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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterizing ozone production in the Mexico City Metropolitan Area: a case study using a chemical transport model" *by* W. Lei et al.

Anonymous Referee #1

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Review of "Characterizing ozone production in the Mexico City Metropolitan Area: a case study using a chemical transport model" by Lei, de Foy, Zavala, Volkamer and Molina for ACPD

The authors have presented a thorough model investigation of O3 production rates and sensitivity in the MCMA. They have provided information on precursors, O3 concentration, and the response to emission reductions. A convincing case is made that in the urban area (for the episode under consideration), O3 production rates and O3 are VOC limited. A comparison of calculated and measured NOx and VOCs implies that this conclusion will not be reversed because of revisions to an emission inventory. This

article should be of interest to the science and regulatory communities. The primary readership is likely to be researchers who participated in the 2006 Milagro campaign. It should find application as a description of O3 production in 2003 against which the 2006 data can be compared.

One of my major comments might be regarded as merely typographical but please take it seriously. The use of the symbol LN to denote radical loss by formation of PAN's, other organic nitrates, and particulate nitrates (defined in Table 3) runs counter to the usual meaning in which formation of HNO3 is included. If you mistake one usage for the other, the equations don't make sense.

Another major comment concerns the back and forth switching between presenting data for the REP-8 sites and the larger urban domain. Whether a figure is for the REP-8 sites or the larger domain should be prominently noted in the text. The REP-8 sites have a concentrated mix of pollutants and conclusions drawn from them, especially regarding VOC sensitivity, are not expected to be uniformly applicable. This is treated in the paper in e.g. the NOx reduction maps - but these come towards the end of the article.

Also see the comment below on the proportionality between P(Ox) and Q1/2. I just don't see how this comes to be. Is the graph correct?

Overall assessment An excellent study. I believe that the items listed below will increase the clarity and make the paper more useful to Milagro researchers.

Specific comments p7964 line 20 "were updated ever since wherever possible" meaning?

p7968 comparison of observed and predicted spatial distribution of max O3. Is this primarily a wind problem or a speed of photochemistry problem?

p 7969 lines 14-18 Not clear from text whether the REP-8 station where chosen because they did or did not have O3 titrated by local NOx emissions.

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p 7970 line 3 - 13 Overprediction of nighttime NO2 probably indicates missing NOx sinks. I don't follow the argument (based on NOx speciation?) that rules out emissions or boundary layer height as a cause of the overprediction.

p 7971, lines 16 - 20. The adjustments to the VOC inventory are from a limited data set. Does this statement apply to this study or to Velasco et al. (2006)?

p 7972 Equation 1 Equation should be written so that it is clear that [NO] is outside of the radical sign

p 7972 Equation 2 The qualifier [NOx] $>$ 1 ppb is confusing. This is an equation that applies for VOC limited O3 production. Except in the most unusual of circumstances NOx will be significantly greater than 1 ppb. Also, [NOx] $>$ 1 ppb is not a sufficient criterion for this equation to apply.

Section 3.2.2 It should be emphasized that the model results shown in Fig. 7 are from the REP-8 sites (noted in figure caption) which have very high concentrations of primary pollutants. It is clear from Fig. 7b that there are no points from clean air because these points would have very high VOC/NO2 reactivity ratios. A broader point should be made that conclusions regarding VOC sensitive O3 formation may not be applicable for the whole domain.

p 7973 discussion of Fig 6. also p 7976 line 20-21 In most locations one finds that P(O3) decreases at high NOx concentration. According to Eq 3, this is due to points with low values of kVOC/kNO2, such as would occur in power plant plumes. Table 1 indicates an absence of NOx point sources in Mexico City. As noted in the text, Fig. 7b shows that VOCs and NO2 are in a near constant ratio and furthermore Q increases with kVOC. This explains the observation that P(O3) does not decrease at high NOx.

p 7974, line 12-13 Fig. 7c shows that P(Ox) is proportional to Q1/2 with very little scatter. This is an unexpected result. If I combine P(Ox) ˜ Q1/2 with P(Ox) ˜ (kVOC/kNO2) Q (Fig 7d leaving out LN), I get kVOC ˜ kNO2/Q1/2. Fig 7e shows that kVOC ˜ Q to

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about the 1/2 power, which means that kNO2 must be proportional to Q to about the 3/2 power to make everything consistent. I can't think of any reason why this should be - and even if there was an approximate reason it would not explain the great correlation in 7c.

p7976 line 15 The HCHO inventory was multiplied by 9. Is the source of HCHO still mostly secondary?

p 7977 lines 15 - 17 OPE is proportional to the VOC/NO2 reactivity ratio for low and high NOx, as long as NOx is greater than a threshold. The higher values for OPE probably correspond to points that are not part of Fig. 7. It is unlikely that these points have VOC limited O3 formation. Some higher values for OPE were reported for petrochemical plumes in Houston.

p 7978 line 7 Both the enhancement time and peak time What is enhancement time? Peak of what?

p 7978 line 11 - 13 Missing reactivity and radical sources as previously discussed There was discussion of HONO but I thought that the model did a good job of matching VOCs.

p 7980 line 14 Fig 2, lower left panel - should be Fig 3

p 7981 line 14 - 15 should be contrasted with the NOx-only reduction case. I'm not sure which Figures this refers to - or whether it refers to a Figure that is not shown.

p 7982 line 14 I would expect that with a smaller percent NOx reduction more points would have a positive P(Ox) difference.

Figure 1 to 3. It is hard to make out the locations of the REP-8 sites. Axes should be labeled with lat and lon. I realize that the model grid may not align with NS and EW and that the labels may have to be put in by hand. However, I believe that a lot of people will be looking at these figures trying to get their bearing relative to measurement sites in the 2006 campaign. The location of the CENICA site should be on the map. Although,

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the location of T0, T1, and T2 are not important for the 2003 study, it would be a valuable addition for the readers of this paper.

Figure 10 I can't see difference in color between "top boundary" and "deposition"

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7959, 2006.