TAbMEP Assessment: ICARTT PAN Measurements

1. Introduction

Here we provide the assessment for the peroxyacetic nitrate (PAN) measurements taken from three aircraft platforms during the summer 2004 ICARTT field campaign [*Fehsenfeld et al., 2006*]. This assessment is based upon four wing-tip-to-wing-tip intercomparison flights conducted during the field campaign. Recommendations provided here offer a systematic approach to unifying the ICARTT PAN data for any integrated analysis. These recommendations are based upon the instrument performance demonstrated during the ICARTT measurement comparison exercises and are not to be extrapolated beyond this campaign.

2. ICARTT PAN Measurements

Three different PAN instruments were deployed on the three aircraft. Table 1 summarizes these techniques and gives references for more information.

Table 1. PAN measurements deployed on aircraft during ICARTT

Aircraft	Instrument	Reference
NASA DC-8	Automated Dual GC with cryofocusing (AD-GC)	
NOAA WP-3D	PAN Thermal Decomposition Chemical Ionization Mass Spectrometer (TDCIMS)	
FAAM BAe-146	Dual Channel GC-ECD (GC-ECD)	*Whalley et all. [2004]*

3. Summary of Results

Table 2 summarizes the recommendations drawn from the intercomparisons. The following sections describe the processes that led to the recommendations. Table 2 recommends a bias correction (see section 4.1 for details) that can be applied to each data set to maximize the consistency between them. The recommended 2σ uncertainty in Table 2 is the larger of either the uncertainty reported by the PI or the quadrature-sum of the recommended bias correction listed in Table 2 and twice the adjusted precision determined for each instrument (see Table 4). When there are multiple intercomparisons available for the same instrument, the maximum adjusted precision value is used.

Table 2. Recommended ICARTT PAN measurement treatment

Aircraft	Instrument	Reported 1σ Uncertainty	Recommended Bias Correction[a]	Recommended 2σ Uncertainty
NASA DC-8	AD-GC	20%	$-23.7 - 1.13\ PAN_{DC-8}$	$\{(-23.7 - 1.13\ PAN_{DC-8})^2 + (0.574\ PAN_{DC-8})^2\}^{1/2}$ pptv
NOAA WP-3D	TDCIMS	10%	$61.0 - 0.147\ PAN_{WP-3D}$	20%
FAAM BAe-146	GC-ECD	5% + 5 pptv	$-25.9 + 0.188\ PAN_{BAe-146}$	10% + 10 pptv

[a] The "true PAN mixing ratio" = measurement – recommended bias correction (as discussed in Section 4.1).

4. Results and Discussion

4.1 Bias Analysis

Figures 1 and 2 illustrate the need for quantifying the bias between instruments. The difference between the simultaneous measurements reported by two instruments is plotted against the PAN mixing ratio reported by one of the instruments. The apparent biases in Table 3 are calculated from orthogonal linear regression (ODR) analysis (shown in the correlation plots in Figs. A1 - A3). ODR is used to approximate the bias between the paired instruments' dependence on the PAN mixing ratio. Apparent bias is defined as the difference in a measurement on one aircraft platform referenced to the same measurement made on the DC-8 (i.e. DC-8 - WP-3D). For convenience, the apparent bias is given in the form a + b*PAN_{DC8}. In this form, it is easier to propagate the apparent biases so the best estimate bias can be used to calculate the uncertainties summarized in Table 2. It should be noted here that the intercept should not simply be interpreted as a measurement offset; instead it is used in conjunction with the slope to best describe the linear trend found in the data.

The best estimate bias is defined as the difference between the instrument being analyzed and the true PAN mixing ratio as a function of the instrument being analyzed. This can be calculated by subtracting the true PAN mixing ratio from the respective apparent bias equation from Table 3 and expressing the result in terms of the instrument being analyzed. The average of the apparent biases for three instruments (23.67 pptv + 0.136 PAN_{DC8}) is assumed to be the "true PAN mixing ratio" from the DC-8 PAN measurement. In effect, this procedure assumes that the true PAN mixing ratio is the average of the three instruments, and the apparent bias correction is used in calculations to most closely approximate the true PAN mixing ratio for each instrument.

It should be noted that the initial choice of the reference instrument is arbitrary, and has no impact on the final recommendations. The given bias corrections were based upon the instrument performance demonstrated during the intercomparison periods.

