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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.

Z.-H. Shon et al.

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REPLY TO REVIEWER #2 General comments: 1. 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

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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? ANS) As key parameters used for PSS calculation, reactive nitrogen species (such as NO, NO2, and NOy), and ozone were measured with 1-second time resolution. For peroxy radicals, HO2 and RO2 were measured with 3-second time resolution. J was measured with 5-second time resolution. 1-min merged data files were created to align species measured with varying time resolutions and these files are used in this study. Detailed information on the MILAGRO Data Policy and Management Plan is given in the web site, http://www.eol.ucar.edu/projects/milagro/data/MILAGRO_DataPolicy.html. The NASA Langley group (Jim Crawford et al.) created merges of the ICARTT-format files. For the data analysis, 1-min merged data sets available on MILAGRO/INTEX-B/IMPEX archive (ftp://ftp-air.larc.nasa.gov) were used for PSS analysis. The difference in data points between Figure 1 and Table 2 resulted from non-coexistence of measurement parameters on a common time base (mainly from the missing data in HO2 and RO2). For the  calculation, 1-min merged data for each variable (J, k, [O3], [NO], [NO2], and peroxy radicals) were used and then  values were averaged. The plots of for BB and TIC in the Figure 2 were removed in the revised manuscript, due to limited number of data points for BB (8) and TIC (4). More information on the data handling was added in the revised manuscript.

2. 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. ANS) There was no nighttime data in this analysis. For FTCO, the data (n=4%, solar zenith angle (SZA) $>85^{\circ}$) near sunrise and sunset exist and for FTMA sunset data (n=8%, SZA $>85^{\circ}$) exist. Mean NO2/NO ratio was reanalyzed for the case of less than solar zenith angle $< 85^{\circ}$. The

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reanalyzed mean ratio was added to the Table 3 in the revised text. For PSS parameter calculation, data sets of SZA $>85^{\circ}$ were not used. If the data set includes high SZA data, we also recognize higher uncertainty for PSS interpretation near sunrise and sunset because model and measured values are less reliable due to greater fractional errors in measured values, especially J2 and [NO] (Ridley et al., 1992; JGR 97, 10375-10388).

3. 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. ANS) According to our reanalysis of NO2/NO ratio with time of day for different air masses, there were no distinct trend. Thus, this analysis was not included in the revised manuscript. For BB and TIC, less than 2 hour time window exist; about 4 hour for BL and FTMA. For FTCO, full daytime time window exists. In the revised text, discussion on NO2/NO ratio for different air mass types was removed because we considered this is not key subject in this paper.

4. 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? ANS) We decided to remove back trajectory plots in the revised manuscript. The altitude value in the plots represent above sea level. Reanalysis of back trajectories was carried out. Detailed description of data grouping for air mass categorization is given in the first paragraph of Section 3.1 (and Table 2).

5. 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

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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. ANS) We analysed NOx/NOy vs NOy to see how well they agree with air mass subdivision into the 5 classes (See Fig. 1). Detailed discussion on air mass origin is given in the revised text.

6. 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. ANS) According to the previous PSS analysis by Ridley et al. (1992, JGR 97, 10375-10388), the uncertainty for PSS parameter (J2[NO2]/k1[O3][NO]) was about 25% on average (with higher value up to 60% near sun rise and sunset), which is similar to our estimates. For our PSS parameter calculation, data sets of SZA $>85^{\circ}$ were not used. If the data set includes high SZA data, we also recognize higher uncertainty near sunrise and sunset because model and measured values are less reliable due to greater fractional errors in measured values, especially J2 and [NO] (Ridley et al., 1992).

7. 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? ANS) Since the PSS interpretation for BB and TIC is not statistically significantly robust, the plots for BB and TIC in the Figure 1 were removed in the revised manuscript.

Typos and presentation: 8. p2276, line 5 in Abstract, "indicator" Better to find another word as indicator also has the meaning of indicator species. ANS) The word of “indicator” was replaced with “indicator species ratio”

9. 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. ANS) A lot of numbers in lines 14-23, p2280 were added to the Table 3 in the revised manuscript.

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10. 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. ANS) Following sentence was added to the revised manuscript. “Note that  $<$1 indicates that the calculated [NO2] is less than observed [NO2] and that concentration levels of observed peroxy radicals (e.g, [HO2] and [RO2]) are significantly too low to sustain PSS.”

11. P2881, line 10-11 "was not always statistically significant for BL, FTMA, and FTCO" 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. ANS) The sentences in lines 10-11, p2281 were rewritten. See the revised manuscript. Statistical summary of linear regression between NO2/NO and {k1[O3] + k3[HO2] + k4[RO2]}/J(NO2) and PSS parameter (Φ) was added in the revised text.

Table Statistical summary of the PSS parameter (Φ) and linear regression between NO2/NO and {k1[O3] + k3[HO2] + k4[RO2]}/J(NO2) Air Mass Slope Slope SE S T-value P-value Φ(meanśstd) Φ(median) BL 1.14 0.012 0.75 91.97 0 1.19ś0.24 1.14 FTCO 1.30 0.029 2.79 45.50 0 1.06ś0.37 1.04 FTMA 0.89 0.018 1.48 50.18 0 0.93ś0.27 0.92 All 1.13 0.017 2.42 66.75 0 1.08ś0.37 1.06

12. P2281. line 17-18, "higher (NOx/NOy) ratio compared to other air masses" Not higher than BL which is 0.54. ANS) The sentences P2281, lins 17-18 were removed. Discussion on the PSS parameter for BB was eliminated.

13. 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 ... ANS) Two sentences in lines 5-7, p 2282 were replaced with “Except for the BL, the mean NO2 level for the BB was higher than those in other air mass categories by at least a factor of 1.3 and as much as a factor of 11 for the FTCO.”

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14. p2282, line 16, "asl" above sea level ANS) Explanation for acronym “asl” is given in the first paragraph of Introduction section.

15. 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. ANS) In the revised text, the 1/phi values in the literature were expressed as phi values.

16. p2283, line 16, "correlation intensity" Should be "correlation" ANS) The phrase of “correlation intensity” was replaced with “correlation.”

17. p2284, line 21 "intercorrelated" Is this the correct word? ANS) The word of “intercorrelated” is replaced with “interrelated.”

18. 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? ANS) In the abstract of revised text, the phrase of "indicating both photochemically young and reactive air masses” was removed. In the Conclusion, it was replaced with “indicating less photochemically aged air masses of polluted plume exiting Mexico City Metropolitan Area”.

19. 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. ANS) In the revised Figures, the scales of x-axis were altered.

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