Atmos. Chem. Phys. Discuss., 8, S1006–S1010, 2008
www.atmos-chem-phys-discuss.net/8/S1006/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characteristics of the NO-NO_2-O_3 systemin different chemical regimes during the MIRAGE-Mex field campaign" *by* Z.-H. Shon et al.

Anonymous Referee #2

Received and published: 26 March 2008

Review of "Characteristics of the NO-NO2-O3 system in different chemical regimes during the MIRAGE-Mex field campaign" by Z.H. Shon et al.

This study presents results on the photostationary state and ozone production efficiency based on measurements taken from the C-130. Results are given for 5 types of air masses. In contrast to other studies, the authors find that the observed NO2/NO ratio is very nearly the same as that obtained from a calculation which uses observed peroxy radicals. The data subsets for which agreement is less good appear to me to have limited statistical significance. The subject matter is appropriate for ACP and should be of interest to a broad segment of atmospheric chemists.

The explanation of methods needs improvement. There are possible flaws in the analysis, i.e. definition of data subsets, uncertainty limits, statistical significance, time of day dependencies. Hopefully these can be easily cleared up. Below are items that need further explanation and/or may suggest changes in methodology.

General comments:

Data handling: The only time scale mentioned in this paper is that reactive nitrogen species and O3 were measured at 1 Hz. More information is needed on how the data was handled. If I add up the number of points in Table 2, I get a number that is plausibly 60 times less than the number of seconds of C-130 flight time. The number of data points in Fig. 1 and other figures are lower than the number of points in Table 1. What is the time resolution of each instrument? How was the averaging done; what averaging time? were instruments put on a common time base, perhaps dictated by the slowest instrument or the need to improve signal to noise? If the averaging time was ˜ 1 minute, how were cases handled in which that minute contained more than 1 type of air mass? What accounts for the lower number of points in Fig. 1(and other figures based in this data)? Given that phi may be an average over roughly 1 minute or longer, was phi calculated with high frequency data, then averaged? Or was phi calculated with averaged data? If the later, what effect do changing concentrations (large variations through narrow Tula or biomass burning plumes) or changing solar intensity (clouds) have on the calculation?

How were night time and high solar zenith angle points handled? There are values of NO2/NO above 10 which must be either very early or late in the day. These points have a large effect on the linear regressions. I would expect that an error analysis would show very high uncertainties for these points.

Is it meaningful to present an average NO2/NO ratio for different air mass types given the dependence that this quantity has on time of day? Some of the air masses have data primarily from a single day, and perhaps from a narrow time window.

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Back trajectories: In Fig. 4, the ending heights of the back trajectories for BL, BB, and Tula air masses are ˜ 5000 – 5500m AGL. Unless there is a typo and you mean above mean sea level, these trajectories end in the free troposphere. 5500 m above sea level is 3200 m above Mexico City. The boundary layer does reach 3200m, at least on some days. But most of the time 3200m will be in the free troposphere. How was it decided which air samples are from the boundary layer and which from the free troposphere?

As to the origin of the air masses, it is probable from the high values of Ox and NOz in marine and free troposphere categories that these air masses had a recent anthropogenic influence This is not unexpected given the C-130's mission to find urban plumes that had aged 1 or 2 days. The high concentration points in these air masses have a lot of influence on the regression slopes. The origin of these air masses needs to be explained.

P2281, lines 6-7, uncertainty range from 23 to 25% for different air mass types. Theses numbers seem to be low. Further, I am surprised that the uncertainty is nearly the same for all air mass types. In general measurements get more difficult at low concentrations.

P2281, interpretation of PSS ratio for BB and TIC According to Fig. 1 there are only 8 BB and 4 TIC points. What is the statistical significance of the results?

Typos and presentation:

p2276, line 5 in Abstract, "indicator" Better to find another word as indicator also has the meaning of indicator species.

P2280, lines 14-23. There are a lot of average and median concentrations. This section might be easier to follow if some or all of the numbers were in a Table, instead.

P2280, Eq. 2. It would help the reader to note that phi $<$ 1 corresponds to 1) calculated NO2 $<$ observed NO2 and 2) observed HO2, RO2 too low to sustain PSS.

P2881, line 10-11 "was not always statistically significant for BL, FTMA, and FTCO"

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Incorrect choice of words? As written, the sentence implies that for each of the sets (BL, FTMA, and FTCO) results are sometimes statistically significant and sometimes not. But that would require that these sets are further split into subsets – which does not appear to be the case.

P2281. line 17-18, "higher (NOx/NOy) ratio compared to other air masses" Not higher than BL which is 0.54.

P2282, lines 5-7. Better to say, Except for the BL samples, the mean NO2 level for the BB was higher than those in other air masses ...

p2282, line 16, "asl" above sea level

P2282, paragraph starting on line 23. All of the PSS results in this paper are of phi. In comparing your results to those in the literature it would be easier reading if the literature values were presented as phi, rather than 1/phi. If you feel it necessary, you could state (maybe in a footnote) that in the papers cited, results are presented as 1/phi. The goal is to make it immediately obvious that your phi is about equal or slightly greater than 1, while the literature results have phi $<$ 1.

p2283, line 16, "correlation intensity" Should be "correlation"

p2284, line 21 "intercorrelated" Is this the correct word?

P2284, line 27, Abstract, and Conclusion "indicating both photochemically young and reactive air masses" As used the meaning is vague. Is an air mass both photochemically young and reactive or are some air masses one and not the other? What makes an air mass photochemically reactive.? If it is a high OPE, what would you call that air mass at an earlier time when it was in the BL and had a lower OPE?

Figures 3, 5 and 6. The insets make these figures difficult to read and are not necessary. I recommend using an axis range that is appropriate for each data set. The reader can be alerted to the change of scales in the figure captions. Alternately, axis breaks can be employed such as in Fig. 1.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 2275, 2008.

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Interactive Comment