Table 3. ICARTT PAN bias estimates

Aircraft	Instrument	Apparent Bias[1] (a pptv + b PAN)	Best Estimate Bias (a pptv + b PAN)
NASA DC-8	AD-GC	0	-23.7 - 0.136 PAN_{DC-8}
NOAA WP-3D	TDCIMS	73.8 - 0.00931 PAN_{DC-8}	61.0 - 0.147 PAN_{WP-3D}
FAAM BAe-146	GC-ECD	-2.80 + 0.398 PAN_{DC-8}	-25.9 + 0.188 $PAN_{BAe-146}$

[1] DC-8 is taken as an arbitrary reference. Apparent bias is expressed as a liner function of PAN on the DC-8.

4.2 Precision Analysis

The instrument precision assessment is summarized in Table 4. The Internal Estimate of Instrument Precision (IEIP) analysis procedures were applied for the one continuous, fast measurement (WP-3D). The IEIP procedure is an effective method to estimate "short-term" precision, which accounts for signal variation during a short period of assumed constant PAN measurements. Because this assumption is not always valid, the IEIP estimate tends to provide an upper limit of the instrument short-term precision. Over longer time scales, however, some instruments are subject to lower precision (i.e. larger variability), which includes variability that arises from uncorrected changes in the zero level or sensitivity of the instrument. These additional contributions to the variability are not likely reflected in the IEIP derived precision, but the intercomparison flights do provide a reasonable check on their influence. This effect was examined through the comparisons of the "expected variability" and "observed variability" given in Table 4. The expected variability is the quadrature-sum of the corresponding IEIP precisions. The observed variability is the standard deviation derived from the three intercomparisons shown in Figs. 3 and 4, denoting the relative difference between the paired instruments. Each standard deviation is expected to be equal to the quadrature-sum of the separate IEIP precisions of the two intercompared instruments. Because IEIP could not be calculated for DC-8 and BAe-146 data, the WP-3D IEIP precision values were taken as WP-3D adjusted precision values and used with the observed variability to calculate the adjusted precisions for the DC-8 flight. Adjusted precision could not be calculated for the BAe-146 flight. For this reason, the PI reported uncertainty was used for BAe-146 data. Based on the results presented in Table 4, the worst "adjusted precision" (or the largest value) is taken as a conservative precision estimate for each ICARTT PAN instrument and is used for the derivation of the recommended 2σ uncertainty in the last column of Table 2.

It should be noted that within the data, many values were measured below the lower limit of detection (LLOD) and were replaced with the recommended value given by the PI. In some instances, specifically the WP-3D data for 7/22 and the BAe-146 data, these LLOD values became significant outliers and were removed from the data set for the difference and relative difference calculations (Figs. 1-2 and 3-4, respectively). The removal of these values allowed for calculation of more accurate and reasonable observed variability values. The LLOD values were included in all other calculations and plots.

Table 3 shows that the measurement bias is a function of PAN mixing ratio. Thus, the bias may have a significant impact on the observed variability. To minimize the effect of bias, we corrected for bias before computing the observed variability, but only when this reduced the variability. For instance, the observed variability in the case of DC-8/WP-3D on 7/22 was estimated at 54.3% without correction. This value was reduced to 29.0% when bias correction was applied. The observed variability values given in Table 4 are computed after the bias correction. The final analysis results are shown in Table 2. Over 90% of the data falls within the combined recommended uncertainties for each intercomparison, which is consistent with the TAbMEP guideline for unified data sets.

Table 4. ICARTT PAN precision (1σ) comparisons

Flight	Platform/ Instrument	IEIP Precision	Expected Variability	Observed Variability	Adjusted Precision
7/22	DC-8	N/A	N/A	29.0%	28.7%
	WP-3D	4.5%			4.5%
7/31	DC-8	N/A	N/A	24.1%	23.9%
	WP-3D	3.1%			3.1%
8/7	DC-8	N/A	N/A	19.6%	18.5%
	WP-3D	6.6%			6.6%
7/28	DC-8	N/A	N/A	34.1%	N/A
	BAe-146				

Appendix A
Figures A1 through A4 show the time series of the PAN measurements and aircraft altitudes for each intercomparison flight as well as the correlations between the two PAN measurements.

References
Fehsenfeld, F. C., et al. (2006), International Consortium for Atmospheric Research on Transport and Transformation (ICARTT): North America to Europe—Overview of the 2004 summer field study, *J. Geophys. Res., 111*, D23S01, doi:10.1029/2006JD007829.

