Atmos. Chem. Phys. Discuss., 13, C10332–C10344, 2013
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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.

W. Zhou et al.

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Received and published: 23 December 2013

Reply to referee-1:

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.

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.

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?

Reply: No measurement of OH or HO2 radicals on aircraft during TexAQS 2000 and 2006 were available. The TexAQS-II Radical and aerosol Measurement Project (TRAMP) measured OH and HO2 radicals on the Moody Tower on University of Houston campus (Mao et al., 2010). The TRAMP OH and HO2 dataset was utilized to evaluate the capability of the DSMACC model in simulating OH and HO2 radical. Our results show that the model did capture the magnitude and diurnal variation of OH and HO2 radicals as shown the figures below. The performance of the DSMACC model is comparable to another box model (Chen, 2010). Both diurnal steady state and instantaneous steady state have been used in previous radical modeling. In these results, 37 organic species have been constrained. The intermediates that are produced by the box model are predominantly short-lived and are expected to be in steady state. Near emission sources, steady-state assumptions may be violated (particularly near NOx emissions). More constraints, including peroxides, would be preferred if measurements were available. The results shown in this paper, however, come from a variety of locations and at a variety of NOx and HC concentrations, and NOx:HC ratios. Given the multiple species being constrained and the variety of conditions, we are confident that the conclusions in this paper are robust.

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Figure R-1-1. Observed and Modeled diurnal profile of OH radical (ppt) averaged over TRAMP in 2006

Figure R-1-2. Observed and Modeled diurnal profile of HO2 radical (ppt) averaged over TRAMP in 2006

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.

Reply: As with all box modeling, vertical transport is not explicitly considered. However, the modeling is informative in characterizing the instantaneous ozone formation chemistry. The photolysis of HONO may play an important role in HOx initiation in the Houston area around sunrise, though other OH sources typically dominate as the day progresses (Ren, 2013). To test the sensitivity of the O3 production rate to HONO, we added HONO to the TexAQS 2006 inputs for DSMACC model in an amount corresponding to the 243 ppt median observed at Moody Tower during the TRAMP field campaign. The difference of OPR between the original case and the case with HONO is presented in Figure R-1-3 below. We found that adding HONO increased OPR by only about 3.5% on average and the maximal OPR value by 5%. This test indicates that the TexAQS 2006 was not significantly influenced by HONO when the aircraft measurement mostly occurred during early afternoon hours.

Figure R-1-3. The calculated ozone production rate with TexAQS 2006 data (blue: no HONO data, red: HONO =243ppt).

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

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only propagate radical. The primary radical sources include O1D + H2O, photolysis of HONO, photolysis of HCHO or alkenes + O3. One way to have additional radical production is through HCHO, as it is a radical amplifier. The authors compare the HO2 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. Reply: the manuscript analyzed the HO2 budget for both studies. HO2 was the key radical for calculating ozone production, the budget of which was essential to understand change of P(O3) from 2000 to 2006. To further support the discussion, the budget analysis of HOx for TexAQS 2000 and 2006 are summarized in Figure R-1-4 and R-1-5. The HOx production was 3.6×108 molec cm-3 s-1 in TexAQS 2000 and 1.6 ×108 molec cm-3 s-1 in TexAQS 2006. In both years, the major chemical reactions to generate HOx radicals were HNO4-> HO2+NO2, O1D+HO2->2OH, HYPOPRO decomposition, HCHO photolysis, CH3O-> HCHO +HO2, HOCH2CH2O ->HO2.

Figure R-1-4. Loss and production processes of HOx radicals for high P(O3) samples during TexAQS 2000

Figure R-1-5. Loss and production processes of HOx radicals for high P(O3) samples during TexAQS 2006

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(O3) and high LN/Q, due to high level of NOx and fast removal of radicals by OH + NO2. 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(O3) values are associated with high concentrations of NOx, and likely inside plumes. Most

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rapid ozone formation doesn't necessarily mean highest ozone concentration. Therefore the discussion on P(O3) and LN/Q is confusing and could be misleading.

