Atmos. Chem. Phys. Discuss., 8, S4526–S4530, 2008
www.atmos-chem-phys-discuss.net/8/S4526/2008/

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.

Z.-H. Shon et al.

Received and published: 7 July 2008

REPLY TO REVIEWER #1 Clarification of these points and suggestions for improving the analysis are offered below. 1. Section 3.1: In this section, regression analysis is used to examine the consistency between the data and PSS expectations. Instead of the simple regression approach used here, a much more rigorous result could be achieved by using regressions that consider the uncertainty associated with the quantities on both axes. The only uncertainty mentioned in the manuscript is that for the PSS parameter. It is unlikely that the uncertainty in the terms for the numerator and denominator of the PSS expression are the same. Thus, the symmetric shading around the regression lines in figure 1 is misleading. ANS) Reanalysis of linear regression for PSS calculation was carried out using statistical analysis software (Minitab). This was

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

included in the revised text. The uncertainties for the numerator and denominator of the PSS expression are different each other. The symmetric shading around the regression lines represents the 1 sigma value of the uncertainty, so it is symmetric. In revised text, we removed the shading and included the prediction intervals of the linear regression. In Fig. 2, the upper and lower (dotted) lines represent prediction intervals in 95% confidence level.

Table Statistical summary of linear regression between NO2/NO (x variable) and {k1[O3] + k3[HO2] + k4[RO2]}/J(NO2) (y variable) and PSS parameter (Φ) air mass Slope Slope SE S T-value P-value delta(Φ)/Φ(%) Φ(meanśstd) Φ(median) BL 1.14 0.012 0.75 91.97 0 21 1.19ś0.24 1.14 FTCO 1.30 0.029 2.79 45.50 0 22 1.06ś0.37 1.04 FTMA 0.89 0.018 1.48 50.18 0 21 0.93ś0.27 0.92 All 1.13 0.017 2.42 66.75 0 - 1.08ś0.37 1.06

2. While I understand the need to differentiate the BB and TIC groups from the rest of the data, the regressions in Figure 1 for BB (8 points) and TIC (4 points) cannot be considered robust and should be eliminated due to a lack of observations. ANS) In PSS parameter analysis, the linear regression analysis for the BB and TIC was eliminated in the revised text. In Fig. 2, regression plots for BB and TIC were removed. In Fig. 3, plots for BB and TIC were also removed.

3. In section 3.2, there is no discussion of the relative importance of O3 and peroxy radicals on the NO2/NO ratio. Without this piece of critical information, it is impossible to know the degree to which NO2/NO ratios may be useful as an indicator of photochemical activity. ANS) The relative importance of ozone and peroxy radicals in the NO2/NO ratio was calculated and was discussed in the revised text.

Table Contribution of O3 and peroxy radicals to the NO2/NO ratios   (k1[O3])/J2 (k3[HO2]+k4[RO2])/J2 BL 3.05 (65) 1.63 (35) FTCO 3.39 (70) 1.44 (30) FTMA 3.25 (70) 1.38 (30)

4. The explanation of PSS deviations (p.2281, lines 14-18) does not make sense to

ACPD

8, S4526–S4530, 2008

me. This system equilibrates too quickly for age alone to be important. Deviations from PSS must indicate missing chemistry not represented in the PSS expression. ANS) The explanation of PSS deviations (p. 2281, lines 14-18) were eliminated. In the equation 1, the missing chemistry term (XO + NO → X + NO2) was added in the PSS expression. Possibility of missing chemistry as one of the reason in the deviations from PSS was more discussed in the revised text.

5. The premise that iodine (or halogen) chemistry could be responsible for shifting the NO2/NO ratio is offered as conjecture and is not well supported (page 2281). The iodine levels needed to correct FTMA (which is shown to be in PSS within the measurement uncertainties) are more than twice those seen in the marine boundary layer. What would be the source of IO radicals at these altitudes and distances from marine influence? ANS) For the source of IO radicals, photolysis of iodocarbons (CH3I, CH2I2, C2H5I, and CH2ICl), followed by the reaction of O3 and I can produce IO. The source strength for iodocarbons such as CH2I2, C2H5I, and CH2ICl could possibly exceed that for CH3I (Davis et al., 1996 and references therein). In high biological productivity regions, CH3I concentration in the coastal air reached as high as 43 pptv (Oram and Penkett, 1994; Atmospheric Environment 28, 1159-1174). Based on the analysis of air mass back trajectory for FTMA, the air mass originated from the Pacific coast of Mexico, where is the region of upwelling of nutrient-rich seawater (Bulgakov et al., 2005; Physical Oceanography 15, 27-36). In the tropical region, there is the strong vertical mixing of CH3I from boundary layer to free troposphere (see Davis et al., 1996). Thus, the possibility of supply of the iodine levels to correct FTMA can not be excluded. Thus, this content was included in the revised text.