Figures

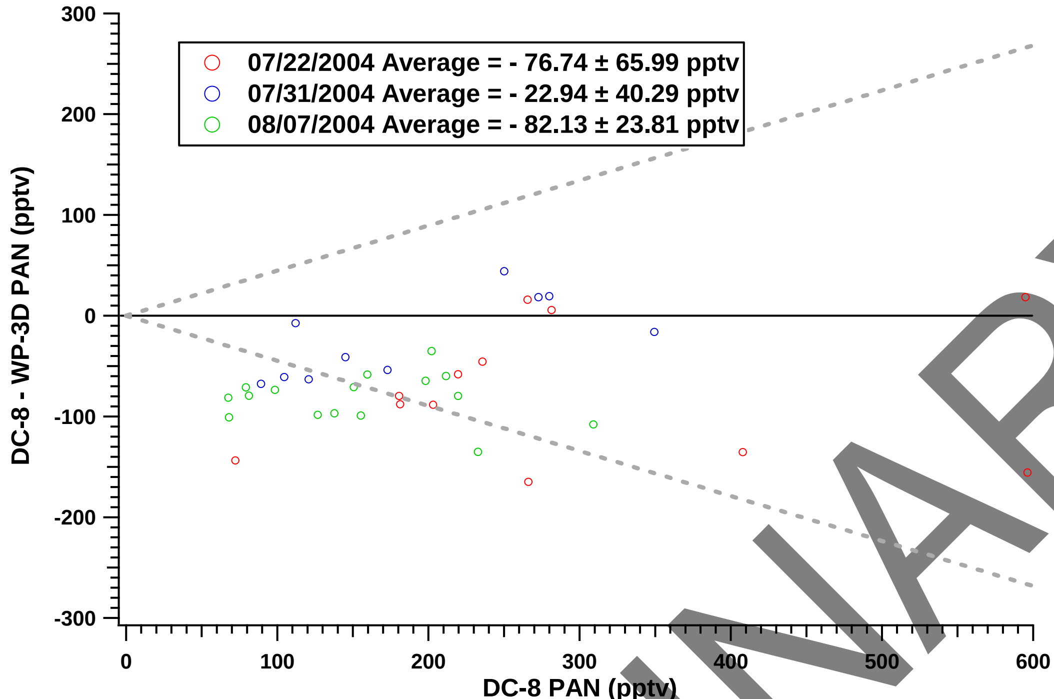

Figure 1: Difference between PAN measurements from the three DC-8/WP-3D intercomparison flights as a function of DC-8 PAN. The dashed lines indicate the range of the results expected from the reported 2σ measurement uncertainties.

