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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterizing ozone production and response under different meteorological conditions in Mexico City" *by* W. Lei et al.

W. Lei et al.

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Response to the referees' comments
We thank the two anonymous referees for their constructive and valuable comments, which help to improve the quality of this article.

Referee #1
General comments
The authors have extended their CTM calculations for Mexico City to two different categories of O3 episodes. This relatively compact paper reaches the important conclusion that all three types of episodes exhibit basin-wide VOC limited conditions. The Lagrangian analysis of P(Ox) as a function of chemical age is one of the best illustrations

of the effects of emission controls on O3 production that I have seen. I recommend publication after minor revisions.

[RESPONSE]: Appreciate the nice comments. To more vigorously and accurately illustrate the P(Ox) evolution in the plume, we have improved the identification of the plume trajectories by visually locating the plume every hour (during 12-17 CDT) every day, and accordingly we have upgraded Figs. 9 and 10, although they do not change the discussions and conclusions.

Specific

1) P 12055, line 18-20. Cold surge ..leading to afternoon convection ... highO3 in the city center due to stable conditions; Why the link between convection and stable conditions?

[RESPONSE]: Before the convection starts in the afternoon, the weather is cloudy and more stable when high O3 occurs. Therefore there is no contradiction between stable and convection. We have clarified this link in the text. In addition we have modified Fig 1 which is more definitive about the circulation model during the MCMA-2003 campaign.

2) P 12058, line 12-13. Emission variations in different EI base years and locations; How was the range of adjustment factors listed in Table 1 used in the model? Was a central value chosen? Was there a spatially dependent adjustment?

[RESPONSE]: We thank the referee for pointing out this confusion. Originally the model was run using both EI 2002 and EI 2004, and comparisons at different sites were conducted, hence there was a range in the adjustment factor. Subsequently we decided to use linearly interpolated emissions from EI 2002 and EI 2004 for this study, and examined the overall comparison among all stations where measurements (especially VOCs) were available. We have eliminated the range of the adjustment factors in the revised version.

3) P 12059, line 19; horizontal convection; horizontal advection?

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Interactive Comment

[RESPONSE]: It has been changed to advection in the text.

4) P 12059, line 5 and following. Sensitivity of predicted basin wide average O3 to a 0.5m/s wind shift. This interesting result makes one reflect on the limits to which O3 (a basin-wide average at that) can be predicted. Fast, de Foy and colleagues have done extensive comparisons between observed and predicted wind fields. To what accuracy can wind fields generally be predicted?

[RESPONSE]: We have added some statements in the text based on the findings from de Foy's month-long MM5 evaluation (de Foy et al., 2006): "de Foy et al. (2006) find that the MM5 model bias for April 2003 in the MCMA is between -0.5-0.0 m/s for surface winds and the variance of errors is 1.0- 1.5 m/s (c.f. Fig. 5 in de Foy et al.); the model bias for the upper level winds is similar (c.f. Fig. 18 in de Foy et al.). This suggests that the wind speed modifications used in the above tests are within the model uncertainty, and it also suggests that there is room for improving the meteorological model".

5) P 12059 line 23-29 O3-south episode and Sunday, Easter Week emission changes Stephens et al have a paper in ACPD (8, 8357-8383, 2008) on weekday, weekend differences in O3, NOx, and CO. Their findings are in agreement with your result. Similar O3 on weekends but less CO and NOx compared with weekdays.

[RESPONSE]: Thanks for providing us this information. We have cited the relevant findings of Stephens et al.

6) P 12060, line 3. I am not sure whether 13-15 April has been previously defined (in this paper) as an O3 South episode.

[RESPONSE]: We have added the episode definition for the period of 13-15 April in the revised text.

7) P 12060, line 20. Under cold surge conditions OPE values appear to be less NOx dependent. This is not apparent in the Figure because of the congestion of data points (see below).

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[RESPONSE]: Data points in Fig 5 have been diluted by introducing every 3rd data points.

8) P 12060 line 27; P 12061 line 12. Low P(Ox) in fresh air. I think all of the ingredients for an explanation are here but it is not quite spelled out. P(Ox) is proportional to Q according to Fig. 6d. The high NOx, high VOC air which has not aged, probably has a low concentration of O3, perhaps near zero due to titration. This cuts down on O3 photolysis and O3+olefins as radical sources. HCHO and other radical precursor compounds that accumulate with age can be expected to be low also.