Reply: The 1-second samples and canister data covered a wide range of NOx concentrations in TexAQS 2000 and 2006 (see the figures below). The data presented in Figure 9 and 12 in the manuscript are a good reflection of all concentration levels measured in the Houston atmosphere during the campaigns. The table in the manuscript presents high, median, and low NOx concentration levels, which provide a comprehensive cross-section of P(O3) and LN/Q both in and outside the most polluted plumes. We agree that the aircraft routes targeted polluted plumes and thus do not represent a volumetric average of Houston air. However, polluted plumes are especially important for attainment of ambient air quality standard for O3, which are based on annual fourth highest O3 observations. While it is true that peak P(O3) does not necessarily coincide with peak concentrations, understanding the chemical processes that form O3 is critical to efforts to control it.

Figure R-1-6. The campaign-average NOx concentration during TexAQS 2000 and 2006; 2000_ALL: the 1-second samples of NOx concentration for TexAQS 2000, 2000_WAS: the canister-basis NOx concentration for TexAQS 2000, 2006_ALL: the 1-second samples of NOx concentration for TexAQS 2006, 2006_WAS: the canister-basis NOx concentration for TexAQS 2006.

Figure R-1-7. The 1-second sample of NOx for all flights during TexAQS 2000

Figure R-1-8. The 1-second sample of NOx for all flights during TexAQS 2006 (the black circles are the canister samples)

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C10332/2013/acpd-13-C10332-2013-supplement.pdf

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

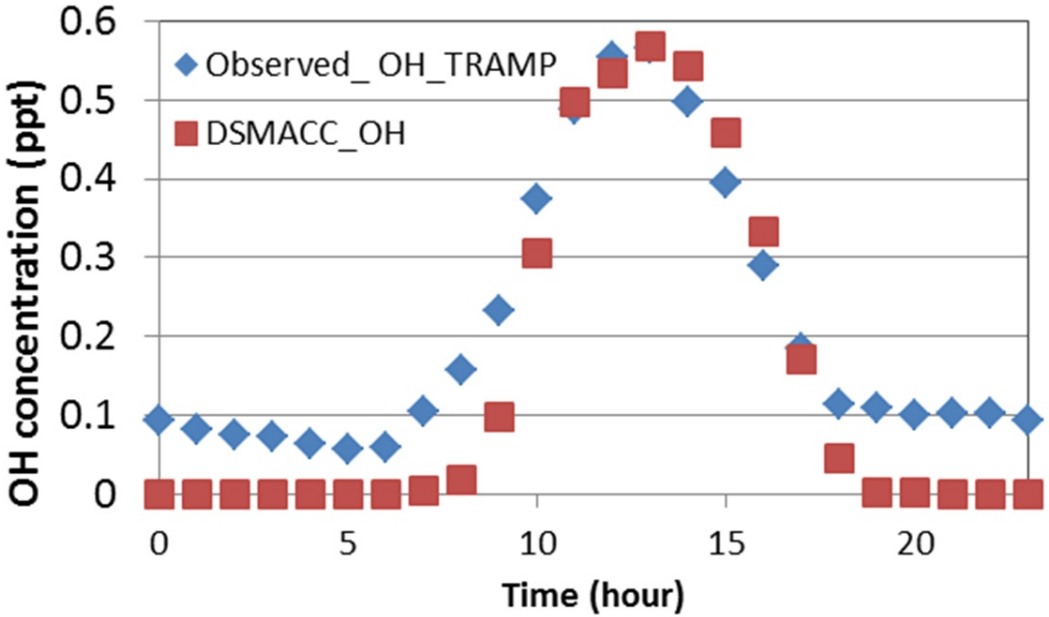

Fig. 1. Observed and Modeled diurnal profile of OH radical (ppt) averaged over TRAMP in 2006