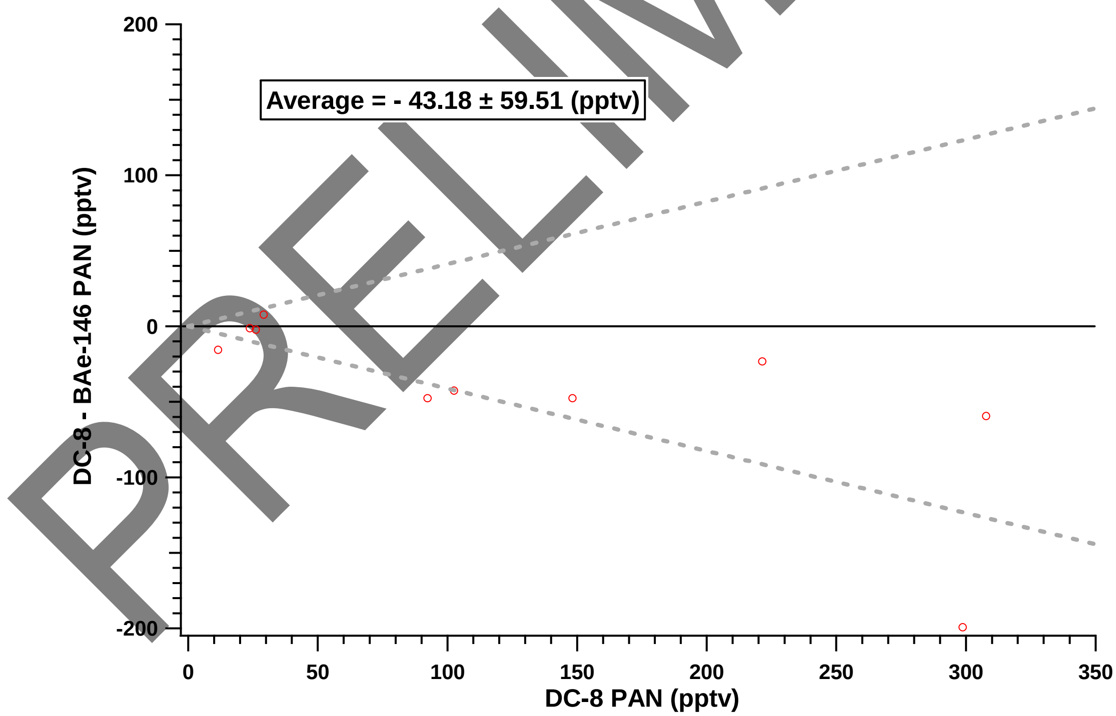

Figure 2: Difference between PAN measurements from the DC-8/BAe-146 intercomparison flight as a function of DC-8 PAN. The dashed lines indicate the range of the results expected from the reported 2σ measurement uncertainties.

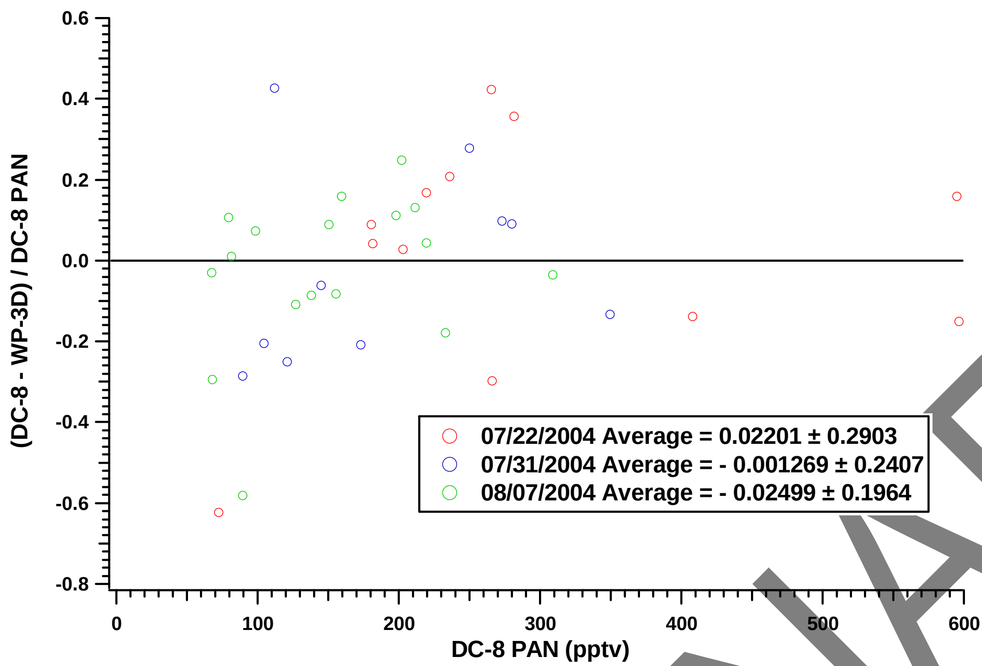

Figure 3. Relative differences between PAN measurements from the DC-8/WP-3D intercomparison flights as a function of DC-8 PAN. Corrections were made to all three data sets to account for bias in the correlation with DC-8.