[RESPONSE]: We thank the referee for the in depth elucidation of the decrease of P(Ox) in fresh air. We have added the following statements in the text: "In the less aged air with high NOx and VOCs, the O3 concentration is lower due to the titration process and the radical scavenging by NOx, which leads to lower radical sources from the O3 photolysis and other radical precursors (such as aldehyde photolysis and alkene ozonolyis) because of slower photochemical process. Since P(Ox) is strongly dependent on the radical sources (Fig. 6c), lower Q values lead to lower P(Ox)". With regard to the relatively lower P(Ox) during the O3-South episode, since the air has similar aging as in the O3-North episode, we attributed it to the lower emissions during this period.

9) P 12062 line 28; P 12063, line 2. description of P(O3) as a function of chemical age. This is difficult to see on the graph. A box and whisker plot might be better.

[RESPONSE]: We agree with the referee that a box and whisker plot may better depict the relation P(Ox)-chemical aging for the plumes at the source area and downwind, but for the plume along the trajectory, binning the chemical aging data would smear the bifurcation feature of the relation. Therefore for the trade-off we decide to keep the original plot while reducing the data points by half.

10) Fig. 4. It would be helpful to add in the caption that these are the 2 days in which the model did not perform well.

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[RESPONSE]: Caption has been added. Furthermore we have upgraded Fig. 4 in several ways, such as the plume's average location and pathway during the O3-North episode is reflected by the area where the episode-averaged peak O3 concentration exceeding 120 ppb, the source and downwind areas where the data are sampled in Figs 9 and 10 are indicated, and the locations of the three VOC sampling sites are marked.

11) Fig. 5 and 6 have a high density of points. The O3 South data hides the other two cases. Perhaps this will look better in a larger figure, but only if the data points stay small. Options are to reduce points by spatial averaging or by plotting every nth point. A box and whisker plot using binned data could work if there is room to display three boxes for each division of the independent variable.

[RESPONSE]: Data points in Figs 5 and 6 have been reduced by using every 3rd data points.

12) Fig. 9. Caption identifies blue squares, which are green in my version.

[RESPONSE]: Caption has been corrected.

Referee #2
General (major) comments:
1. The literature review of the authors is limited to two recent papers, which might give the wrong impression on the amount of literature available on the subject. There is a vast amount of literature that has been published on the influence of meteorological conditions on photochemical air pollution. Authors should acknowledge this literature, and try to make reference to classic papers in this area.

[RESPONSE]: We thank the referee for the suggestion. We acknowledge that there are numerous studies on the influence of meteorology on photochemical air pollution. We attempt to focus this article on the influence of meteorology on O3 sensitivity chemistry.

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We have revised the literature overview and have included additional references.

2. P. 12056, line 14. Briefly describe the model configuration and modeling domain. Even though this information has been published elsewhere, it will help to get an overall idea on how the modeling was conducted. For example, in Table 1 several emission categories are indicated (e.g., ALKx, OLEx, etc.) What do they stand for? What species were considered for each category? Is this a direct function of the chemical mechanism used by the model? If such, what chemical mechanism was used?

[RESPONSE]: A brief description of the model configuration and modeling domain has been added: "Briefly, the model domain covers 52x52 grids with a grid resolution of 3 km centered in Mexico City; there are 15 vertical layers extending from the surface to about 5 km a.g.l with the bottom model layer interface of about 64 m a.g.l. The chemical initial and boundary conditions were the same as those used in Lei et al. (2007). Photolysis rate frequencies were pre-computed with the TUV model (Madronich and Flocke, 1998) for clear sky, and were corrected for the cloud effects using the approach of Chang et al. (1987)."

In the revised text we have also clarified the chemical mechanism (SAPRC99) used in the model, in which ALKx, OLEx and AROx are model's lumped VOC species.

3. P. 12056, line 22. Why were two distinct emissions inventories used?

[RESPONSE]: The official EI is released every two years. To estimate the emissions in the year of 2003 as realistic as possible, we interpolated them from EI 2002 and EI 2004. We have clarified this in the revised manuscript.