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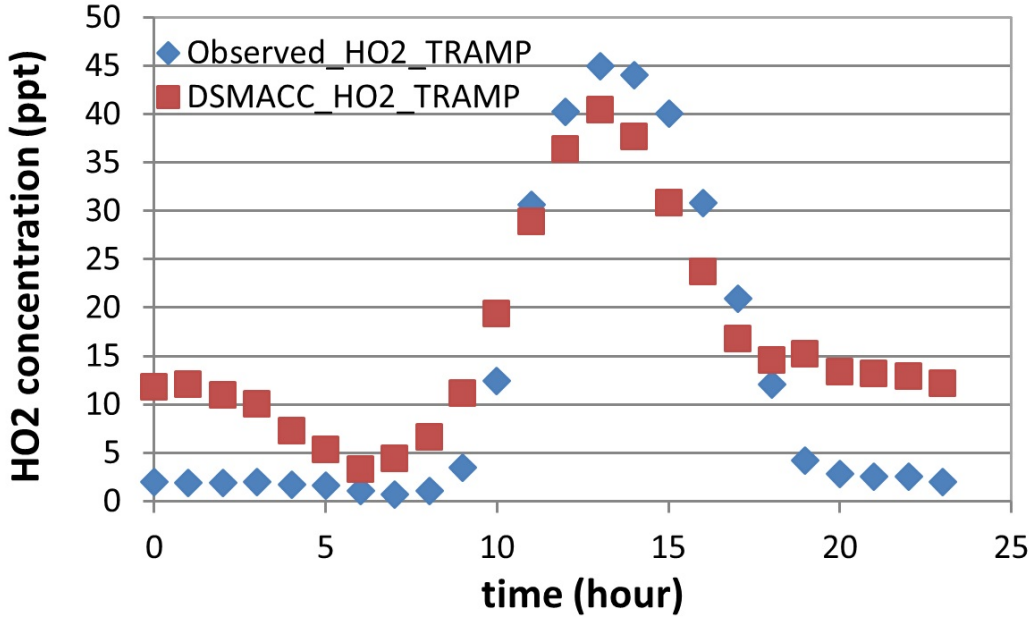

Fig. 2. Observed and Modeled diurnal profile of HO2 radical (ppt) averaged over TRAMP in 2006

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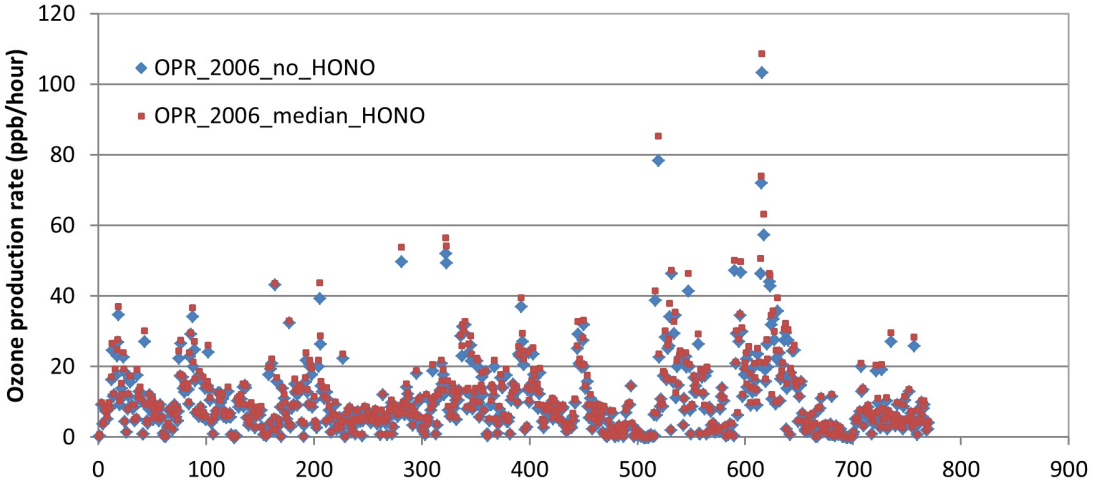