6. Section 3.2: In section 3.1, the authors demonstrate that much of the data conform to PSS. This means that the partitioning of NOx is generally understood to be a function of ozone, peroxy radicals, altitude (or temperature), and actinic flux (NO2 photolysis). If the partitioning of NOx can be understood in terms of PSS, then why is the partitioning being examined using regression of NO2 versus NO? From Table 2 and Figure 2, it

ACPD

8, S4526–S4530, 2008

is evident that the subgroups span a significant range of altitude and/or ozone values. Both of these parameters have a profound influence on the NOx partition given the importance of the strongly temperature dependent NO+O3 reaction. The main problem with the regressions in figure 3 is that they are being driven primarily by the high NOx data points. Closer examination shows that many of the low NOx points are not well represented by the regression lines. Here is where the authors should elaborate on the relative importance of the various terms in the PSS expression. Do radicals play a substantial role in the partitioning of NOx or is it dominated by ozone? What about the relative roles of hydroperoxy and organic peroxy radicals? Are the contributions from peroxy radicals large enough that they could be inferred from PSS assumptions? These are important pieces of information as the NO2/NO ratio plays an important role in determining NOx lifetime as loss processes are primarily through reactions involving NO2 rather than NO. ANS) The partitioning of NOx is reanalyzed based on ozone and peroxy radicals (see Table). In general, the conversion of NO to NO2 mainly resulted from the reaction with O3 except for BB. The contribution of ozone and peroxy radicals to the ratio was included in the revised text. Statistical summary of NO2/NO, NOx/NOy, and OPE with different altitudes for FTCO and FTMA is given in Table below, but this was not included in the revised text because we considered this is not key subject in this paper.

Table Contribution of O3 and peroxy radicals to the NO2/NO ratios (median) Air mass category A=(k1[O3])/J2 B=(k3[HO2]+k4[RO2])/J2 BL 3.18+/-1.40(3.04) 66% 1.62+/-0.47 (1.58) 34% FTCO 2.33+/-4.74(1.17) 61% 1.52+/-1.36 (1.27) 39% FTMA 3.35+/-2.48(2.94) 71% 1.37+/-0.85 (1.28) 29%

7. It is not clear to me what value the trajectories add to this analysis (Figure 4 and associated discussion) ANS) The trajectory figure was removed.

8. I also do not find any utility in the use of regression statistics to assess the NOx-NOy ratios for the various groupings (Figure 5 and associated discussion). In many cases high NOx/NOy is correlated with fresh NOx from strong sources. This is most evident in

ACPD

8, S4526–S4530, 2008

Interactive Comment

figure 5e, but in all of the figures, there is clear evidence that the regressions are being driven by the high NOx points and that the majority of the data lie below the regression line as the lifetime of NOx is generally less than that of the NOy reservoir, rendering the NOx-NOy relationship nonlinear. ANS) We removed the regression between NOx and NOy as suggested by the reviewer. We added NOx/NOy vs NOy analysis to see how well they agree with air mass subdivision into the 5 classes (See Fig. 1). Detailed discussion on this is given in the revised text.

9. Section 3.3 With the exception of panel 6e, the OPE results in figure 6 are being driven by the extremes in O3 from individual flights and should not be construed as representative of the grouping as a whole. OPE is also expected to be altitude dependent, which may explain some of the scatter in these figures. ANS) The altitude dependence of OPE was investigated. See figure below. The OPE results were not driven by the extremes in O3.

10. The comparison of OPEs with those for a remote marine environment (Davis et al.) are misleading. The OPEs derived from figure 6 are based on net ozone per unit NOx. A closer inspection of the Davis results shows that those OPE estimates were based on gross ozone per unit NOx. This difference in definition make the comparison invalid as gross production and destruction rates can often be orders of magnitude greater than the net change in ozone. ANS) The OPEs for Davis et al. was removed and new comparison was added.

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