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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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We want to thank the reviewer in particular for the many positive comments.

Here are responses to some issues raised by the review.

General comments

1. The reviewer discussed the 2006 observations and noted in particular that the observations show that PAN is high and HNO_3 is low. We do not currently have access to this data, but the quoted results are especially interesting. We have added some discussion of measured PAN from Marley et al., 2007, at the suggestion of Referee 3. Marley et al. found that PAN and PAN/O_3 ratios during the 2003 campaign were both

much lower than in 1997. The PAN/HNO_3 ratio may be lower also, but we have not seen direct measurements to show this.

2. The reviewer made some interesting comments about the evolution from VOC-sensitive conditions to NO_x-sensitive conditions between the hours of 12-13 and 15-16. He/she noted that model peak NO_y decreases significantly between 12-13 h and 15-16 h, and that greater dilution due to vertical mixing can lead to more NO_x-sensitive conditions.

We have added a brief discussion of the reasons for the shift to NO_x-sensitive conditions. There are several possible causes: greater vertical dilution (as suggested by the reviewer); photochemical aging; and higher biogenic VOC emissions (although this may have less significance for Mexico City). The large decrease in peak NO_y between 12-13 h and 15-16 h(from 60 ppb to 25 ppb) only occurs on March 4 and may be due to the specific meteorology on that day (with higher wind speeds during the afternoon). Peak NO_y also decreased on the other two days, but the decrease was smaller (from 45 to 35 ppb on March 2 and from 40 to 35 ppb on March 14).

The discussion in the paper on page 20521, lines 19-21 was intended to highlight the difference between the response of O3 concentrations and the response of the instantaneous production rate for O_3. If the instantaneous production rate shifts from VOC-sensitive in the morning to NO_x-sensitive during the afternoon (a common pattern), then the sensitivity for O_3 concentrations will shift several hours later. We have modified this paragraph to make it more clear.

The revised text is as follows:

Results also suggest a shift from a primarily VOC-sensitive environment before 14h to a more NOx-sensitive environment after 16h. The instantaneous production rates for O3 in the model (as opposed to the O3 concentrations) shift from being primarily VOC-sensitive in the morning to primarily NOx-sensitive after noon. This prediction might be tested though evaluation of instantaneous production rates based on measured NO

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and HO2 (as in Shirley et al., 2006). A shift from VOC-sensitive conditions during the morning hours to NOx-sensitive conditions during the afternoon has been found previously in many locations (e.g. Milford et al., 1994, Kleinman et al., 2005) and may be due to photochemical aging or to increased vertical dilution.

Specific comments

1. Abstract: We revised the ambiguous sentence as follows:

The model predicts a mixed pattern of ozone-precursor sensitivity in Mexico City, with VOC-sensitive conditions in the morning and NOx-sensitive conditions in the afternoon, in contrast to results from other models for more recent events that predicted strongly VOC-sensitive conditions throughout the day.

2. Boundary conditions and low values of H_2O_2: The reviewer's concern about the impact of boundary conditions on H_2O_2 is important. We have added the following sentence (p. 20515, lines 1-3 in original manuscript):

The low H_2O_2 may be due in part to the model boundary conditions (with zero H_2O_2), although we do not anticipate elevated H_2O_2 upwind from Mexico City.

3. The reviewer asked whether the steady state solution for PAN (Equation 1) applies to the aged plume. Our view is that PAN has a photochemical lifetime of 1 hour or less for the conditions described here, so that the PAN concentration will "chase" the steady-state value with a time lag of less than 1 hour. The PAN concentration should not be exactly equal to the steady-state value (since PAN concentrations change throughout the day), but this provides a good basis for evaluating the behavior of PAN. This is summarized on p. 20506. We expect PAN to approach the steady state solution but not reach it exactly.

4. Elevated PAN and high VOC in Mexico City: The reviewer noted that the abstract and text attributed the high PAN entirely to temperature. We have modified the abstract and the text. Temperature is now presented as a likely contributing factor but not the only

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factor. The conclusion states that the high PAN/O_3 ratio is attributed to temperature, but the next sentence clarifies by stating that the high PAN/HNO_3 ratio cannot be explained by temperature and must be due to different VOC.

We do not expect that propane would contribute significantly as a precursor of PAN. Although propane concentrations are very high in Mexico City, its rate of reaction is slow. Propane accounts for approximately 7% of total VOC reactivity in Mexico (Velasco et al., 2007), slightly less than both propene and ethene. Propene and other light alkenes also have a higher yield of CH_3CO_3 than propane. For these reasons we refer to light olefins rather than propane in the revised discussion.

We are also not convinced that the Mexico anthropogenic VOCs should lead to a higher PAN/O3 ratio than a region such as Nashville that is dominated by biogenic VOCs, because the biogenics are also PAN precursors. However, we agree that the impact of specific VOC on PAN is an important possibility, especially given the results reported by Marley et al. (2007). We have modified the text with this in mind.

Modified text (p. 20516, line 25):

...The Nashville event was associated with a multi-day regional pollution episode with up to 85 ppb O3 in rural upwind locations, so it is expected that rates of ozone production would be lower in Nashville than in Mexico for a given O3 concentration.

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/O3 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/O3 can also be explained by the influence of temperature on the PAN decomposition rate. Maximum surface temperature during the model events ...

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