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Atmospheric Chemistry and Physics Discussions

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

S. Sillman and J. J. West

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We want to thank the referee for the many thoughtful comments and suggestions, and in particular for bringing our attention to journal articles that we had overlooked. Here are responses.

Response to General Comments:

The reviewer's main concern was the appropriateness of the emissions adjustment from West et al., 2004, and also the possible influence of the chemical boundary conditions (BCs). We have added discussion and caveats to address this, as described below.

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Emissions adjustment: We agree with the reviewer that the emission adjustment relative to the base case inventory (3X VOC, 2X CO) is subject to debate. The discussion in Section 5.3 is intended to make this clear, and also makes clear that predictions for ozone-precursor sensitivity depend on this assumption. We have revised this section and also modified the abstract and conclusions to emphasize the uncertainty in emissions.

The factor-of-3 adjustment was extensively documented in West et al., 2004. This included comparisons with measured total VOC and speciated VOC at three sites in Mexico City. A similar finding about VOC emission inventories was also reported by Arriaga-Colina et al. (2004). The subsequent analyses by Lei et al. (2007) and Velasco et al. (2005, 2007) do provide a basis for questioning whether the the factor-of-3 increase from West et al. is too high, but these analyses also have large uncertainties (made clear in the articles themselves). We do not think we need to revisit these issues, as the current manuscript does not add new understanding of the issues.

The reviewer noted that there was little change in emissions between 1998 and 2002 in emission inventories for Mexico City. However, there is considerable measurement-based evidence suggesting a reduction in VOC emissions over this period, including Zavala et al. (2008) (cited in the text), Stephens et al. (2008), and Marley et al. (2007). There were also significant differences in the VOC:VOC and VOC:NO_y ratio in measurements from West et al. (2004) and Lei et al. (2007), on which they based their emission adjustments for the 1997 and 2003 events.

The reviewer mentions the possibility of excessive vertical mixing in the CIT model. This may be based on a suggestion from Velasco et al. (2007). Velasco et al. reported that the CIT with a factor-of-3 emissions adjustment showed good agreement with measured olefins and other VOC species, and speculated whether the good agreement could be due to the compensating effect of too-high emissions and too-strong vertical mixing. However, the model-measurement comparison in Velasco et al. (2007) showed good agreement throughout the afternoon time period. Vertical mixing is rapid during

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the afternoon (e.g. Velasco et al.,2008) and vertical dilution is controlled primarily by the height of the mixing layer rather than the model mixing rate. Comparisons between model and measured VOC:NO_y ratios reported by West et al. (2004) also support the factor-of-3 emissions adjustment and are less sensitive to possible errors in vertical mixing. We think that the question of mixing rate accuracy does not need to be addressed here, but we have added a caveat to the text (see 2 paragraphs below).

Lastly, we note that the main conclusions of the manuscript are not affected by uncertainties in the emission inventory. The manuscript seeks to identify measurements that might be used to identify VOC-sensitive and NO_x-sensitive photochemistry. If anything, this gives further emphasis to the question of emissions uncertainty.

The text has been modified as follows (at page 20522 in original ACPD paper):

The most likely reason for the difference in sensitivity predictions between West et al. (2004) and Lei et al. (2007) is the decrease in VOC emission rates and VOC/NO_x emission ratios between 1997 and 2003. Results from Zavala et al. (2008) suggest that CO and VOC emissions from mobile sources decreased by approximately 40% over this time period while NOx emissions remained unchanged. Marley et al. (2007) also reported evidence of a significant decrease in emissions of light olefins based on changes in ambient PAN concentrations. Other possible reasons for the difference include different estimations of VOC emissions and different meteorological conditions during the simulated events. It has also been suggested that vertical mixing is too rapid in the CIT model used here (Velasco et al., 2007), which can also lead to a more NO_x-sensitive simulation, but West et al. (2004) report good agreement with NO_y measurements, suggesting that errors in vertical mixing may not be large.

