Response to Anonymous Referee #3

**Below we respond to each of the referee's general comments:**

*1. Incomplete introduction:* As discussed in our response to Referee 1 and 2, a revised manuscript will include significant efforts toward rewriting the introduction of the manuscript to avoid inconsistencies and provide a more thorough discussion of previous observations near this sampling region. We address Referee 3's specific concerns (1-8) in the following section.

*2. Use of C-130 data from INTEX-B:* While we agree that including the C-130 data from INTEX-B would expand the observations, we view this as beyond the scope of this manuscript. Specifically, the intent of this manuscript is to assess the photochemical state of the remote North Pacific.

*3. TD-LIF discussion and references:* Since the initial writing of this manuscript three important papers have been published that both describe the application of the TD-LIF technique toward aircraft observations as well as provide comparison of the TD-LIF ΣPNs measurement with both GC-ECD and TD-CIMS techniques. Specifically, Wooldridge et al., 2010 report a slope of 0.93 ± 0.06, intercept of 0.042 ± 0.007, and $R^2 = 0.77$ for the in-flight wingtip-to-wingtip comparison of the TD-LIF ΣPNs and C-130 TD-CIMS PAN and PPN measurements during the INTEX-B in flight comparison of 15 May 2006. Details on all the in-flight DC-8 and C-130 intercomparisons can be found in Kleb et al (2011). Both of these important citations will be included in a revised manuscript. Beyond this, Perring et al [2010] describes aircraft observations from the MILAGRO campaign, including ΣANs. Beaver et al [2012] demonstrate agreement between independent AN measurements made using CIMS and TD-LIF ΣANs measurements at the surface (BEARPEX 2009), $R^2 = 0.89$, slope = 0.91.

In the revised manuscript, we will expand the instrumental section to provide a brief description of the aircraft TD-LIF instrument at its duty cycle for measurement of $NO_2$, ΣPNs, ΣANs, and $HNO_3$.

*Wooldridge et al., Atmos. Meas. Tech. 3, 593-607, 2010.*

*Perring et al., Atmos. Chem. Phys., 10, 7215-7229, 2010.*

*Kleb et al., Atmos. Meas. Tech., 4, 9-27, 2011.*

*Beaver et al. Atmos. Chem. Phys., 12, 5773-5785, 2012.*

With regard to detection of particulate nitrate, laboratory measurements (unpublished) has shown that TD-LIF is sensitive to volatile nitrate. The resulting $NO_2$, formed following the thermal dissociation of the precursor compound, would be detected in the corresponding TD-LIF channel (e.g., semi-volatile organic nitrate aerosol are detected as ΣANs). Specific discussion of alkylnitrates in the aerosol phase can be found in Rollins et al 2012.

*Rollins et al., Science, 337, 1210-1212, 2012*

*4. NO measurements:* Nitric oxide was measured *via* chemiluminescence by Georgia Tech during INTEX-B. A revised manuscript will include a discussion of the instrument uncertainties (accuracy, precision, systematic error) at the concentrations found in the lower troposphere where NO is routinely below 50 pptv. Typical combined uncertainty ($1\sigma$) for research grade chemiluminescence measurements is 10 pptv, 10%. The impact of this uncertainty on the calculated $\Delta(O_3)$ will be discussed. During preparation of this manuscript the PI for

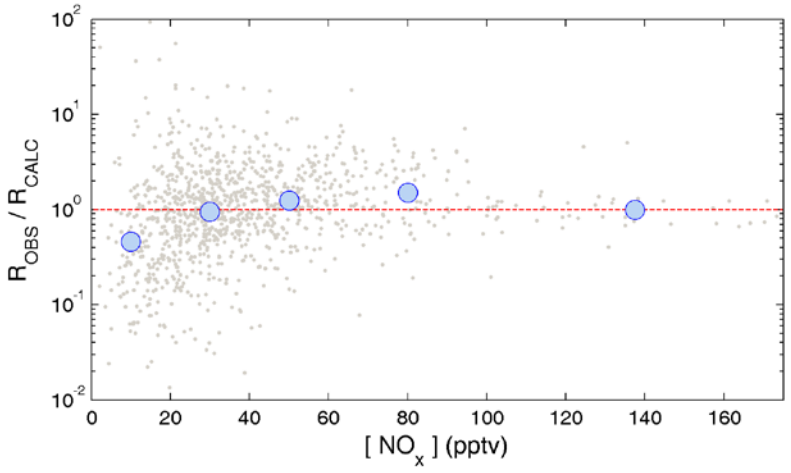
the NO measurement was offered co-authorship. However, we stress that systematic bias or calibration uncertainty are most important in the calculation of $\Delta(O_3)$, as random error can be reduced with time averaging.