Fig. 3. The calculated ozone production rate with TexAQS 2006 data (blue: no HONO data, red: HONO =243ppt)

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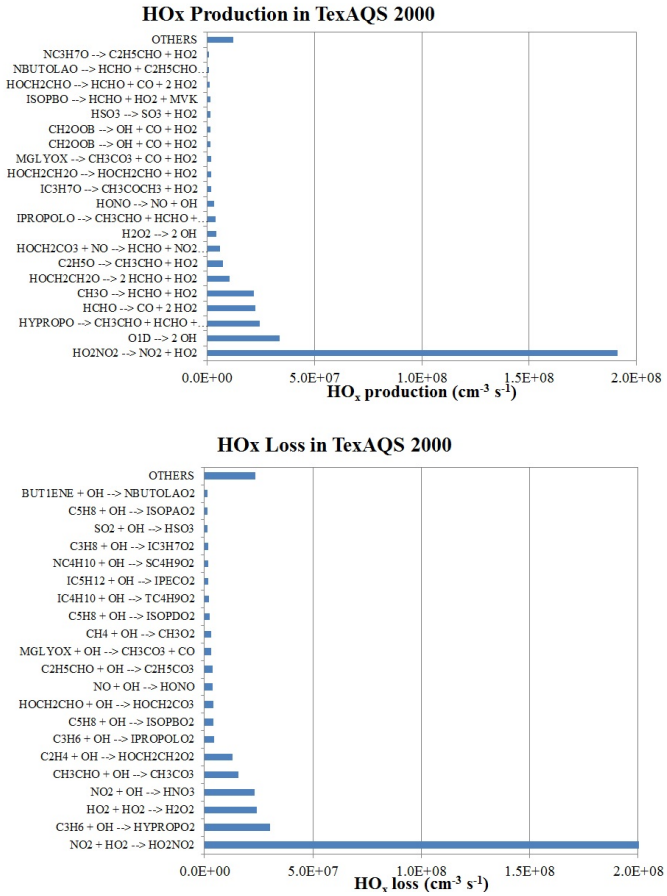

Fig. 4. Loss and production processes of HOx radicals for high P(O3) samples during TexAQS 2000

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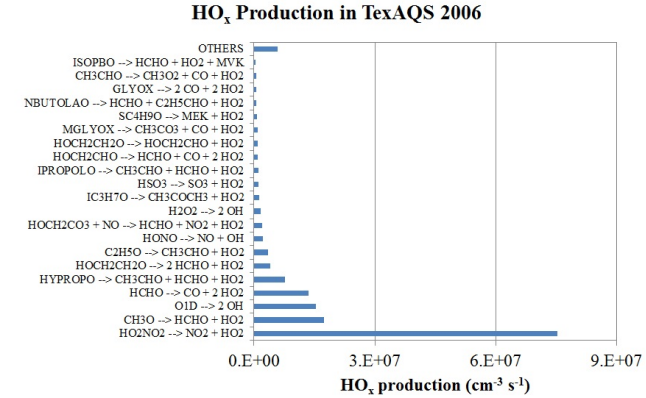

