**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Ozone response to emission changes: a modeling study during the MCMA-2006/MILAGRO campaign" *by* J. Song et al.

Anonymous Referee #1

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Review of "Ozone response to emission changes: a modeling study during the MCMA-2006/MILAGRO campaign" by Song et al for ACPD

Song et al have done chemical transport model calculations for 6 time periods with different meteorological conditions during the MILAGRO field campaign. They have compared model predictions with surface and aircraft measurements finding generally good agreement. Several CTM calculations have already been published and it is valid to ask, why another.

The heart of this paper is in the calculation of the relative effects of emission reductions of NOx and VOCs. The result that ozone production in Mexico City is VOC limited in high concentration regions and tends towards NOx limited as an air mass is advected away from the City has also been found in other calculations. That said, there are

elements of the current analysis that are unique and can serve as a model for others doings this type of study. I refer specifically to material presented in Figs. 12 and 13. The later figure presents results on ozone sensitivity as a function of photochemical age. Though the general tendencies shown in this plot are recognized, I'm not certain if the literature contains a more straight-forward demonstration of the transition between VOC and NOx sensitive conditions. Figure 12 presents calculated results showing how production rates change when emissions are changed. This figure is unique and provides much needed justification for analyzing chemical production rates. Further explanation is given below.

The comments below are mainly on clarity coupled with a few digressions on what I think is going on and what is important.

This paper should be published with minor modifications.

General Comments Several discussions about sensitivity would be more complete if the authors brought up the effect that a higher concentration of NOx (keeping VOC/NOx constant) leads to a more VOC limited system. There is theoretical justification and I believe even experimental evidence that dilution which usually accompanies aging cause VOC sensitivity to increase.

Figure 12a give the dependence of P(Ox) to P(H2O2)/P(HNO3). This type of figure is usually constructed by changing NOx and VOC concentrations at a point in time and space and seeing how P(Ox) responds. The arrangement of points in Fig 12a, in particular, the P(H2O2)/P(HNO3) at which the NOx and VOC curves cross looks very much like the theoretical prediction and the calculations where local concentrations have been changed. Except, and this is a big exception, here emission rates, not local concentrations have been changed. Somehow, the dependence of local concentration (upon which production rates depend) follows the change in emissions. This graph provides a much needed justification for using local production rates as a way of determining sensitivity to emission changes.

Specific Comments p 23422 "Brute-Force" please explain

p 23427 line 18. putting reference to de Foy et al., 2008 at end of sentence implies that de Foy identified 6 meteorological cases. Is that true?

p 23429 SAPRC99 mechanism Please explain category of species or reactivity range represented by ALK4, ALK5, ARO1, ARO2, etc. Line 4: ALK4 and ALK5 are identified as having high OH reactivity. Is this compared with alkanes such as propane? Highly reactive compounds in urban emissions are generally dominated by C3 and higher olefins.

p 23430 line 4-5 Model – measurement comparison for reactive olefins. Are there sites where a comparison with olefins (individual compounds rather than lumped reactivity from FOS) can be made?

p 23431 top paragraph. Changes in NOx and VOC Lower VOC

p 23434, line 6 The term ozone production efficiency is most often applied to the quantity $P(O_3)/P(NO_z)$ or the slope of a graph of O_3 or O_x versus NO_z. I don't know of any standardized term for $P(O_3)$/radical source. My suggestion is that you spell it out in the text so that the reader does not have to rely on the x-axis label in Fig. 9.

p 23437 ozone sensitivity versus NO_z/NO_y This is not the same sort of relation as obtained from $P(H_2O_2)/P(HNO_3)$. It is driven by the association of low NO_z/NO_x with high concentrations of NOx, i.e. a dilution effect.

p 23437-23438 Comparison with 2003 Lei et al (2008, 2009) apparently did the 2003 calculations? Are the models identical, or nearly identical, apart from emission inventory changes so that one can have confidence in the comparisons of ozone sensitivity. Are there any meteorological differences between 2003 and 2007 that would cause an ozone sensitivity change? An example would be better ventilation in one year.

p 23438 line 6-7 ozone formation in 2006 more VOC-limited than in 2003 due to reduced VOC/NOx ratio NOx emissions in 2006 are slightly higher than in 2003 (page

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23431). This by itself would make ozone production more VOC sensitive. Changes in VOC/NOx could add to this tendency.

p 23440 line 12-13. Ozone sensitivity aloft. Ozone is usually well mixed in the boundary layer, so a different sensitivity aloft refers mainly to the free troposphere.

p 23436 Section 3.4.2, literature values of $P(H_2O_2)/P(HNO_3)$ Are the values cited all for production rates or are they for the corresponding concentration ratio $[H_2O_2]/[HNO_3]$?

p 23436 Section 3.4.2, calculated values of $P(H_2O_2)/P(HNO_3)$ The range for separating VOC and NOx sensitive conditions, 0.1 to 0.35, looks to be narrower in Fig. 12a. Is there an objective criteria in terms of the percent of points where the blue points are above or below the red points?

Fig. 4. According to caption OLE_eq [ppbv] is propene equivalent olefin concentration. Please clarify if propene equivalents are in ppb compound rather than ppb carbon as in the original definition by Chameides.

Table 2. Additional lines for individual compounds or categories of compounds would help the reader "see" what is described in the text.

Fig. 12. It would be helpful to the reader to have some landmarks on the graph, such as T0, T1, and T2. This would cut down on page turning back to Fig. 1.

Fig. 13 It would be helpful to the reader to identify young air mass on the left and aged air mass on the right.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 23419, 2009.