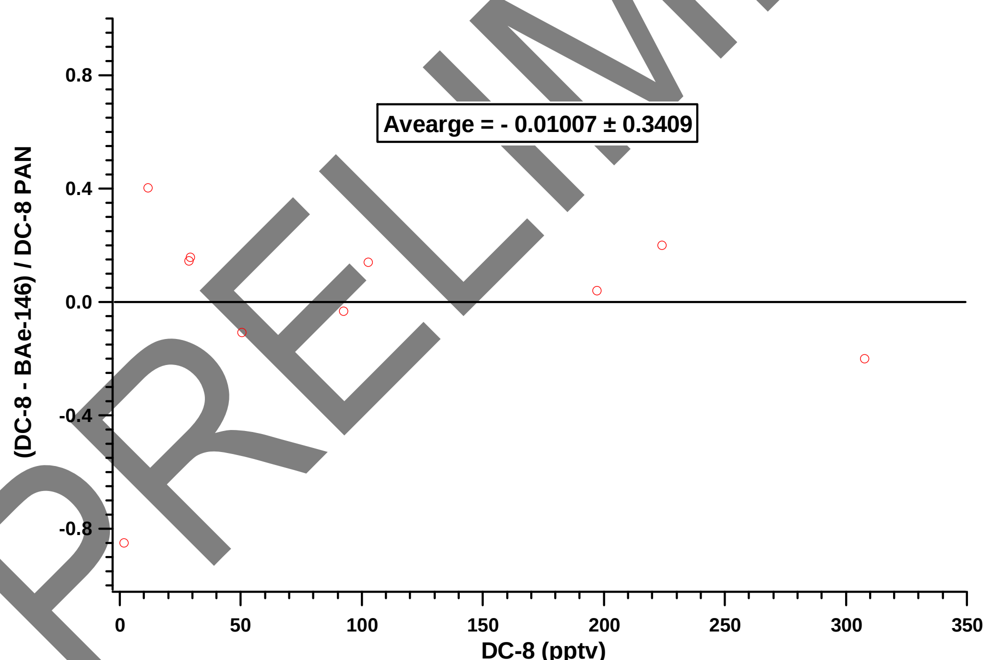

Figure 4. Relative difference between PAN measurements from the DC-8/BAe-146 intercomparison flight as a function of DC-8 PAN. Corrections were made to the BAe-146 data to account for bias in the correlation with DC-8.