West et al. (2004) and Lei et al. (2007) both increased VOC emissions with respect to their base inventories, but Lei et al. increased emissions by 65 % whereas West et al. increased emissions by 200 %. The resulting total VOC emissions were 1425 kton per year in West et al. and 900 kton per year in Lei et al. The lower VOC emissions

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in Lei et al. result in a more VOC-sensitive model. The adjustment by Lei et al. also varied for individual VOCs, including a factor-of-9 increase for HCHO and no increase for alkenes. The resulting VOC speciation differed from West et al. West et al. and Lei et al. both evaluated their model results using measured O_3, VOC and NOy and both interpreted the available NO_x measurements as representing NO_y. The smaller emissions adjustment used by Lei et al. were also supported by measurement-based analyses, although with some uncertainty (Velasco et al., 2005, 2007). It is also possible that the different emissions adjustments used by West et al. and Lei et al. reflect reductions in ambient VOC between 1997 and 2003. Accuracy of the emission inventory (including both total VOC, VOC/NO_x ratios and VOC speciation) has historically had a large impact on model predictions for ozone-precursor sensitivity (e.g. Pierce et al., 1998).

Boundary conditions: The reviewer is correct that the same boundary conditions were used in all simulations in this study. The possible impact of chemical boundary conditions was already discussed in West et al. (2004). Both West et al. (2004) and Lei et al. (2007) found that boundary conditions had little influence on their results (assuming a reasonable range of values). In particular, both studies concluded that boundary conditions would not affect the conclusions about emissions. They also found little impact on ozone production.

Response to Specific Comments:

1. The reviewer suggested that grids near the model boundaries should be excluded from the analysis. We have effectively done something very similar. Most of the analysis is based on the model response to reductions in VOC and NO_x and excludes locations with changes in O_3 below 5 ppb. This effectively eliminates locations near the upwind boundary that do not have significant photochemical production or loss of O_3 through processes within the model domain. Concentrations near the downwind boundary reflect photochemistry and transport within the model domain rather than the boundary and do not need to be omitted. Finally, the results in Figure 1 are presented

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in the form of species correlations. In this type of display the near-boundary locations show the 'starting values' at the model boundary (showing the boundary values of O_3 and NO_y). Properly interpreted, this is useful information and does not need to be omitted.

The reviewer specifically recommended omission of locations within 4 grids of a model boundary. Omission of the outer 4 grids is commonly done for prognostic meteorological models which provide input for chemistry/transport simulations, but it is usually not necessary for the chemistry/transport simulation itself. Our simulations of chemistry and transport are not near the boundaries of the much larger meteorological simulations.

2. The reviewer referred to several differences between the model set-up in West et al. (2004) and Lei et al. (2007).

First, the model domains are different. While this has some effect on results, there are large differences in predicted O_3-precursor sensitivity for the urban center, and also for predicted O_3-precursor sensitivity associated with peak O_3. In each case, Lei et al. found predominantly VOC-sensitive conditions while West et al. found mixed conditions, including some NO_x-sensitive conditions. For example, contrast the result for 15-16h in Figure 2(b) of this manuscript with Figure 12 in Lei et al., 2007. Figure 2(b) shows that ozone responds more strongly to reduced NO_x than to reduced VOC throughout our entire model domain at 15-16h, while Figure 12 in Lei et al., 2007 showed a stronger response to reduced VOC. This cannot be attributed to different domains or locations.

The reviewer pointed out that Lei et al. (2008) have also discussed the tendency towards NO_x-sensitive conditions later in the day as the Mexico plume moves downwind. This is an important finding, which we had overlooked. We have added discussion of the progression towards NO_x-sensitive conditions as the plume moes downwind, citing Lei et al. (2008), in the text. However the results from Lei et al. (2008) still show

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VOC-sensitive conditions for the Mexico City urban area. This is stated clearly in Lei et al. (2007) in the discussion of Figures 7 and 12. (Lei et al. 2008 used the same model results.) So there is no question that the ozone-precursor sensitivity results are different for the models by West et al. and Lei et al.

The suggestion that the different results are due to boundary conditions is unlikely, given that both West et al. and Lei et al. tested the model response to boundary conditions, and that emission rates within the model domain used by West et al. greatly exceed rates in the surrounding area.

The reviewer asked us to repeat our simulation using the same grid and emissions as in Lei et al., or using the same model (CAMx) as used by Lei et al. While these types of direct model intercomparisons are useful, they are beyond the scope of this study.

We have included the possibility that excessive vertical mixing may cause the CIT model to be NO_x-sensitive (see response to general comments above.)

We have added the following discussion to include the results from Lei et al., 2008 (at p. 20521, line 24 in the original ACPD text):

Lei et al. (2008) also reported a shift towards NO_x-sensitive conditions later in the day associated with photochemical aging in the plume downwind from Mexico City.

