Atmos. Chem. Phys. Discuss., 8, S10547–S10550, 2009
www.atmos-chem-phys-discuss.net/8/S10547/2009/

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

Anonymous Referee #2

Received and published: 20 January 2009

Review of “Reactive nitrogen in Mexico City and its relation to ozone-precursor sensitivity: results from photochemical models” by Sillman and West for ACPD

This is an ambitious article that discusses unique features of the Mexico City nitrogen budget and its impact on the sensitivity of O3 to NOx and VOCs. The analysis is very well thought out. No hand waving here. There is a direct connection between high formation rates of PAN and the indicator ratios found in Mexico City. There are many items that are treated in a sentence or two which could have major implications for others doing sensitivity analysis.

The main conclusion is that in 1997, O3 production in Mexico City was VOC sensitive

in the morning and NOx sensitive in the afternoon. There have been measurement campaigns in 2003 and 2006. CTM calculations as well as other analysis methods show a more VOC limited atmosphere in the later years which could, as the authors suggest, be due to changes in NOx to VOC emission ratios. This article does not need to be expanded to treat 2006 observation, but my hope is that such an effort is in progress. Calculations for 2006 would greatly benefit from high quality data on NOz components.

The general comments listed below do not require any modifications to the text, though the authors can certainly make use of whatever is useful.

I recommend publication with minor revisions.

General Comments

NOx budget. NOx budgets have been constructed from C-130 data collected in 2006. Possibly also from ground site observations. Not much of this has been published. From material presented at meetings, which should be publicly available, the 2006 observations show that PAN is high and HNO3 low, in agreement with the current model results. I would be very interested to see if the predicted large contribution of organic nitrates is supported by observations.

Changes in O3 sensitivity between the hours 12-13 and 15-16. Part of the reason is given on Page 20521, lines 19-21. I agree that model results are consistent with instantaneous production rates for O3 shifting from being primarily VOC sensitive in the morning to NOx sensitive after noon. I suggest that this is primarily due to very rapid growth of boundary layer height starting around noon plus dilution due to advection as the urban plume spreads out. NOy is conservative over time periods of hours but there is a dramatic decrease in peak concentrations of NOy from 60 ppb (12-13) to 25 ppb (15-16) (Fig. 1) which can only be due to dilution. NOx reacts away, but the steep decrease in peak NOx with time is probably due primarily to dilution. O3 formed under VOC limited conditions will likewise be diluted. Peak O3 concentrations

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at 15-16 are comparable or larger than peak values at 12-13. This implies that ozone production rates in the 13 – 16 time frame, occurring under under increasingly NOx limited conditions, are rapid enough to keep up with dilution. Dilution controlled ozone sensitivity has precedent in Sillmans Lake Michigan study.

Transition values for NOx and VOC sensitivity Many numbers are presented in the text. Collecting them in a Table might make for easier reference.

Specific Comments

Abstract, lines 25-26 The model with mixed sensitivity predicts much lower.. Ambiguous. Is the reference here to another model, different locations, different years, etc.?

Page 20515, lines 1-3 Low values of H2O2 along with NOx sensitive chemistry. An excellent point that this is due to low values of HNO3 which in turn are due to HNO3 being a smaller fraction of NOz than in other locations. However, at these low levels I have concerns that H2O2 concentrations will depend on model background conditions.

Page 20156, line 15 steady state equations (R1) should be steady state equation (1)

Page 20516, line 26. Low PAN because of low rates of O3 production in aged Nashville plume. This is based on (1) which is a steady state solution. Is it expected that the steady state condition applies in the aged plume? Also, one might expect the Nashville plume to transition from anthropogenic to biogenic VOC precursors as it is advected away from the city. This would change the relation between O3 production rate and [OH][CH3CHO].

Page 20516-20517 line 2. Regarding high PAN formation rates in Mexico City and the statement that it is less likely that the cause is a different VOC speciation. This appears in several places starting with the abstract. Very high propane concentrations have been measured in Mexico City. I assume the authors have done the math showing that propane does not contribute enough CH3CHO to make Mexico City PAN formation distinctive.

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Page 20518, lines 9-11. Neglect of PAN in constrained steady state calculations may pose a problem in Mexico City where PAN is a large fraction of NOx oxidation products. An excellent point.

Page 20520, lines 12-13 the formation of peroxides exceeds formation of HNO3 should be 2 times formation of peroxides

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

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