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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.

Anonymous Referee #1

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This manuscript presents an analysis of the NO2-NO system during the MIRAGE-Mex field campaign to test understanding of current photochemical theory. It is noteworthy that this data set offers an opportunity to assess NOx catalytic cycling without the use of model calculations to infer peroxy radicals as both hydroperoxy and organic peroxy radicals were measured from the NSF C-130 aircraft. The exclusive use of regression analyses to examine the data could be improved and is at times inappropriate. As a result, there is little information of value presented other than the confirmation of PSS for most of the data within the measurement uncertainties.

Clarification of these points and suggestions for improving the analysis are offered

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below.

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.

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.

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.

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

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?

Section 3.2:

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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 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.

It is not clear to me what value the trajectories add to this analysis (Figure 4 and associated discussion)

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 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.

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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.

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.

Summary

While I believe that this data set is of excellent quality for assessing the NO2-NO system, I am left feeling disappointed that a more thoughtful analysis was not pursued. The use of regression statistics is in most cases inappropriate and the resulting conclusions are not well supported. I would encourage the authors to focus their analysis more heavily on the terms in the PSS expression to understand differences within and between the data groups.

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

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