TAbMEP Assessment: ICARTT HNO_3 Measurements

1. Introduction
Here we provide the assessment for the nitric acid (HNO_3) measurements taken from two aircraft platforms during the summer 2004 ICARTT field campaign [*Fehsenfeld et al.*, 2006]. This assessment is based upon the three wing-tip-to-wing-tip intercomparison flights conducted during the field campaign, plus a comparison between the two NASA DC-8 instruments on all ICARTT research flights. Recommendations provided here offer a systematic approach to unifying the ICARTT HNO_3 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 HNO_3 Measurements
Three different HNO_3 instruments were deployed on the two aircraft. Table 1 summarizes these techniques and gives references for more information.

Table 1. HNO_3 measurements deployed on aircraft during ICARTT

Aircraft	Instrument	Reference
NASA DC-8	Mist chamber (MC)	
NASA DC-8	Chemical ionization mass spectrometer (CIMS)	
NOAA WP-3D	Chemical ionization mass spectrometer (CIMS)	

3. Summary of Results
The standard of analysis for ICARTT HNO_3 is the DC-8 MC versus WP-3D CIMS comparison. Both instruments were well established prior to the ICARTT campaign and they compared well with each other. The DC-8 CIMS instrument was not incorporated into the standard because it was the first time that instrument was used on the DC-8. 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 precision value is used.

In this comparison, two methods of determining bias were used. The bias for DC-8 MC and WP-3D CIMS is best described linearly. The central tendency of DC-8 CIMS, however, is best described by a more complex function. For the DC-8 CIMS instrument "water dependent sensitivity corrections were applied using the DLH water mixing ratio and water dependent sensitivity curves measured in the laboratory." Figure A3 shows a clear trend between the DC-8 HNO_3 residual and DC-8 DLH mixing ratio. Due to this trend the DC-8 CIMS recommended bias correction equation in Table 2 incorporates DLH. Details of analysis and the corresponding bias equation are in section 4.1.

For the WP-3D CIMS instrument, the bias correction is smaller than the uncertainty reported by the PI, so no bias correction needs to be made to this data set. For the DC-8 MC instrument, the reported PI uncertainty was less than the quadrature-sum, so the quadrature-sum is used as the recommended 2σ uncertainty.

Table 2. Recommended ICARTT HNO_3 measurement treatment

Aircraft	Instrument	Reported 2σ Uncertainty	Recommended Bias Correction	Recommended 2σ Uncertainty
NASA DC-8	MC	60-70% for <25 pptv 40% for 25-100 pptv 30% for >100 pptv	$-3.65 - 0.14\ HNO_{3\ MC}$ [b]	$\{(-3.65 - 0.14\ HNO_3)^2 + (0.456\ HNO_3)^2\}^{1/2}$ pptv
NASA DC-8	CIMS	Reported point by point	y0=-432.06, A1=301.93, x0=24.009, t1=79.79, A2=447.2, t2=15516, A3=0.084171 [a]	
NOAA WP-3D	CIMS	Precision: 40 pptv, Accuracy: 100 pptv + 30%	$2.85 + 0.109\ HNO_{3WP3D}$ [b]	$\{40^2 + (100 + 0.3\ HNO_3)^2\}^{1/2}$ pptv

[a] Correction in the form y0 + A1*exp(-(DLH – x0)/t1) + A2*exp(-(DLH – x0)/t2) + A3*DC-8 CIMS
[b] Correction in the form a + b*H_2O

4. Results and Discussion

4.1 Bias Analysis

Figures 1-3 illustrate the need for quantifying the bias between instruments. The difference between the simultaneous measurements reported by two instruments is plotted against the HNO_3 mixing ratio reported by one of the instruments. The DC-8 MC and WP-3D CIMS apparent biases in Table 3 are calculated from orthogonal linear regression (ODR) analysis (shown in Fig. A4). ODR is used to approximate the bias between the paired instruments' dependence on the HNO_3 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. WP-3D - DC-8). For convenience, the apparent bias is given in the form a + b*$HNO_{3\text{-}MC}$. In this form, it is easier to propagate the apparent biases and 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 HNO_3 mixing ratio as a function of the instrument being analyzed. This can be calculated by subtracting the true HNO_3 mixing ratio from the respective apparent bias equation from Table 3 and putting the result in terms of the instrument being analyzed. The average of the apparent biases for the DC-8 MC and WP-3D CIMS instruments (3.65 pptv + 0.14 HNO_3) is assumed to be the best estimate of the "true HNO_3 mixing ratio." The DC-8 CIMS is not included in the average since another method was used to approximate the central tendency of the data. In effect, this procedure assumes that the best estimate of the true HNO_3 mixing ratio is the average of the two instruments, and the apparent bias correction is used in calculations to most closely approximate the true HNO_3 mixing ratio for the DC-8 MC and WP-3D CIMS instruments.