We have also expanded the discussion of NO_x/NO_y (p. 20522, line 25 in the original ACPD manuscript) as follows:

The VOC-sensitive response in Lei et al. was associated with NO_z/NO_y equal to 0.7 or lower (equivalent to NO_x/NO_y equal to 0.3 or higher), and the region with low NO_x/NO_y coincides with high O_3. In the model by West et al. high O_3 coincided with NO_x/NO_y from 0.2 to 0.6 and the lower values ($NO_x/NO_y < 0.4$) had NO_x-sensitive chemistry. In addition to having lower NO_x/NO_y, the model by West et al. predicted NO_x-sensitive chemistry for somewhat higher NO_x/NO_y than was reported by Lei et al. (2007, 2008)

3. The reviewer reminded us about the importance of VOC speciation and reactivity-

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weighting. We have added a description of the different speciation between West et al. and Lei et al. (see revised text in response to general comments, above).

4. The reviewer described results from Marley et al (2007) with regard to PAN and VOC. We thank the reviewer for bringing our attention to the results of Marley et al. We have added discussion of these results in Section 5.1 and changed the wording so that the high PAN is not attributed solely to low temperatures.

The revised text (modified at p. 20516, line 25 in the original ACPD):

... Another possibility is that the speciated VOC in Mexico and in Paris contained a higher proportion of specific precursors of PAN than the VOC in Nashville. This is a likely possibility for Mexico because subsequent measurements showed large decreases in both PAN and the PAN/O_3 ratio, as a result of large reductions in emission of light olefins (Marley et al., 2007).

While these are possibilities, the differences in PAN and PAN/O_3 can also be explained by the influence of temperature on the PAN decomposition rate....

5. The reviewer wrote that there is significant overlap between sensitivity regimes in Figure 3. There is certainly overlap between locations categorized as 'NO_x-sensitive' and 'mixed', and also between 'mixed' and 'VOC-sensitive'. This is inevitable, because these categories are directly continuous with each other. It is certainly not possible to expect no overlap between categories that can include locations with very little differences in predicted sensitivity. However, there is almost no overlap between locations characterized as 'NO_x-sensitive' and 'VOC-sensitive'. The discussion of Figure 3 is expressed in these terms.

In Figure 3c, regarded in isolation, NO_x-sensitive locations all have NO_y below 20 ppb, while all VOC-sensitive locations have NO_y above 20 ppb, so there can be no question of overlap. It is somewhat more relevant to compare the VOC-sensitive region in Figure 3c with NO_x-sensitive regions at different times, which include higher NO_x and

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may have overlap. This is shown in Figures 3(g) and 3(h). Figure 3(g) shows a large separation between NO_x-sensitive and VOC-sensitive regions with a small number of exceptional locations (VOC-sensitive locations in the NO_x-sensitive region and vice versus.) Referring again to Figure 3c, the VOC-sensitive locations most likely to 'overlap' have 25 ppb NO_y and 115 ppb O_3. There are a small number of NO_x-sensitive locations in Figure 5g with 25 ppb NO_y and O_3 as low as 120 ppb, which is the closest to an overlap. There are somewhat more locations with 25 ppb NO_y and O_3 at 120 ppb in Figure 3h. All this is consistent with the description of Figure 3.

6. The reviewer asked about the lack of correlation between H_2O_2 and HNO_3 in Figure 6. Here it is important to distinguish between the ratio between species and possible correlation. We found a large difference between predicted H_2O_2/HNO_3 ratios between NO_x-sensitive and VOC-sensitive locations, but not necessarily a correlation between H_2O_2 and HNO_3. Similar results were reported previously for other locations (Sillman and He, 2002). We have tried to make this clear by distinguishing between the terms 'correlation' and 'ratio'.

We have added the following to the paper:

As in previous studies (Sillman and He, 2002), there is little correlation between H_2O_2 and HNO_3 except possibly in subregions with either uniformly NO_x-sensitive or uniformly VOC-sensitive conditions. However there is a large difference in H_2O_2 and HNO_3 values associated with NO_x-sensitive and VOC-sensitive chemistry.

7. The reviewer suggested that excessive vertical mixing in the CIT could bias the model towards NO_x limitation. A note to this effect has been added (see revised text in the response to general comments above).

References:

Velasco, E., Márquez, C., Bueno, E., Bernabé, R. M., Sánchez, A., Fentanes, O., Wöhrnschimmel, H., Cárdenas, B., Kamilla, A.,Wakamatsu, S., and Molina, L. T., At-

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