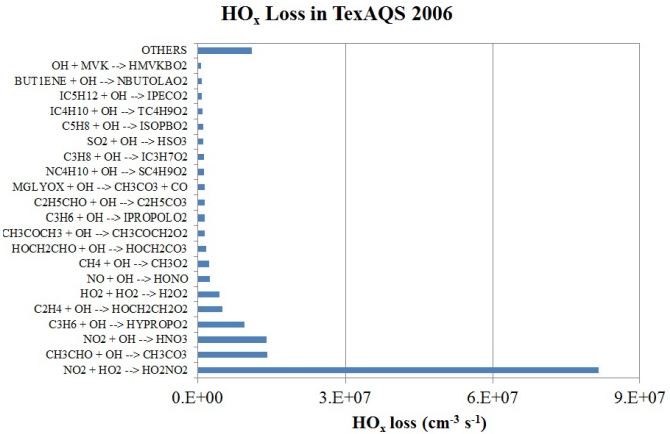

Fig. 5. Loss and production processes of HOx radicals for high P(O3) samples during TexAQS 2006

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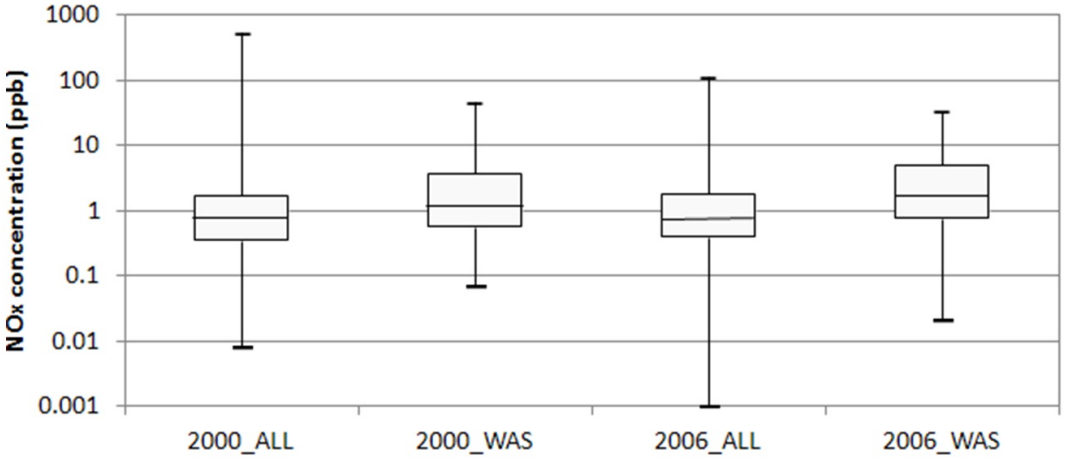

Fig. 6. The campaign-average NOx concentration during TexAQS 2000 and 2006

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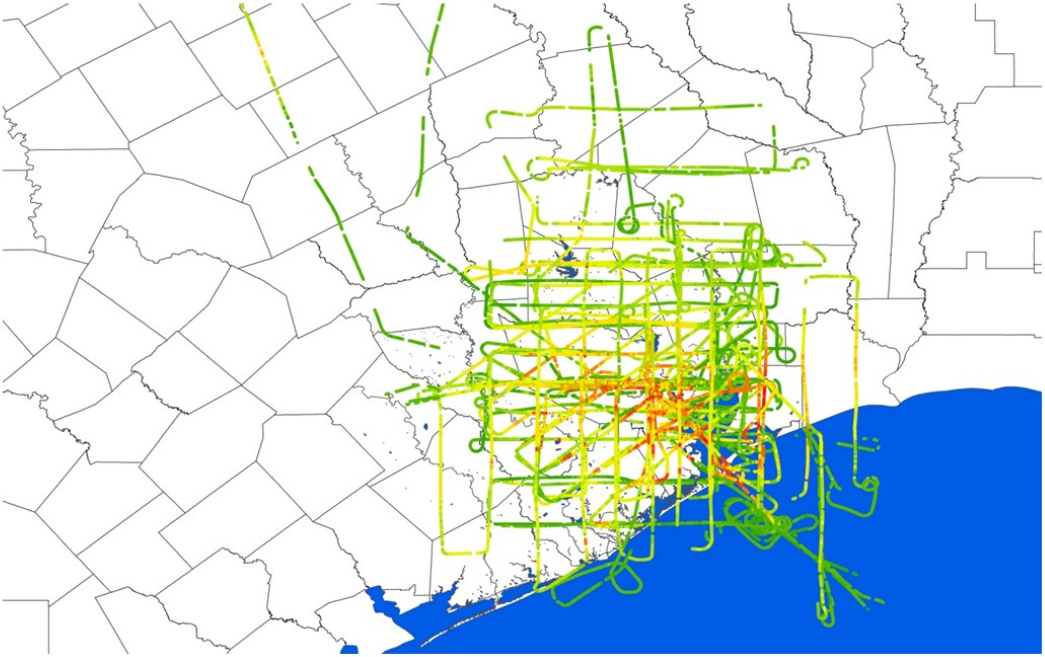

