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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

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The reviewer made a number of suggestions for additional model sensitivity tests and analysis. Here are responses.

1. The reviewer discussed NO_z extensively and suggested that the paper should focus primarily on NO_z. From these comments, it appears that the reviewer may have misunderstood some of the results. We have modified the introduction to clarify this.

The purpose of the study is not to identify species that are strongly correlated with each other, such as O_3 and NO_z. Instead, it is to find species that consistently show different values in model locations that are predicted to have NO_x-sensitive chemistry, as opposed to the values in locations that are predicted to have VOC-sensitive chem-

istry. These species may also show strong correlations in plots such as Figure 1, but the correlations are not necessary.

For example: consider the results for O_3 and NO_z in Figure 4(d). The model predicts a strong correlation between O_3 and NO_z, but the correlation is virtually identical for NO_x-sensitive and VOC-sensitive locations. This means that a model may show good agreement with the measured O_3-NO_z correlation even if its predictions for O_3-precursor sensitivity are incorrect.

By contrast, consider the results for H_2O_2 versus HNO_3 (Figure 6c) and for O_3 versus NO_x (Figure 7c). These species are not strongly correlated. However, the NO_x-sensitive locations in the model show very different values for these species in comparison with the VOC-sensitive locations. This means that measured values for these species, if compared to the NO_x-sensitive and VOC-sensitive patterns in the figures, provide an indirect evaluation of the accuracy of model predictions for O_3-precursor sensitivity. If (for example) a model predicts primarily NO_x-sensitive chemistry for Mexico City but the measured O_3 versus NO_x coincides with the VOC-sensitive locations in Figure 7c, it strongly suggests that the model O_3-precursor predictions are incorrect. This is not foolproof, of course, but corrections to the model to improve the model-measurement agreement for O_3 versus NO_x would be likely to change the predicted O_3-precursor sensitivity as well.

We have modified the introduction to clarify this.

2. The reviewer requested various additional model results, including the following:

(i) Repeat the model using similar emissions as in Lei et al., 2007.

(ii) Rerun the model with different temperatures.

(iii) Rerun the model with different vertical transport.

(iv) Add tracers to identify the size of different radical sink rates.

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8, S11779–S11781, 2009

Interactive Comment

(v) Run tests for the impact of initial/boundary conditions on results.

(vi) Show results with NO_x and VOC emissions reduced by a smaller amount (rather than 50%).

These are all good suggestions, but they are well beyond the scope of the present study. We believe that the current results are valid and useful without these additional tests, especially for our conclusions relating indicator species and ratios to the model ozone-precursor sensitivity.

In the case of emissions changes: we have run tests with lower VOC emissions (not identical to Lei et al., but in that direction). These result in a more VOC-sensitive simulation, and the predicted species correlations such as O_3 versus NO_x also shift in the direction associated with VOC-sensitive conditions (as identified in Figure 7c, for example). We found, for example, that ambient NO_x increases significantly in a model with lower VOC emissions and unchanged NO_x emissions. This is consistent with the higher ambient NO_x in the VOC-sensitive simulation described by Lei et al.

Vertical transport is generally determined by hour-by-hour and day-to-day meteorology. We have already included a range of conditions over the three modeled events.

The impact of boundary conditions was discussed in West et al., 2004. Results showed little sensitivity to initial and boundary conditions, so long as boundary values were within a reasonable range. Lei et al., 2007 reached a similar conclusion.

The 50% reduction in NO_x and VOC has been a standard basis for presenting model results, both in Mexico City and elsewhere. Our interest here is to distinguish broadly NO_x-sensitive conditions from VOC-sensitive conditions, in order to identify ambient concentrations associated with each. These designations are unlikely to change for different percent reductions.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 20501, 2008.