4. P. 12056, line 26. Authors indicate that "...an extensive array of ground measurements for VOCs were made..." and used in their study. However, then they indicate that VOC measurements were only conducted in three sites. Finally, in the conclusions (and before in the text) they indicate that "...VOC comparisons were still made over limited locations...". There seems to be lack of consistency in these comments.

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[RESPONSE]: Extensive measurements can be defined in terms of the coverage for time duration, species number and technique, which are the case for the MCMA-2003 field measurements, not necessary in terms of space coverage.

5. P. 12057, lines 7-8. It is indicated that some emissions estimates where compared against values obtained by Zavala et al. (2006), though I did not find any further comments or evidence on this in the following sections of the paper.

[RESPONSE]: Thanks for pointing out the inconsistency. The relevant finding of Zavala et al. (2006) was used indirectly for agreement check. We have deleted this sentence and added the citation in the comparison discussion.

6.1 One key issue of the paper is the emissions manipulation. Authors indicate that they used the procedure devised by Lei et al. (2007) to evaluate the emissions for these new model applications. As the model is driven heavily by emissions, more needs to be said about these and the procedure devised by Lei et al. (2007). As implied by the paper, emissions were adjusted until they obtained a "satisfactory agreement". How and on what basis were the emissions adjusted? Was this based on a stochastic approach? Was this a one-at-a-time change for each species, or was it a multivariate approach? What do they mean by "satisfactory agreement"? What was the metric used to assess this? How sure are you that you got the "right" combination of adjustments given the non-linear response that one could get from these changes? These questions might have an answer in the Lei et al. (2007) paper, though I believe that the issued is so relevant, that further comments are needed in this paper.

[RESPONSE]: We have added a brief description of the estimation procedure: "In brief, first, a spatially and temporally resolved and chemically speciated initial emission estimate was constructed from the annual emissions in the official emission inventory; second, the initial emission estimate was then adjusted based on the RAMA observations of CO and NOy and the MCMA-2003 field measurements of speciated VOCs. Model runs with varying emission scaling factors for each gaseous primary

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model species were repeated and simulated, and morning rush hour (6-9 AM) concentrations of CO, NOy and speciated VOCs were compared with measurements until a good model-measurement agreement for these species was reached. The comparisons were carried out for all primary model VOC species except higher aldehydes (CCHO and RCHO) whose measurements were unavailable or incomplete".

As illustrated this is a one-at-a-time adjustment approach (in fact emissions of multiple species can be adjusted at the same time). Since the comparison was made primarily during the morning rush hours for each (lumped) primary species (no O3 was involved), there was no or little nonlinearity involved, and hence there is no " the right combination" issue. "Satisfactory agreement" has been reworded to "good agreement".

6.2 Following the above discussion, authors indicate that from Figure 2 it can be implied that they got "good agreement" between VOCs observations and simulated values. Be more quantitative (how "good" is "good"?), and compare with what others have obtained elsewhere. Clarify in Figure 2 what the lines represent (1-sigma values? 2-sigma? max and min?) What episode is being presented in Figure 2? Throughout the paper, the term "uncertainty" is used to express the plausible error in the emissions. I have trouble with how the authors are using the concept of uncertainty.

[RESPONSE]: The "good" agreement can be checked through visualization alternatively; actually we have done linear fitting between observed and simulated 6-9 AM concentrations for species in Fig 2 (not shown). This figure summarizes the comparison for lumped alkane, olefin and ARO2, in fact model species ALK1-5, ETHE, OLE1-2 and ARO1-2 were checked individually. For most species, the slopes were better than 0.8. The error bars in Fig 2 have been clarified as 1-sigma std dev. The comparison was made during the Cold Surge and O3-North episodes (clarified), although measurements were not available every day during these episodes (each data point in the scatter plot represents the data of one day). Since the word "uncertainty" was not correctly used rigorously, we have change the wording in the text.

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6.3 Given that they refer to the uncertainty of an empirical quantity, it is expected that a corresponding probabilistic analysis accompanies the description of the variable. For example, in P. 12058, line 5, authors state that "...are accurate (within 10P. 12058, line 12. It is not clear what is meant by "variations in different EI base years and locations". The modeling is conducted for the year 2003, so why are there different. base years? Was a location-by-location analysis conducted? This is not presented.

[RESPONSE]: "uncertainty" has been avoided in the text relevant to emissions, and the range of the adjustment factors has been removed (see the response to Referee #1's comment #2). The initial 10% was referred to the variation of the range (0.9-1.1).

