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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "On the export of reactive nitrogen from Asia: $NO_x$ partitioning and effects on ozone" *by* T. H. Bertram et al.

**Anonymous Referee #3**

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**General comments:**

Bertram et al. present an analysis of observations in the central North Pacific troposphere that were made during the INTEX-B field study in spring 2006. They reach five main conclusions: 1) peroxyacyl nitrates play a controlling role in NOx production in aged Asian outflow, 2) the remote Pacific is extremely sensitive to future changes in NOx loadings, 3) the experimentally determined crossover point between net Ox destruction and net Ox production is at 60 pptv NOx, 4) the flux of reactive nitrogen through the meridional plane of 150°W was 0.007±0.002 TgN per day, which provides an upper limit of 15% on the export efficiency of NOy from East Asia, and 5) episodic dry subsidence events play an important role in the intercontinental transport of ozone and its precursors from East Asia to North America. These are far-reaching conclu-



sions that are only marginally supported in the manuscript as it presently stands, and the discussion has many errors and shortcomings. Indeed each of these five conclusions would require a paper of its own to provide proper support by thorough analysis of all available data in this region and season, as well as much improved discussion of how the present analysis fits into the previously published work that has addressed these same issues. I recommend that this paper be rejected, and suggest that the authors consider what conclusions they can robustly support with thorough analysis and discussion in a very extensively revised paper. Following are some of my specific concerns with the present manuscript.

1. In my view the introduction is incomplete and lacking in rigor. It should be more objective, complete and accurate. A much more thorough review of relevant previous work must be given. Some specific concerns are listed in the Specific Comments (1-8) below.

2. INTEX-B involved two highly instrumented aircraft - the NASA DC-8 and the NCAR C130 - yet this paper discusses only the DC-8 data. Both of the aircraft measured the species necessary for the discussion in this paper. The analysis in this paper should include data from both aircraft, comparing and contrasting results from the different measurement techniques used on the two aircraft. Such comparisons and contrasts will provide many opportunities for 1) intercomparing measurements of important species, and 2) providing a much more robust analysis. I realize that the DC-8 focused on the central North Pacific and the C-130 focused on the eastern North Pacific, but there is no reason to suspect very different environments as long as any episodes of North American outflow are avoided in the analysis of the C-130 data. INTEX-B also included measurements from other aircraft and ground sites that may be useful in the analysis.

3. A much fuller discussion of the thermal dissociation – laser induced fluorescence measurements is required, particularly with regard to accuracy, precision and specificity of the measurement of $\Sigma$PNs, $\Sigma$ANs and $HNO_3$ from an airborne platform. The

two references given (Thornton et al., 2000; Day et al., 2002) discuss only laboratory and surface site measurements. Measurements from an aircraft platform with rapidly changing ambient conditions is a much more difficult endeavor. Three specific questions immediately arise: How do these measurements compare to similar measurements on the C-130 during intercomparison flights, which I believe were conducted as part of INTEX-B? Are the systematics of the total NOy concentrations and the NOy partitioning determined from the measurements on the two aircraft in the remote North Pacific troposphere consistent? What is the response of the thermal dissociation – laser induced fluorescence instrument to aerosol nitrate, which may be encountered in some environments?

4. Section 2 discusses the measurement of NOy species, but does not mention NO, yet Section 3 discusses NOy defined as NOx +$\Sigma$PNs+$\Sigma$ANs+$HNO_3$. How was the NO concentration obtained in order to calculate NOx? This is important, as NO concentrations can equal or exceed those of $NO_2$ in the mid troposphere [e.g., Nakamura et al., 2003] and NO dominates NOx in the upper troposphere. The accuracy of the NO measurement is particularly important in the analysis of $O_3$ production rates that are summarized in Fig. 5, since an accurate NO measurement is particularly important in quantifying the rate of Reaction (7), and these relevant NO concentrations are undoubtedly quite small in the remote North Pacific troposphere. At such low concentrations measurement artifacts often have been found to be significant problems. A full discussion of the NO measurement technique including accuracy, precision and potential systematic errors including interferences is required in this paper.

