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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.

W. Lei et al.

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Response to Comments from Referees

We would like to thank the referees for valuable comments that greatly improve the quality of the manuscript. Changes are made accordingly as follows.

Response to Referee #1

(1) Regarding the symbol of LN. We have corrected the definition of LN, and a new symbol of LN' is added in Table 3. And accordingly LN and LN' are properly used in the text (Eq. 1,2,3, and Fig. 8 (original Fig 7) axes.

(2) Back and forth switching of REP-8 sites and the larger urban region: As the referee

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points out that the conclusions drawn from the REP-8 sites may not be applicable to a broader area, now we have presented all our results in the urban region except in Figs. 4 and 12 (original 11).

(3) Proportionality between P(Ox) and Q1/2. We have changed it to the proportionality between P(Ox) and Q. Our previous proportionality was purely based on the data itself, not on the radical chemistry.

(4) p 7964,"were updated ever since wherever possible". Specifications are made.

(5) p 7968, max O3 comparison due to wind problem or speed of photochemistry problem. We conducted test runs of these factors, and test results are added to the text. We tend to think it is primarily due to the former, and the interactions between these 2 factors may magnify the disagreement.

(6) p 7969, choice of the REP-8 stations. This is clarified in the text as "with less influence from nearby local emission sources".

(7) p 7970, explanations of Nighttime NOy hangover. We change the statement. (Our initial rational was that if the overprediction of NO2 was due to the emissions, then we should have seen the overprediction of NO, which did not occur. But we neglected the fact of the NOx "activity"–the NO-NO2 interconversion and other chemical transformation at night -Thanks for the questioning). After comparing the NOy/CO ratios derived from the emissions and from the simulations, we are quite sure the NOy "residual hangover" (the part other than that due to PBL mixing) is due to the relatively larger fractional emissions of NOy (compared to CO) during nighttime and very early morning.

(8) p 7971, lines 16-20, Statement on the VOC emission adjustments. It applies to both this study and Velasco et al (2006), and is clarified in the text.

(9) p 7972 Eq 1, corrected.

(10) p 7972 Eq 2 criterion, corrected.

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(11) Section 3.2.2 domain of Fig 7, results are presented in the urban area, see (2).

(12) p 7973 The explanation of the P(Ox)-NOx relationship. Thanks for providing the explanations, and they are used in the text.

(13) p 7974 P(Ox) ˜ Q1/2, corrected, see (3).

(14) p 7976 We have not carried out the HCHO partitioning study yet using CAMx (will be doing in the near future). But according to Garcia et al. (2006, ACP, 6, 4545-4557), in our sampling time window (12-17PM), the HCHO primary source should still be secondary.

(15) p 7977 High OPE points are unlikely VOC-limited. We agree. As a matter of fact, Fig. 13 (Fig. 12 original) suggests that most of these high OPE points are from the south-southeast part of the urban analysis area.

(16) p7978 enhancement time and peak time. We have clarified in the text.

(17) p 7978 Missing reactivity and missing radical sources. “Missing reactivity” has been removed.

(18) p 7980 Should be Fig 3. Corrected.

(19) p 7981 “ should be contrasted with the NOx-only reduction case”. There are descriptions of the referred figure in the text (p7980 l 27-28 original).

(20) Response of P(Ox) to a 30% reduction in NOx. Likely, but since we have not done the test run, we don’t know the answer yet.

(21) lats and lons in Figs 1-3. Lats and lons are labeled in Fig 1. Topography is also added in Fig 1a to facilitate the identification of the MCMA area. We change the notation of “City Limit” to “Urban Analysis Area” to designate the central urban area where mos of the monitoring stations are locatedThe location of the 2003 campaign supersite CENICA is added. We have considered referee’s suggestion of adding the locations of MILAGRO supersites T0, T1 and T2. To do so we would have to have

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reference in the text to the MILAGRO campaign not related to this study, which would make this fairly long paper longer; without the reference the addition would confuse some general readers. Therefore we decide not to include these locations.

(22) Figure 10 (new Fig 11): The color code has been changed and the quality of the figure has been improved.

Response to Referee #2

General comments One major concern of the referee is about the novelty of our ozone modeling study in Mexico City. First, as we are aware of, there are very few, if not none, 3-D O3 modeling studies that are constrained by as comprehensive O3 precursor field measurements (CO, NOx and VOCs) as we have done, particularly speciated VOCs. These measurements should greatly reduce the emission uncertainty of precursors especially VOCs, which is a major uncertainty in O3 modeling. Therefore we expect the conclusions drawn from our study will be more reliable. Second, we attempt to distinguish our study from many other 3-D modeling studies in characterizing the O3 photochemistry by using O3 photochemical formation rate (P(O3)) instead of O3 itself. P(O3) provides more insight of the O3-NOx-VOC chemistry than O3 itself, and it is relatively less prone to transport compared to O3 itself, and thus the uncertainty in the results due to the uncertainty of meteorological input can be reduced to some extent. Finally, we focus our analyses on the afternoon hours by which we believe we are in a better position to evaluate the sensitivity of O3 formation to VOC and NOx, because during this time period the O3 formation in urban plumes tends to be more NOx-limited by nature. From the arguments of possible heterogeneous sources of radicals and the conclusion from this paper of VOC-limited (or radical-limited) midday O3 formation, it would be intriguing to dig into the radical budget issue, which we are planning to undertake.

Another major comment of the referee is about the small model domain. We think there may be a misunderstanding here and we believe our model domain is quite adequate

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for our study that focuses on the urban area. First, the domain (160x160 km2) covers the whole MCMA area (and the outer buffer area as well), which well contains the urban area (1500 km2). Second, as shown in Fig. 2, we only have emission data within a very confined metropolitan area, and emissions outside the domain is specified by the chemical boundary conditions (BCs). Consequently expanding the model domain is not expected to significantly improve model performance. Third, one important criteria of determining whether a domain is big enough or not is whether the question of interest is affected by the chemical BCs. We have carefully examined the chemical BCs based on measurements at MCMA boundary stations such that the BCs are close to their real average states. We also tested the impacts of the BCs on the pollutant fields by disturbing the BCs by 50%, and we did not find noticeable influences of most chemical species in the urban area except long-lived species such as CO. Finally, meteorological studies have showed that in general the pollution in MCMA is caused by the same day emissions, due to the fact of the rapid venting out of pollutants and less frequent occurrences of recirculation in the basin.

The Third major issue is about the substandard performance evaluation. We have included 25% and 75% percentile bars/area in Fig. 4; additionally an O3 time series obtained using the initial emissions is added to Fig 4a, which should give a sense of necessity of adjusting VOC emissions. A scatter plot (Fig. 5) of observed vs modeled O3 surface concentrations over all RAMA monitoring stations is also added to the manuscript, in which three performance statistics (normalized bias, normalized gross bias and average accuracy of peak) are also shown. We are pleased with this new plot, as it shows more promising agreement than Fig. 3 does.

Specific comments Origin of the VOC reactivity. Additional wording is included and references are provided. The reason why we use Fig. 8 is, as seen from Eqs (1), (2) and Fig 7, P(O3) is closely connected to KVOC; we try to check which VOC species contribute significantly to the ozone production.

More sophisticated assessment of emission reductions (such as emission changes in

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specific emission sources). We are currently undertaking these tasks.

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