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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) peroxyacetyl nitrates play a controlling role in NO_x production in aged Asian outflow, 2) the remote Pacific is extremely sensitive to future changes in NO_x loadings, 3) the experimentally determined crossover point between net Ox destruction and net Ox production is at 60 pptv NO_x, 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 NO_y 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-

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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 Σ PNs, Σ ANs and HNO_3 from an airborne platform. The



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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 NO_y concentrations and the NO_y 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 NO_y species, but does not mention NO, yet Section 3 discusses NO_y defined as NO_x + Σ PNs + Σ ANs + HNO₃. How was the NO concentration obtained in order to calculate NO_x? This is important, as NO concentrations can equal or exceed those of NO₂ in the mid troposphere [e.g., Nakamura et al., 2003] and NO dominates NO_x in the upper troposphere. The accuracy of the NO measurement is particularly important in the analysis of O₃ 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 O₃ production rates in Section 4.1 and Figure 5 depend upon measured OH and HO₂. 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-

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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 NO_x 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.

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8. In Section 4.2 the authors calculate the average flux of NO_y 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 NO_y 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 NO_y concentration in each bin. This latter step is valid if and only if wind speed and NO_y 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 NO_y 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 NO_y 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 NO_y 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 NO_y 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 NO_y from East Asia.

9. The discussion and analysis in Section 4.4 on the role of episodic subsidence events in O₃ production also has critical shortcomings. First, the authors use the criterion of O₃/CO>1.25 to remove strong stratospheric influence. However, this is not adequate; Figure 3 of Nowak et al (2004) summarize the sources of O₃ measured during the ITCT 2K2 study. The authors' criterion would remove only the most intense stratospheric events, but would leave air parcels with O₃ > 125 ppbv with most of that O₃ 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-

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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 O₃ in the remote atmosphere." However, there is substantial evidence that O₃ 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

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opportunity to test model representations of the transport and chemical evolution of NO_x 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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Nakamura, K., et al. (2003), Measurement of NO₂ by the photolysis conversion technique during the Transport and Chemical Evolution Over the Pacific (TRACE-P) campaign, *J. Geophys. Res.*, 108(D24), 4752, doi:10.1029/2003JD003712.

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