*Kleb et al., Atmos. Meas. Tech., 4, 9-27, 2011.*

*5. Uncertainty in OH and $HO_2$ and resulting impact on $\Delta(O_x)$ calculation:* OH and $HO_2$ were measured *via* laser induced fluorescence by Penn State during INTEX-B. A revised manuscript will include a discussion of the instrument uncertainties (accuracy, precision, systematic error) at the concentrations found in the lower troposphere. For INTEX-B, an accuracy of ± 32% (2σ) for OH and $HO_2$ has been reported by the PI. This will reflect issues with calibration, however we note that the OH interference is primarily found in regions of high BVOC and we expect this to be of lesser importance in these airmasses. The impact of this uncertainty on the calculated $\Delta(O_3)$ will be discussed. During preparation of this manuscript the PI for the $HO_x$ measurement was offered co-authorship. Again, we stress that systematic bias or calibration uncertainty are most important in the calculation of $\Delta(O_3)$, as random error can be reduced with time averaging.

*Kleb et al., Atmos. Meas. Tech., 4, 9-27, 2011.*

*6. PSS calculation:* The referee suggests that we include a calculation of photochemical steady-state for the ratio of $NO_2$/NO for comparison with the observations as a useful test of the validity of the measurements at low $NO_x$ concentrations (for ALT < 5km). The results of this analysis are included below and will be described in full in a revised manuscript. In the figure to the left, we plot the ratio of the observed $NO_2$/NO ratio to that calculated via PSS from measurements of $O_3$, $HO_2$, and $J(NO_2)$ and model calculations of $RO_2$ as a function of measured $NO_x$. The results (also shown in the table below) suggest that systematic error in the measurement of NO or $NO_2$ may be important at $NO_x$ concentrations below 20 ppt. This is likely either a systematic positive bias in NO or negative bias in $NO_2$. A revised manuscript will provide discussion of the impact of this bias on the calculated $\Delta(O_3)$.



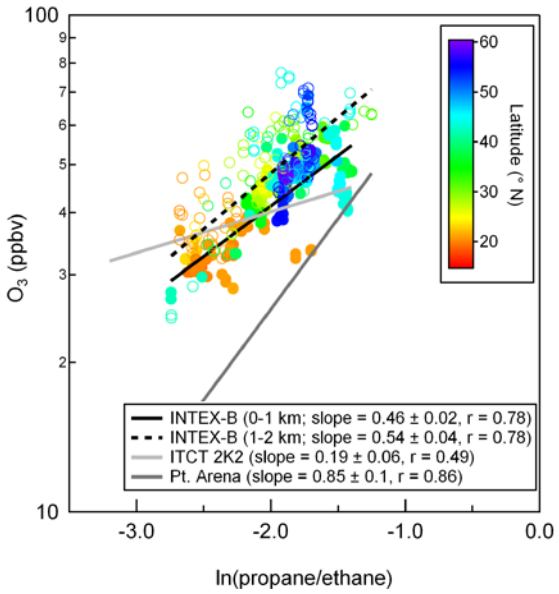

| **[$NO_x$] (pptv)** | **# 1-min samples** | **Median (Ratio)$_{OBS}$ / (Ratio)$_{CALC}$** |
|---|---|---|
| **0 – 20** | 219 | 0.46 |
| **21-40** | 448 | 0.96 |
| **41-60** | 126 | 1.25 |
| **61-100** | 225 | 1.5 |
| **101-175** | 45 | 0.99 |

*7. Comparison of Δ($O_x$) with Parrish 2004 analysis:* Referee #3 suggests that we expand our discussion of the net ozone production rates as calculated for INTEX-B and compare/contrast them with those observed previously both *via* direct calculation and inferred through correlation with hydrocarbon ratios. This is a very important suggestion and will be addressed directly in the revised manuscript.

