

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

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Response to Referee #1

The authors are grateful to the referees for their thoughtful and thorough reviews, which has substantially improved the quality of this paper. Following are our response to the comments (comments of Referees in *italic* and responses in TNR).

*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.*

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*The heart of this paper is in the calculation of the relative effects of emission reductions of NO<sub>x</sub> and VOCs. The result that ozone production in Mexico City is VOC limited in high concentration regions and tends towards NO<sub>x</sub> 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 doing 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 NO<sub>x</sub> 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.*

We thank the referee for the gracious comments.

**General Comments.** *Several discussions about sensitivity would be more complete if the authors brought up the effect that a higher concentration of NO<sub>x</sub> (keeping VOC/NO<sub>x</sub> 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.*

The following paragraph has been added in Sect. 3.4.3 (separated from the original Sect 3.4.2) NO<sub>x</sub>-VOC sensitivity vs chemical aging), which briefly discusses other factors that affect the O<sub>3</sub> sensitivity with focus on dilution: “The O<sub>3</sub> sensitivity is discussed above in the context of emissions and chemical aging represented by NO<sub>z</sub>/NO<sub>y</sub>. In fact, O<sub>3</sub> sensitivity is also influenced by other factors (Sillman, 1999), such as VOC/NO<sub>x</sub> ratio, VOC reactivity and the severity of the event (including dilution). Although the ratio of NO<sub>z</sub>/NO<sub>y</sub> is used to represent the chemical aging, it is often affected by emissions, since the level of NO<sub>y</sub> reflects the NO<sub>x</sub> emissions (and mixing) and NO<sub>z</sub> is affected

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by radical concentrations, which are affected by both VOCs and NO<sub>x</sub>. In addition, the chemical aging is usually accompanied by the process of dilution, which alone can shift the NO<sub>x</sub>-VOC sensitivity to the VOC-limitation regime (Milford et al., 1994; Sillman, 1999). Milford et al. (1994) found that for plumes with same VOC/NO<sub>x</sub> emission ratios, plumes those with higher NO<sub>x</sub> emissions tend to be more VOC-limited, and plumes with lower NO<sub>x</sub> emissions tend to become NO<sub>x</sub>-limited more quickly as they are photochemically processed. Therefore it should be noted that when discussing the O<sub>3</sub> chemistry - chemical aging relationship, many other physical and chemical processes are often inevitably involved."

*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.*

We thank the referee for the comment.

### **Specific Comments**

*p 23422 "Brute-Force" please explain.*

This has been clarified ( "in which the O<sub>3</sub> sensitivity is examined by changing a certain percentage of precursor emissions").

*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?*

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Yes. This sentence has been rearranged for clarity.

*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.*

This has been explained in the first paragraph of Sect3.1.

*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?*

There were measurements of individual olefin species at T0 as shown in Table 1, and we obtained the emission adjustment factors for model species ETHE, OLE1 and OLE2 based on these measurements, even though only ETHE comparison is shown in Fig 3 as an example. PTR-MS measurements for several aromatics were made by PTR-MS at SIMAT site, but none for olefin species. It would be interesting to inter-compare the FOS and PTR-MS data had the PTR-MS olefin measurements were available.

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

This has been corrected throughout the text (elsewhere in abstract, conclusion, and Sect. 3.5).

*p 23434, line 6 The term ozone production efficiency is most often applied to the quantity P(O3)/P(NOz) or the slope of a graph of O3 or Ox versus NOz. I don't know of any standardized term for P(O3)/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.*

The ozone production efficiency is defined as P(Ox)/P(NOz) and is calculated from the data pairs in Fig 9. This has been clarified in the text.

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*p 23437 ozone sensitivity versus NO<sub>z</sub>/NO<sub>y</sub> This is not the same sort of relation as obtained from P(H<sub>2</sub>O<sub>2</sub>)/P(HNO<sub>3</sub>). It is driven by the association of low NO<sub>z</sub>/NO<sub>x</sub> with high concentrations of NO<sub>x</sub>, i.e. a dilution effect.*

The original Sect 3.4.2 has now been divided into 2 sections, and the following sentence has been added to differentiate the difference of these two relations: "Although both the O<sub>3</sub>-chemical aging relationship and the P(H<sub>2</sub>O<sub>2</sub>)/P(HNO<sub>3</sub>) relation discussed above attempt to use measurements to assess the O<sub>3</sub> formation characteristics, they are different in that the former is derived from the radical chemistry and reflects the in situ chemistry while the latter is usually associated with plume dilution and transport and is embedded with the plume history." In addition, an opening statement has been added to Sect 3.4.2: "Due to its robust theoretical backgrounds, a strong correlation between its constant ratio and the P(Ox) ridgeline and the least uncertainty. . .".