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 HNO_3 bias estimates

Aircraft	Instrument	Apparent Bias[1] (a pptv + b HNO_3)	Best Estimate Bias (a pptv + b HNO_3)
NASA DC-8	MC	0	-3.65 – 0.14 $HNO_{3\text{-}MC}$
NOAA WP-3D	CIMS	7.30 + 0.280 $HNO_{3\text{-}MC}$	2.85 + 0.109 $HNO_{3\text{-}WP3D}$

[1] DC-8 MC is taken as an arbitrary reference. Apparent bias is reported as a line where DC-8 MC is the independent variable to accommodate for the slope and intercept of the bias.

Through the DC-8 MC and DC-8 CIMS comparison it was determined that there is a trend with DC-8 DLH as shown in Fig. A3. In order to encompass the correlation between the two instruments and the dependence on DLH, a 2D equation was used to describe the central tendency. An exponential equation with offset fits well in Fig. A3, but by slightly adjusting the equation so DC-8 CIMS and DC-8 DLH are independent variables and the residual is the dependent variable, the following equation can be derived: y0 + A1*exp(-(DLH – x0)/t1) + A2*exp(-(DLH – x0)/t2) + A3*DC-8 CIMS. Adding another term (A4*DC-8 CIMS^2) did not improve the fit.

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 three continuous, fast measurements. The IEIP procedure is an effective method to estimate “short-term” precision, which accounts for signal variation during a short period of assumed constant HNO_3 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. 4 - 6, 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. In three cases the observed variability is larger than the expected variability, which indicates that the IEIP derived (short-term) precision needs to be adjusted to reflect the longer term fluctuations. Table 4 contains estimates of this “adjusted” precision obtained by proportionally scaling the IEIP estimates so that the expected variability values would equal to that of the observed variability. This adjustment was not done for the DC-8 MC/DC-8 CIMS comparison because such large variability may not be explainable by just instrument precision. For the case where observed variability is smaller than the expected variability, the adjusted precision (last column in Table 4) is set equal to the IEIP precision. 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 HNO_3 instrument and is used for the derivation of the recommended 2σ uncertainty in the last column of Table 2.

Table 3 shows that the measurement bias is a function of HNO_3 mixing ratio. Thus, the bias may have a significant impact on the observed variability. To minimize the effect of bias, we make corrections for bias before computing the observed variability. For instance, the observed variability for DC-8 MC/DC-8 CIMs for all flights is 187% without correction. With correction and the removal of outliers it is 81.8%. The observed variability values given in Table 4 are computed after the bias correction.

Table 4. ICARTT HNO_3 precision (1σ) comparisons

Flight	Platform	IEIP Precision	Expected Variability	Observed Variability	Adjusted Precision
07/22	DC-8 MC	15%	16.8%	25.4%	22.8%
	WP-3D	7.5%			11.4%
07/31	DC-8 MC	15%	19.5%	15.7%	15%
	WP-3D	12.5%			12.5%
08/07	DC-8 MC	15%	16.8%	24.2%	21.7%
	WP-3D	7.5%			10.8%
All Flights	DC-8 MC	15%	16.8%	81.8%	
	DC-8 CIMS	7.5%			

Appendix A

Figure A1 shows the time series of the HNO_3 measurements and aircraft altitudes for each intercomparison flight as well as the correlations between the two HNO_3 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

