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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 #1

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This paper uses the aircraft measurements collected over the Houston area in 2000 and 2006, to understand the change of anthropogenic emissions on ozone production in Houston from 2000 to 2006. The authors applies a box model that is constrained by these aircraft measurements, to understand the discrepancy in radical budget between these two datasets. While this paper is within the scope of ACP, it does not show novel insights and also lacks in-depth analysis. And the conclusion is not well supported. Therefore I cannot recommend to the publication of ACP.

First, I am wondering how confident the authors are about their model simulations. The model is not validated by any observations and most analysis relies on these two model

simulations. Is the diurnal steady state approach applicable to the urban conditions such as Houston? My understanding is that significant amount of intermediate species will be produced by doing so. How do authors deal with this kind of issue in the box model?

Also recent papers have shown the important role of HONO in the photochemistry of urban areas. The major production of HONO is from heterogeneous production (such as surface and aerosols). While HONO is likely small from aircraft measurements, it could play a very important role in radical budget (at least in surface layer) and therefore have important implications on ozone production from surface. This could also imply that a significant amount of ozone is produced in surface layer and transported upward. The box model applied here wouldn't be able to take that into account.

Second, I am confused by the statement of radical decline is due to the decrease in HRVOC emissions. This is not obvious to me. First of all, VOCs reactions with OH will only propagate radical. The primary radical sources include O1D + H2O, photolysis of HONO, photolysis of HCHO or alkenes + O_3. One way to have additional radical production is through HCHO, as it is a radical amplifier. The authors compare the HO_2 budget in Figure 11 (a mixture of primary HOx sources and cycling terms), but it seems more appropriate to compare the budget of HOx. The conclusion of "radical decline is due to the decrease in HRVOC emissions" seems problematic. A detailed analysis on radical budget is required.

Another concern is the sampling bias. A significant portion of these aircraft measurements were sampled in petrochemical plumes, urban plumes or power plant plumes. It seems to me that those points with high NOx values in Figure 9 and 12 are mostly from those plumes. It is not surprising that they have high P(O_3) and high LN/Q, due to high level of NOx and fast removal of radicals by OH + NO_2. However, it doesn't necessarily imply that the Houston area is under VOC-sensitive conditions. In another word, VOC-sensitive condition is only valid in those plumes, and the atmosphere is still under NOx-sensitive conditions outside plumes. Similarly in Figure 9, those high

$P(O_3)$ values are associated with high concentrations of NOx, and likely inside plumes. Most rapid ozone formation doesn't necessarily mean highest ozone concentration. Therefore the discussion on $P(O_3)$ and LN/Q is confusing and could be misleading.

Overall, given the extent of the changes that is required to make this paper publishable in ACP, I would recommend this paper to be rejected.

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