*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.*

Same or nearly identical models were used in MCMA-2003 (the 2007 paper used an older version of CAMx (v4.02) vs v4.4 in this and the 2008 papers). The dilution and transport were similar between MCMA-2003 and MCMA-2006. We have added the following statements: "Lei et al. (2007, 2008) investigated the relationships between ozone production rate, radical primary source, and VOC-to-NO<sub>2</sub> reactivity using identical or similar model (an older version in the 2007 paper)", "Meteorologically, Shaw et al.(2007) evaluated the vertical mixing during MILAGRO and found it to be similar to prior studies. de Foy et al.(2008) found that March 2006 was climatologically representative of the warm dry season. Compared with April 2003, there were fewer wet days and more warm winds from the south but overall the transport patterns were similar."

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*p 23438 line 6-7 ozone formation in 2006 more VOC-limited than in 2003 due to reduced VOC/NO<sub>x</sub> ratio; NO<sub>x</sub> emissions in 2006 are slightly higher than in 2003 (page 23431). This by itself would make ozone production more VOC sensitive. Changes in VOC/NO<sub>x</sub> could add to this tendency.*

The relevant statements have been changed as follows: "The difference is probably mainly due to the reduced VOC reactivity and lower VOCs in the estimated emissions in 2006, as indicated by the overall ~20 % decrease in VOC emissions and significant decreases in emissions of reactive alkenes and aromatics. The 6% increase of NO<sub>x</sub> emissions can also contribute to the tendency, but probably with a minor impact due to the moderate increase". Also refer to the response to the p23431 comment.

*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.*

From the Spencer et al. (2009) paper, it is not clear whether their study focuses on the PBL or the free troposphere. To avoid over-interpret or misinterpret their results, the following statements have been REMOVED: "Finally, it is the urban area near the surface that is VOC-limited; the situation could be different aloft. Spencer et al. (2009) argues that if missing radical sources are accounted for, O<sub>3</sub> production over the MCMA (below 7 km a.s.l.) could be NO<sub>x</sub>-limited or the regime may shift to NO<sub>x</sub>-limited at higher NO<sub>x</sub> levels."

*p 23436 Section 3.4.2, literature values of P(H<sub>2</sub>O<sub>2</sub>)/P(HNO<sub>3</sub>) Are the values cited all for production rates or are they for the corresponding concentration ratio [H<sub>2</sub>O<sub>2</sub>]/[HNO<sub>3</sub>]?*

We have modified to cite values from Tonnesen and Dennis (2000), who used P(H<sub>2</sub>O<sub>2</sub>)/P(HNO<sub>3</sub>).

*p 23436 Section 3.4.2, calculated values of P(H<sub>2</sub>O<sub>2</sub>)/P(HNO<sub>3</sub>) The range for separating VOC and NO<sub>x</sub> 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*

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*above or below the red points?*

We have now used the definition: “Here we define the transition regime as the situation where the difference in the O<sub>3</sub> production rate between the two emission scenarios is less than 5% relative to the base case. This definition is similar to the one defined by Sillman (1999) in the context of urban O<sub>3</sub> chemistry”, and with this the range for the transition regime has been refined (0.14-0.24).

*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.*

Thanks for pointing this. The equivalence here is referred to the FOS response to olefin species, i.e., it is instrument response based, not OH reactivity based as defined in Chameides et al. The following statements have been added for the clarification: “The propene equivalence here refers to the sensitivity response of the FOS instrument to olefin species with respect to propene (Velasco et al., 2009), which is different from the OH-reactivity based definition introduced by Chameides et al. (1992)”.

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

Estimated emission rates of alkenes and aromatics during MCMA-2003 and MCMA-2006 have been added in Table 2.

*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.*

This has been done. The location of SIMAT has also been included in 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.*

This has been explained in the figure caption.

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