

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

J. Song et al.

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Response to Referee #2

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

The paper by Song et al. presents a detailed study of the sensitivity of ozone production to NO_x and VOC emissions in the MCMA, using the CAMx 3-D photochemical model. This appears to me to be a solid and thoroughly-conducted contribution, and provides a logical extension and update to the work done by this group on MCMA-2003. In particular, the effect of decreasing VOC emissions/reactivity between MCMA-2003 and

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MCMA-2006 is clearly demonstrated. In my opinion, the paper is suitable for publication in ACP with minor revision, as noted below.

One general question that the authors might want to address in more detail: How well are the VOC budget and the associated OH reactivity toward VOCs actually known? While it appears that the authors have done a very logical and complete job of scaling the emissions inventories to match the available data, I wonder if the authors can offer any further comment on the possibility of the existence (for example) of unmeasured hydrocarbon species, and the impacts that associated uncertainties might have on the overall results obtained.

Thanks for raising this important issue. The emission uncertainty is always a big concern in any CTM modeling, and there is no exception in this study even though we have made a lot of efforts to reduce the uncertainty. We have added the following paragraph in Sect 3.5 on the basis of the MCMA2003 – MCMA2006 comparison, with the hope of addressing the issue further:

“The comparison between the MCMA-2003 and MCMA-2006 O₃ chemistry allow us to estimate, to a certain extent, how emissions uncertainties may affect the conclusions of this study. Our model-based evaluation of VOC emissions relies on the assumption that the observations contain the full spectrum of the lumped model species such that the comparison can be made. However, it is likely that some VOC compounds are missed by the measurement techniques, in particular those with high molecular weights and low atmospheric concentrations. One way to examine the completeness of VOC measurements is to compare the directly observed OH reactivity contributed to VOCs with its VOC measurement-derived counterpart. Such a comparison was made during MCMA-2003 (Shirley et al., 2006), and it was found that the latter was about 20% lower than the former. The consistency between observational evidence (Stephens et al., 2008; Nunnermacker et al., 2008; Wood et al., 2009) and this modeling study regarding the O₃ chemical regimes in the MCMA strongly suggests that the uncertainties introduced by the missing VOCs are not sufficient to change our conclusions. Although

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the magnitude of the unmeasured VOCs is unknown and its estimation is beyond the scope of this study, the comparison between MCMA-2003 and MCMA-2006 O₃ chemistry indicate that up to 25% differences in VOCs (up to 50% for aromatics) do not reverse the chemical regime, but can alter the magnitude of the O₃ sensitivity. It should be pointed out under what emissions reduction scenarios the O₃ sensitivity chemistry is defined. If smaller emission reductions are applied (such as 20%), the O₃ chemical regime response might change". In addition, a brief remark on the effect of biomass burning is added in the conclusions (see response #7 to referee #3).

A more specific, but related question – it appears from the text near the top of p.23429 that the ALK4 and ALK5 emissions did not need to be altered. Were measurements of the species that fit into these lumped categories (pentane and larger alkanes, I think?) available? – they are not currently listed in Table 1.

Thanks for pointing out this that we missed. There were no sufficient number of individual >C4 alkene species measured during the MCMA-2006 that allowed us to lump and compare with simulations. Therefore we used the scaling factors of ALK4 and ALK5 from the MCMA-2003 studies. This has been clarified in the text by the following statements: "The number of >C4 alkanes measured during the MCMA-2006 campaign was not adequate for lumping; we did not use to conduct measurement-model comparisons. The adjustment factors obtained during the MCMA-2003 study, 1.4 and 0.6 for ALK4 and ALK5 respectively, were instead used (Lei et al., 2007; 2008). The downscaling of ALK5 emissions may also be due to their low concentrations and the incomplete detection of these species by the GC/FID measurement. Nevertheless the uncertainty in ALK5 emissions is not expected to substantially influence the O₃ chemistry due to their low concentrations and low VOC reactivity (Velasco et al., 2007)"

Minor comments:

Can a reference be provided for the statement (p. 23423) that RAMA NO_x measurements more accurately represent NO_y?

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The reference of West et al. (2004) has been added.

Page 23428 (bottom) and Figure 2 – Should there not be more data points to compare with, given that there are 15 RAMA sites being used, more than 20 days under consideration, and potentially 5 hourly measurements per station per day (7am – 11am)?

To avoid the high density that would mask the episode signature, each data point in Fig 2 is the 15 RAMA site average. This has been clarified in the figure caption.

Second line of p. 23431 – This should be the VOC/NO_x ratio, not NO_x/VOC, I think?

Yes. It has been corrected.

Bottom of page 23431 – a minor point, but are the O₃ values from CnvS and CnvN days really that different from O₃-S days?

There are discussions on the differences of O₃ concentrations between SV (South venting) days and other episodes, but none between O₃S and Cnv days. We have removed the statement that may have caused the confusion: "rain and high winds reduced photochemistry during Convection days", and have added the following sentence: "High O₃ concentrations were still observed under the convection conditions (O₃-CnvS and O₃-CnvN) because the convection usually occurred in the late afternoons."

Page 23433, and elsewhere – should use ARO2 throughout, no subscript.

It has been corrected.

Top of p. 23434 – Am I right that the Ox production efficiency referred to is the P(O_x)/P(NO_z) ratio, which is not explicitly shown in Fig.9? You might want to add a sentence of explanation here.

We have clarified this problem by revising the sentence as "The mean Ox production efficiency, defined as P(O_x)/P(NO_z) in this study, calculated from data pairs in Fig. 9, is 7".

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p. 23435, and also in the conclusions – I think it is always the case that a reduction in VOCs will lead to a reduction in ozone – i.e., unlike the case with NO_x, VOCs never saturate / inhibit the chemistry.

We agree with the referee's comment with one exception—an urban air with important biogenic VOCs. The following sentence or similar has been added in Sect 3.4.1 and in the conclusions: "This is always the case with few exceptions in the polluted urban atmosphere because of high NO_x, limited radicals and the reduction magnitude of VOC emissions."

p. 23436 – It is not clear which part(s) of the preceding discussion the authors are using to justify the concluding sentence of the paragraph, that "This further suggests that ozone formation in the MCMA urban area is VOC-sensitive". Please clarify.

The 2nd paragraph in Sect 3.4.1 along with Fig 10 and Table 3 were meant to reach the VOC-sensitive conclusion. This has been clarified.

Very bottom of p. 23437 – should be "was" instead of "were", I think.

It has been corrected.

The Sillman and West (2009) paper does not appear in the reference list.

It has been added.

The y-axis label for Fig. 8c is not readable.

The y-axis label was clear in our manuscript; it might have been cut out during the typesetting.

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