Specifically, we will: 1) expand the discussion of the $\Delta O_3$ calculation to provide a more thorough discussion of how measurement uncertainty (specifically systematic bias) in NO, $NO_2$, OH, $HO_2$, and other measurements impact the calculations, 2) provide the altitude dependent, mean and median instantaneous net production rate for the INTEX-B observations and discuss the values in comparison to those in the literature (e.g., CITE-2 1984, $P(O_3)$ = -0.7 ppbv $h^{-1}$, 0-2 km, instantaneous, Chameides et al., [1989] and PHOBEA 1999, $P(O_3)$ = -0.83 ppbv $d^{-1}$, 0-2km, 24-hour avg, Kotchenruther et al., [2001b]). This will include discussion of the role of both surface deposition and stratospheric intrusions in biasing the measurements.

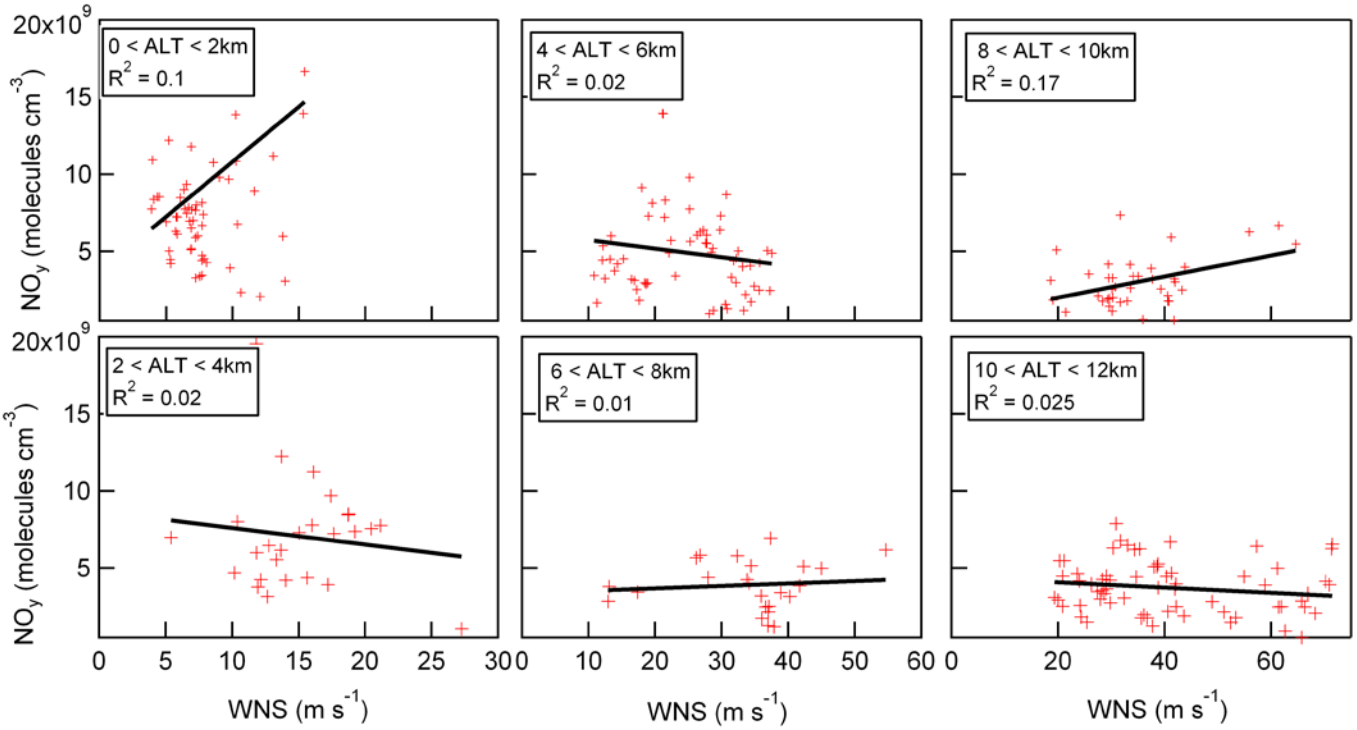
| Altitude | Mean instantaneous $\Delta O_3$ (ppbv $h^{-1}$) | St. Dev (1σ) | Median |
|---|---|---|---|
| **0- 1 km** | -0.10 | 0.21 | -0.09 |
| **1-3 km** | -0.06 | 0.16 | -0.04 |
| **3-5 km** | -0.03 | 0.12 | -0.01 |

and 3) examine the $O_3$-hydrocarbon ratio correlations for the DC-8 during INTEX-B for comparison with Parrish et al 2004. This comparison is shown at right, where the correlation of the natural log transformed $O_3$ levels with the natural log of the propane to ethane ratio are shown for INTEX-B, Pt. Arena, and ITCT 2K2 (0-1 km and 1-2km). This integrated perspective will be compared with the instantaneous measurements discussed above as well as placed within the context of previous observations (ITCT 2K2 and Pt. Arena).