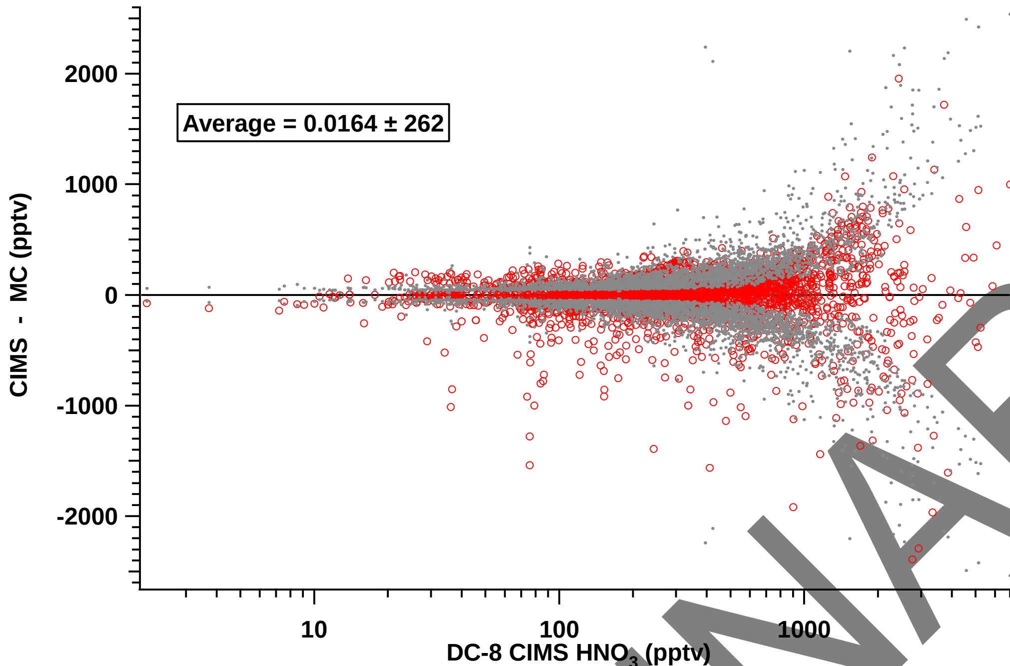

Figure 1: Difference between HNO_3 measurements from DC-8 MC/DC-8 CIMS for all intercomparison flights as a function of DC-8 MC HNO_3. The gray dots indicate the range of the results expected from the reported 2σ measurement uncertainties.

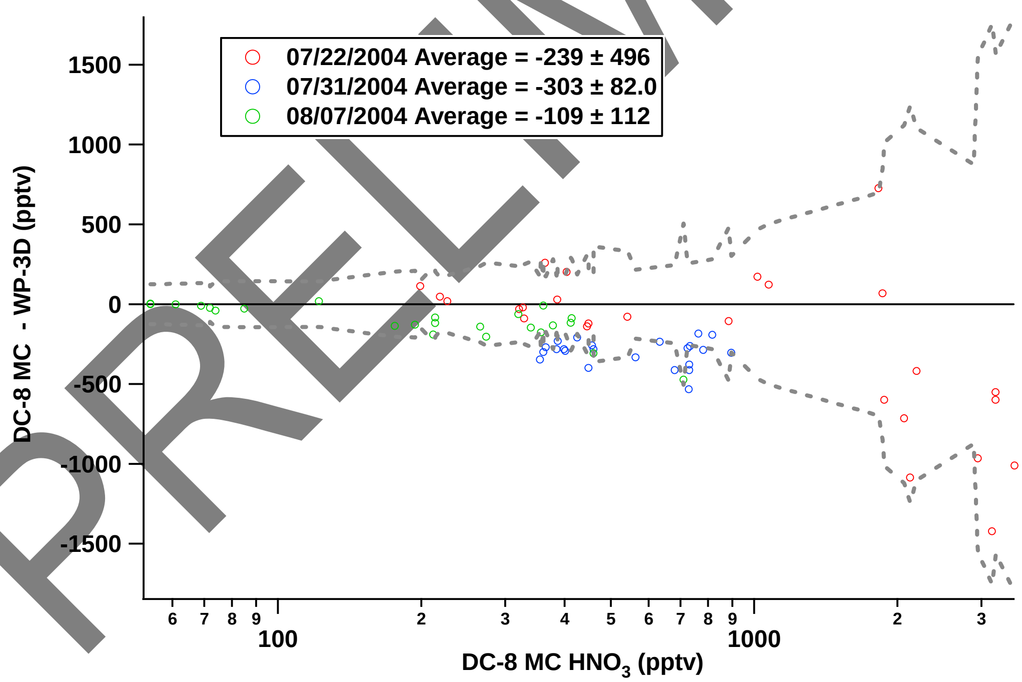

Figure 2: Difference between HNO_3 measurements from the three DC-8 MC/WP-3D CIMS intercomparison flights as a function of DC-8 MC HNO_3. The dashed lines indicate the range of the results expected from the reported 2σ measurement uncertainties.