6.4 A statistical model performance evaluation is conducted for O3, NOy, and CO. Similar values should be presented for VOCs given the availability of the data

[RESPONSE]: Due to the limited sampling size of the VOC data (even though it has been increased significantly compared to the study for the O3-South episode) and the concentration variation (see the 1-sigma values), it is not very appropriate to do similar statistical analysis as for CO and NOy, which had routine measurements for every hour of every day in about 20 RAMA stations. Instead a simple 1-sigma was presented.

7. P. 12059, line 1. How does Figure 4 shows that "O3 was too high because the simulated component (gap flow) was too weak...". Could there be another reason besides the weak gap flow to this observation in the model performance? Any reason why the met model did not capture accurately the prevailing wind conditions on April 10 and 26?

[RESPONSE]: For April 10, it could be due to emissions, but it would be very hard to justified why the emissions would change significantly only on this ordinary day; in contrast, it is more likely due to the wind field. We have softened the tone by stating that the wind field is the probable reason. For April 26, by examining the shift of the high O3 zone, it is easy to blame the wind field. The MM5 simulation was carried out month-wise instead of focusing on a specific day, therefore it is not surprising that the

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meteorological simulation did not do well for some days, particularly for the Cold surge episode in which cloud and rain occurred frequently. The reason why the met model did not capture accurately the wind field (the prevailing wind condition was well captured as a matter of fact) could be due to the problems in the parameterization of the complex land use and PBL, which is beyond the scope of this study. De Foy et al. (2006) has presented the model performance and discussions.

8. P. 12059, line 16. Model performance was "reasonable". What is the benchmark used to make this statement?

[RESPONSE]: Except for O3 which EPA has recommended benchmarks, we are not aware if there are exact benchmarks for CO and NOy. We hope Table 2 can give the reader ideas about the model performance. We have deleted the sentence "The various statistical analysis indicate that O3, CO and NOy were reasonably well simulated, particularly O3."

9. Fig. 5. The way the figure was constructed does not allow getting a clear interpretation of the results. There is high degree of scatter and overlapping of the data clouds. Averaging or other techniques of data reduction might help. 10. Fig. 6. Same comment with respect to Figure 5; too much overlapping limits the interpretation of the plot. Try to use a data reduction technique.

[RESPONSE]: Data points in Figs 5 and 6 have been diluted by using every 3rd data points (see response to comment #11 from Referee #1).

Minor comments:
P. 12054, line 6. I recommend not including the terms in parenthesis (Cold Surge, O3-North, and O3-South). There is no need to be so specific in the abstract.

[RESPONSE]: They have been deleted.

P. 12054, line 8. Instead of using the term "weakly", be more quantitative. First paragraph of the introduction: Review the wording. It seems that the authors are referring to

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photochemistry of polluted air; though, as written, one might indicate that when referring to the photochemistry of the natural troposphere one does not talk about "pollutant precursors".

[RESPONSE]: The effects of meteorology are really hard to quantify; some data points (a small fraction though) do show the influence of the meteorology, hence we indicate this qualitatively. As for the wording of photochemistry, we have specified to photochemistry in "polluted" troposphere or "polluted" atmosphere in the revised abstract and introduction.

P. 12056, line 10. "...improve out understanding of air pollution in megacities." This gives expectations that cannot be satisfied. The comment should be limited to understanding air pollution in Mexico City, which is the objective of the paper.

[RESPONSE]: We have changed the word megacities to Mexico City.

P. 12055, lines 28-29. "evolution" instead of "evolutions". "...response of the urban plume.": response to what? Please clarity.

[RESPONSE]: We have changed accordingly. It is the response to the emission reduction.

P. 12057, line 20. Show on a map the location of the sites where the VOC samples were obtained.

[RESPONSE]: The three sites (CENICA, MER and IMP) are added in the upgraded Fig. 4 (also see the response to comment #10 from Refree #1).

P. 12060, lines 7 and 10. Change "...episode is..." for "...episode are..."

[RESPONSE]: Done.

P. 12060. Figure 7 is mentioned before Figure 6. Line 14: Figure 7 does not reflect what it is being discussed in the text.

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[RESPONSE]: "(Tab. 2, Figs 3 and 7)" has been changed to "(Tab. 2 and Fig. 3)" .

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