Appendix A

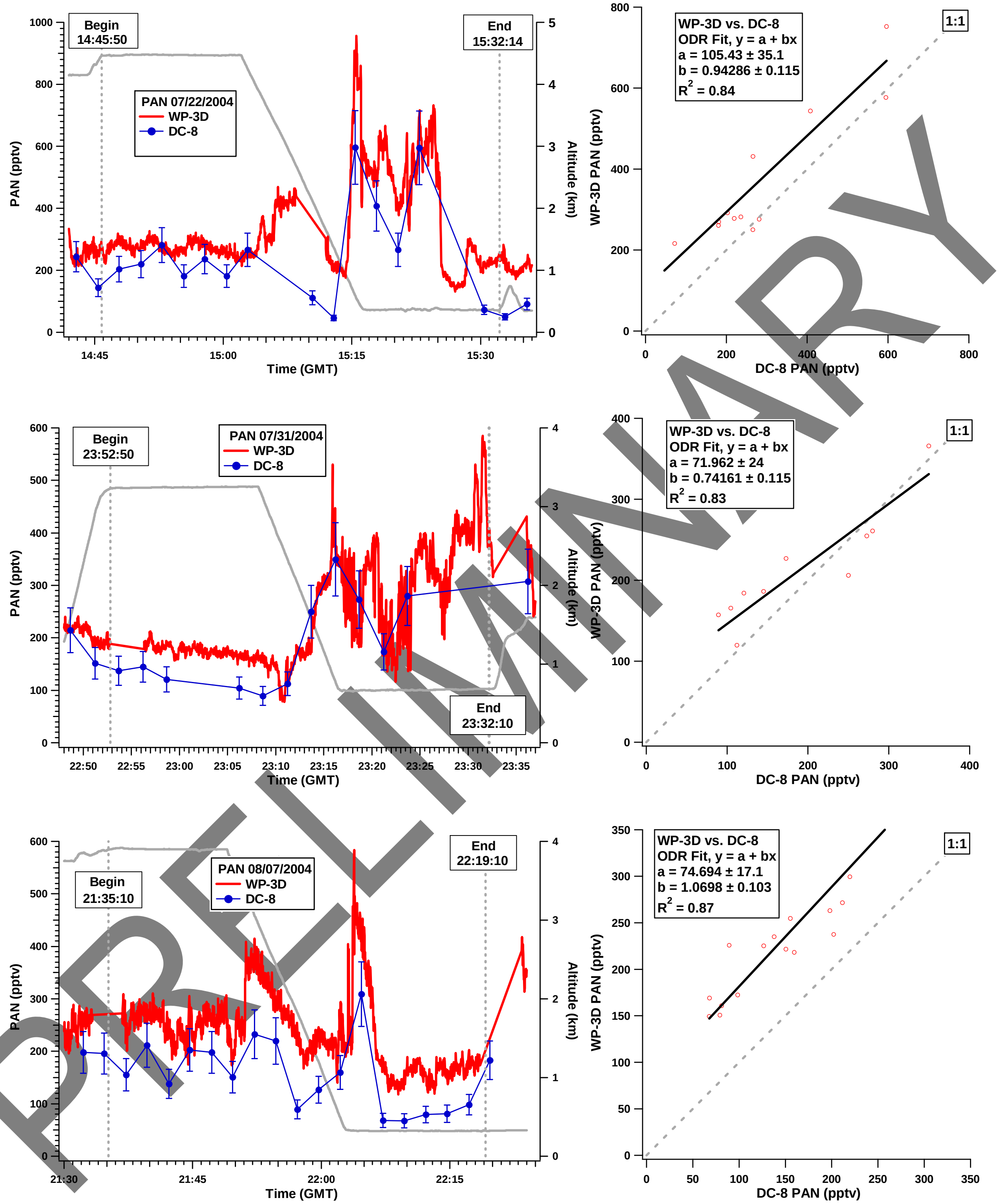

Figure A1: (left panels) Time series of PAN measurements and aircraft altitudes from two aircraft on the three comparison flights between NASA DC-8 and the NOAA WP-3D. (right panels) Correlations between the PAN measurements on the two aircraft.

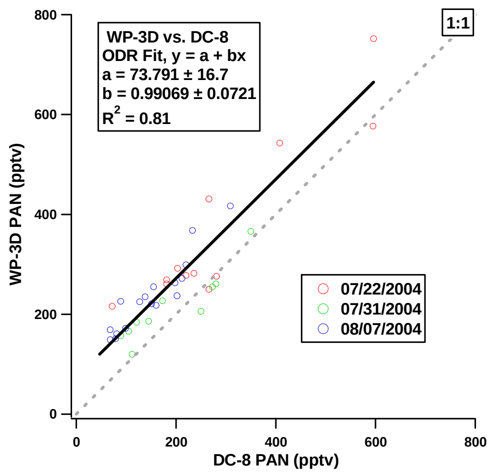

Figure A2: Correlations between the PAN measurements on the two aircraft for all three days.

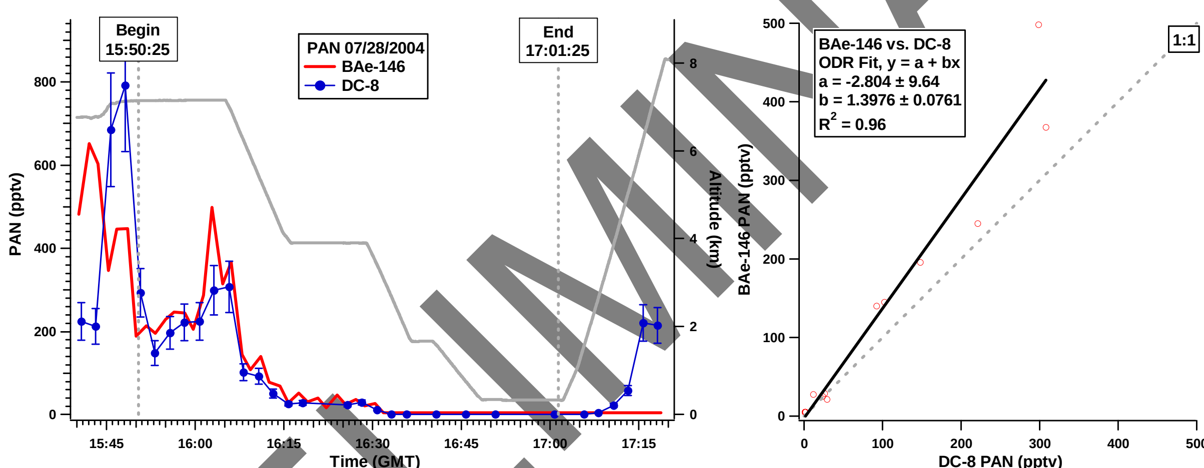

Figure A3: (left panel) Time series of PAN measurements and aircraft altitudes from the intercomparisons flight between NASA DC-8 and the FAAM BAe-146. (right panel) Correlations between the PAN measurements on the two aircraft.