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***Interactive comment on “Reactive nitrogen in
Mexico City and its relation to ozone-precursor
sensitivity: results from photochemical models”
by S. Sillman and J. J. West***

Anonymous Referee #3

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General comments

In this paper the authors examine the relation between reactive nitrogen and secondary species and ozone-NO_x-VOC sensitivity in Mexico City (MC) based on CIT modeling for the year of 1997, and compare with those in other cities they studied previously. Their results show that while some indicator relations established previously still hold for Mexico City, such as the ratios of H₂O₂/HNO₃ and O₃/NO_y, many indicators behave differently, such as higher PAN/O₃ and O₃/HNO₃, due to high organic nitrate production and low HNO₃ formation. They also found a mixed sensitivity of O₃-NO_x-VOC chemistry in MC domain-wise, different from recent model- and measurement-based studies, which they attribute to changes in emissions over time. The paper

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is well written, and contains important scientific merits, particularly the O₃ precursor sensitivity-classified indicator analysis. I suggest publication after the following issues are addressed.

A major concern is that the entire modeling results and conclusions are based on the CIT simulations of West et al. (2004), in which an emission adjustment of a factor of 3 for VOCs and a factor of 2 for CO (3VOC, 2CO) was applied to the 1998 official EI, and a small model domain of 19x20 grids was configured.

The emissions adjustment has been subject to debate (e.g., see Velasco et al., 2007; Lei et al., 2007, 2008; Stephens et al., 2008). A quick check of the official EIs shows that surprisingly there were no significant changes in emissions of CO, VOC and NO_x between 1998 and 2002 (< 13%). This leads to the questioning that some other factors may affect and/or contribute to the difference in emission justification in West et al and Lei et al, such as the chemical boundary conditions (BCs) and excessive vertical diffusions used in the CIT. It appears to me that either the justification of 3VOC and 2CO needs to be further substantiated, or the conclusions in this paper need to be emphasized on this emission premise which is subject to a probable significant uncertainty.

In addition, the small model domain used in this study makes the results and conclusions susceptible to the influence of the chemical BCs. I presume that the authors used same BCs for all model runs. For such a small domain, changes in BCs according to the emissions seem to be necessary, and examinations of the effect of the BCs on the O₃-precursor sensitivity would be helpful to clarify and solidify their findings.

Specific comments

(1) In the analysis model data were sampled on the whole model domain. Due to the small model domain and consequently the probable BC effects, it would be more reasonable to exclude data from grids near the model boundaries, e.g., at least 4 grids from each boundary side should be excluded.

(2) Regarding the comparison of mixed O₃ sensitivity vs predominant VOC-sensitive

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condition in Lei et al. (2007), some clarifications are needed: (a) locations are different-domainwise here vs urban region (near source) in Lei et al. (2007); (b) Lei et al. (2008) also find that the O₃ sensitivity evolves with chemical aging in the pollutant plume (fig 10), showing the change of O₃ sensitivity with location and time. Therefore the comparison should be made in the same area (urban), which would also reduce the possible BC effect to some extent on the O₃ sensitivity. If the O₃ sensitivity difference remains in this updated comparison, then the authors could discuss the possible causes, such as emission change, chemical BCs, excessive vertical mixing, grid resolution, etc. Regarding whether the emission change is the primary driving force for the difference in the O₃ sensitivity (assuming the difference remains), a quick test would be using the same emissions as those in Lei et al. (2007) or using the same model (CAMx in Lei et al.) with 1997 emissions for the verification.

(3) Emission change in West et al (2004) and Lei et al (2007). Just a reminder- the change includes not only the different VOC/NO_x ratio, but also the different reactivity-weighted VOC/NO_x ratio. A uniform factor of 3 adjustment in West et al. (2004), and small adjustments in higher reactive VOCs (olefins and aromatics) in Lei et al. (2007) and different VOC speciation in these two studies should lead to a significant difference in the VOC reactivity.

(4) High PAN concentration in MC explained by temperature. Possibly it is more than just due to the temperature. Marley et al. (2007) report a dramatic reduction in PAN levels observed in 2003 compared to 1997, which they attribute to the reduction in reactive VOC emissions over time due to the recent enactment of emission control strategies. In addition, Lei et al. (2008b) find high HCHO emission rates in MC. Although they have no discussions on the CH₃CHO (a PAN precursor) emissions, it could shed light on the possibility of high PAN precursor emissions in MC.

(5) Fig 3 and relevant text: Although there is a general separation trend for NO_y in different sensitivity regime, there seems to be a broad overlap zone too, most evident in fig 3c.

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(6) Fig 6 and relevant text (p20514-20515, p20523, etc): there is hardly any clear correlation between HNO₃ and H₂O₂ in the VOC-sensitive regime in figs 6a and 6d. How was the H₂O₂/HNO₃ ratio number derived?

(7) Fig 7, p 20522 and p 20524 on low NO_x: the excessive vertical mixing (especially at morning hours) in the CIT would also lead to low afternoon NO_x, and could shift the O₃-precursor sensitivity towards NO_x-limitation.

Technical issues

(1) p20507 l10: change “on 2, 14, and 14 March”; to “on 2, 4 and 14 March”?

(2) p20521 l27: change Let et al to Lei et al.

(3) p20516 lines 16 and 21 (maybe other places too), change “.” to “/” in the ratio notation for consistency.

References

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