*8. Calculation of $NO_y$ flux:* Referee #3 raises three problems with the analysis of section 4.2. We address each of these specifically below.

1) The calculation does use the average westerly component of the wind speed. This will be clearly written in a revised manuscript. $NO_y$ and the westerly component of the wind speed are not correlated in each of the sampling regions. In the figure below we show this for the latitude range of 45 – 45 N from 2-12 km in 2km bins. The $R^2$ value for each bin is also included. A revised manuscript will discuss these important details.




2) As defined previously in the literature, the export efficiency refers to the fraction of boundary layer $NO_y$ that is exported to the free troposphere (e.g., Li et al., 2004). Under this definition, the number reported here cannot represent an upper bound on the export efficiency as the referee notes (due to the potential for subsequent loss of $NO_y$ from the point of injection to the FT and the crossing of the meridonial plane of 150 W. Nonetheless the $NO_y$ flux across this plane represents an important constraint on the transport of reactive nitrogen across the north pacific as it does represent an upper limit on the fraction of Asian $NO_x$ emissions that pass through this sampling window (for this specific sampling period) A revised manuscript will contain significantly revised language.

3) The flux measurements were calculated between 20-55 N (as shown correctly in Fig 6, although incorrectly stated in the MS as 25-55N) and 0-10km in altitude. We have included a citation to Forster et al (2004), that indicates for a 15year average from MAM along the 125 W transect (Fig 2B) that the Asian CO tracer is concentrated between 25-50N and 3-12km. In addition, the revised manuscript will discuss transport features specific to the INTEX-B campaign that have been described previously in the literature. We will include reference to the work of both Walker et al and Zhang et al that have conducted analyses of the trans-pacific transport of $O_3$, $NO_y$, and CO for this time period. Specifically, satellite observations of CO from AIRS and TES and $O_3$ columns from TES were used in combination with kinematic trajectory analyses. In each of these cases, the export of the Asian plume was found to be North of 20 °N at 150 °W.

*9. Discussion of episodic subsidence:* <u>This section has been removed from the manuscript.</u>

**Below we respond to each of the referee's specific comments:**

**1. P.24957, line 17:** As discussed previously the discussion of the fate of temporary reservoirs will be revised, this includes discussion of $NO_3$, $N_2O_5$, and $HNO_3$.

**2. P. 24958, lines 4-5:** Correct. The sentence will be revised.

**3. P. 24958, line 13-14:** Correct. Discussion of the fate of $HNO_3$ will be revised, especially in light of the conclusions of 4.3.

**4. P.24958, line 14-15:** Correct. The photolysis of alkyl nitrates will be added as a loss mechanism.

**5. P.24959, line 1-2:** References are now provided to the work of Perring et al. that specifically discuss comparison of ΣAN measurements from aircraft platforms during INTEX-NA and INTEX-B. Beyond this, references to in-flight comparison of ΣPNs will be provided as discussed above.

**6. P. 24959, line 3-6:** The work of Jaffe and Parrish will be properly referenced for observation of increasing $O_3$ concentrations and their linkage to increasing $NO_x$ concentrations. The reference to Fishman (1979) simply states that $O_3$ production is $NO_x$ limited in these regions. This reference will be retained.

**7. P. 24960, line 1-2:** The intent of this statement was that vertically resolved observations of $NO_y$ have not been made in the remote Pacific (region between 135-180W, 15-60N and 0-12km). This region had only been sampled on occasion during ferry flights (PEM-WEST B, TRACE-P). We view this as a significant contribution, especially given that the majority of ITCT 2K2 flights were conducted very close to the NA continent.

**8. P. 24960, line 3-7:** The revised manuscript will specify that TD-LIF measures classes two specific classes of $NO_y$ compounds (ΣPNs and ΣANs) in addition to $NO_2$ and $HNO_3$.

**9. P. 24968, line 13:** As discussed above, the observations presented here provide a novel opportunity to test model parameterizations as they are the most comprehensive in the region of 135-180W, 15-60N and 0-12 km. Further, they are not subject to sampling artifacts that one might expect from aircraft observations conducted close to the continent.