5. The discussion of $O_3$ production rates in Section 4.1 and Figure 5 depend upon measured OH and $HO_2$. These measurements are extremely difficult, and over the past decade the experimental group responsible for these radical measurements utilized here have struggled with calibration and interference issues. Yet these measurements are not discussed in Section 2, which describes the Experimental Methods. Further, no investigators from this group are included as coauthors of this paper. In or-



der for the discussion in Section 4.1 to be credible, a thorough discussion of the radical measurements and their uncertainties must be included in Section 2, and these uncertainties must be fully and rigorously considered in the subsequent analysis. Preferably, coauthors from the radical measurement group should be included to ensure that the measurement uncertainties are adequately considered in the analysis utilizing these data.

6. The authors calculate the gross rate of $O_3$ production from the right hand side of Eq. (7). A useful test of the accuracy of this determination is to check if this calculated quantity is balanced by the difference between the photolysis rate of $NO_2$ and the rate of reaction of NO with $O_3$. Demonstrating that the measurements are consistent with the well-known photostationary state of NO-$NO_2$-$O_3$ in the presence of significant concentrations of peroxy radicals would provide very useful support for the accuracy of the measured quantities upon which the net $O_3$ production rate is calculated. A thorough analysis of the consistency between the measured $NO_2$/NO ratio and that expected from the photostationary state calculated from measured and calculated concentrations of $O_3$, peroxy radicals, and photolysis rate should be included.

7. The analysis illustrated in Fig. 5b suggests that the tropospheric environment over the North Pacific is, on average, one of net ozone destruction. This analysis appears to be the basis of the second conclusion listed above, that the remote Pacific is extremely sensitive to future changes in NOx loadings. However, Parrish et al. [2004] concluded that the springtime North Pacific troposphere changed from net $O_3$ destruction to a more $O_3$ neutral environment between 1985 and the ITCT 2K2 study in 2002. Their argument was indirect, based upon the correlation of $O_3$ concentration with photochemical age of the air mass as determined from measured hydrocarbon ratios. The present paper should at least discuss these contrasting findings. It would also be useful to examine the $O_3$-hydrocarbon ratio correlations in the DC-8 and C-130 INTEX-B data sets to see if the findings of Parrish et al. [2004] were peculiar to only the studies they consider.

8. In Section 4.2 the authors calculate the average flux of NOy across the North Pacific through the meridional plane of 150°W, and compare this flux to total East Asian emissions to derive an upper limit of 15% on the export efficiency of NOy from East Asia. There are at least three problems with reaching this conclusion. First, the average flux is derived from the sum of the average fluxes derived for individual latitude-altitude bins. The average flux for each bin was calculated from the product of the average wind speed and average NOy concentration in each bin. This latter step is valid if and only if wind speed and NOy concentration are not correlated within the bin. It is not clear to me that a correlation is or is not expected, but the authors must demonstrate a lack of correlation before using this procedure. Further the authors do not make it clear that they used average westerly component of the wind speed (as they must) rather than the mean wind speed (as they state.) Second, even if the authors' calculation is valid, the result can be an upper limit for the export efficiency from East Asia if and only if NOy is conserved between East Asia and the central North Pacific. Given the complexity of the transport patterns in the central North Pacific (see e.g. Cooper et al., 2004) a significant fraction of NOy exported from East Asia is likely lost (via wash out or conversion to aerosol nitrate) en route to the central North Pacific. And as the authors note, additional NOy is likely added from stratospheric intrusions and lightning. Third, the authors consider only the 25° to 55° N latitude range. Transport of East Asian emissions disperses to latitudes outside this range (see e.g. Forster et al., 2004). Consequently, the conclusion of Section 4.2 is not valid. The average NOy flux through the meridional plane may not have been calculated correctly, but even if the calculation is valid, it does not provide an upper limit to the export efficiency of NOy from East Asia.