Fig. 7. The 1-second sample of NOx for all flights during TexAQS 2000

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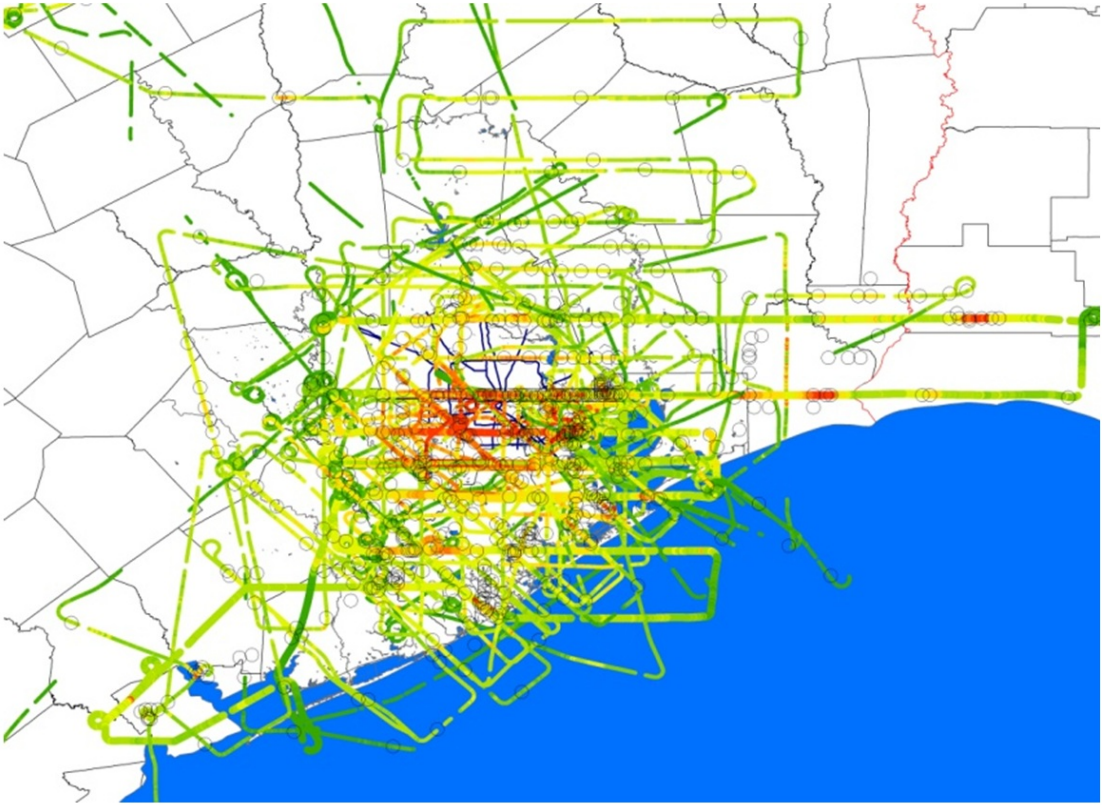

Fig. 8. The 1-second sample of NOx for all flights during TexAQS 2006 (the black circles are the canister samples)

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