9. The discussion and analysis in Section 4.4 on the role of episodic subsidence events in $O_3$ production also has critical shortcomings. First, the authors use the criterion of $O_3$/CO>1.25 to remove strong stratospheric influence. However, this is not adequate; Figure 3 of Nowak et al (2004) summarize the sources of $O_3$ measured during the ITCT 2K2 study. The authors' criterion would remove only the most intense stratospheric events, but would leave air parcels with $O_3$ > 125 ppbv with most of that $O_3$ due to



stratospheric influence. Such air parcels may well account for the high $O_3$ data in the authors' Figure 8a, especially those parcels at high altitude and low water vapor. Clearly the observed $O_3$ concentrations do not provide any indication of rapid net ozone production in dry air; the higher $O_3$ concentrations in the drier air may be due entirely to stratospheric input. Much more detailed model calculations must be presented if the authors wish to establish that high net $O_3$ production rates correlate with low water vapor. This is a complex calculation as reaction of $O(^1D)$ with water vapor is a sink for $O_3$, but also a source of $HO_X$ radicals, which are necessary for $O_3$ formation. Indeed, the authors' Figure 8c show the highest net $O_3$ production rates at both low and high water vapor content.

**Specific comments:**

1. Pg. 24957, line 17 - Reactions 4 and 5 are described as a "loss process", presumably of NOx. However the products of these reactions are only temporary reservoirs of NOx, which will be reformed following sunrise. This wording should be changed.

2. Pg. 24958, lines 4-5 - The argument is made that peroxy acyl nitrates "act as a net source of NOx in warm climates". However, this is incorrect. Significant concentrations of peroxy acyl nitrates would not form in warm climates. Peroxy acyl nitrates act as a net source of NOx when they are formed in a cool environment and transported to a warmer environment.

3. Pg. 24958, lines 13-14 - The authors state "production of $HNO_3$ is viewed as an irreversible sink for NOx." In the context of intercontinental transport, which is the subject of this paper, this statement is not true (see Neuman et al., 2006). The authors recognize this in the analysis summarized in Fig. 7. This statement requires modification.

4. Pg. 24958, lines 14-15 - I believe that photolysis is a significant sink for at least some alkyl nitrates; the authors fail to mention this.

5. Pg. 24959, lines 1-2 - The authors assert that Day et al. [2003] made direct ob-

servations of the sum of the alkyl nitrates in the planetary boundary layer and in the free troposphere. However, their technique does not provide specific identification of individual alkyl nitrates, which can then be summed. Instead they rely on a difference between measurements of two classes of reactive nitrogen species to approximate the sum of all the alkyl nitrates. To my knowledge their technique has not been rigorously compared with other techniques, particularly in the free troposphere, which is the environment that is the subject of this study. If this statement is retained, it requires much more substantial support. The only reference given is Day et al., 2003, which discusses only boundary layer measurements.

6. Pg. 24959, lines 3-6 - The authors state that NOx emission increases "are projected to be responsible for an increase in $O_3$ in the remote atmosphere." However, there is substantial evidence that $O_3$ in the remote atmosphere (at least at northern mid-latitudes) has already increased substantially. The authors must expand this discussion. Has the projected increase already occurred? What is the support for the projection that the authors mention? Certainly one 1979 reference is not adequate.

7. Pg. 24960, lines 1-2 - the authors assert "Until the spring of 2006, the main transport corridor between Asia and North America was left largely unmeasured." This statement is incorrect. In 2001 TRACE-P and in 2002 PEACE measured within this corridor on the Asian end, and in 2002 ITCT-2K2 measured at the North American end. Several other field studies have also investigated this transport. In reality only the central Pacific portion of the corridor was left largely unmeasured.

8. Pg. 24960, lines 3-7 - The authors state that they use "direct measurements of speciated NOy". However, their techniques do not provide specific identification of individual NOy species. Instead they rely on differences between measurements of classes of reactive nitrogen species to approximate the sum of classes of NOy species. This should be clarified.

9. Pg. 24968, line 13 - The authors claim that their observations "... provide a novel



opportunity to test model representations of the transport and chemical evolution of NOy from the Asian continent." They certainly provide an opportunity, but it is not a "novel" opportunity as other studies have been conducted in this region; that adjective should be removed.

**Technical Corrections:**

1. The reference Koike et al., 2007 does not report what the authors seem to believe that it does report. Perhaps they have another reference in mind?

2. The caption to Fig. 6 is garbled.

**References:**

Cooper, O. R., et al. (2004), A case study of transpacific warm conveyor belt transport: Influence of merging airstreams on trace gas import to North America, J. Geophys. Res., 109, D23S08, doi:10.1029/2003JD003624.

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Res., 109, D23S18, doi:10.1029/2004JD004978.

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