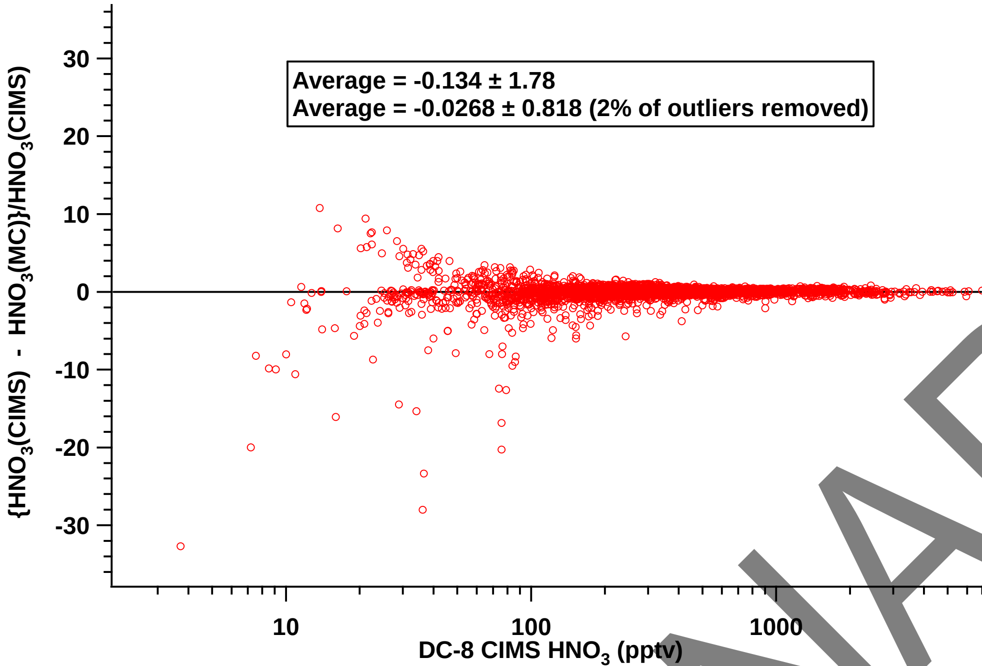

Figure 4: Relative difference between HNO_3 measurements from DC-8 MC/DC-8 CIMS for all intercomparison flights as a function of DC-8 MC HNO_3. A correction to the data was made to account for bias.

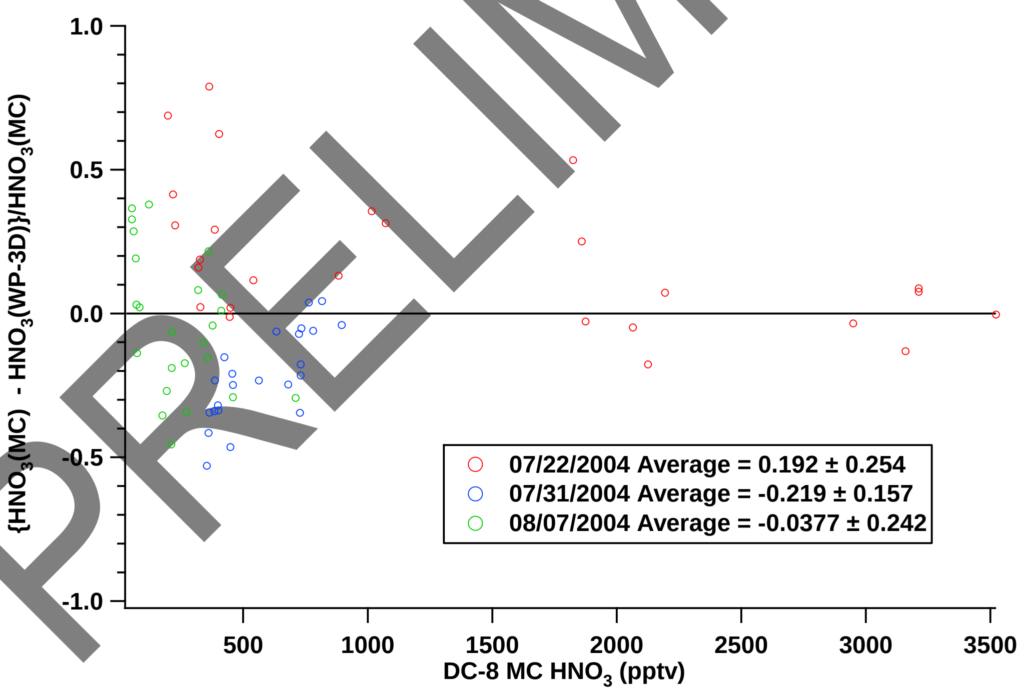

Figure 5: Relative difference between HNO_3 measurements from the three DC-8 MC/WP-3D CIMS intercomparison flights as a function of DC-8 MC HNO_3. A correction to the data was made to account for bias.

Appendix A

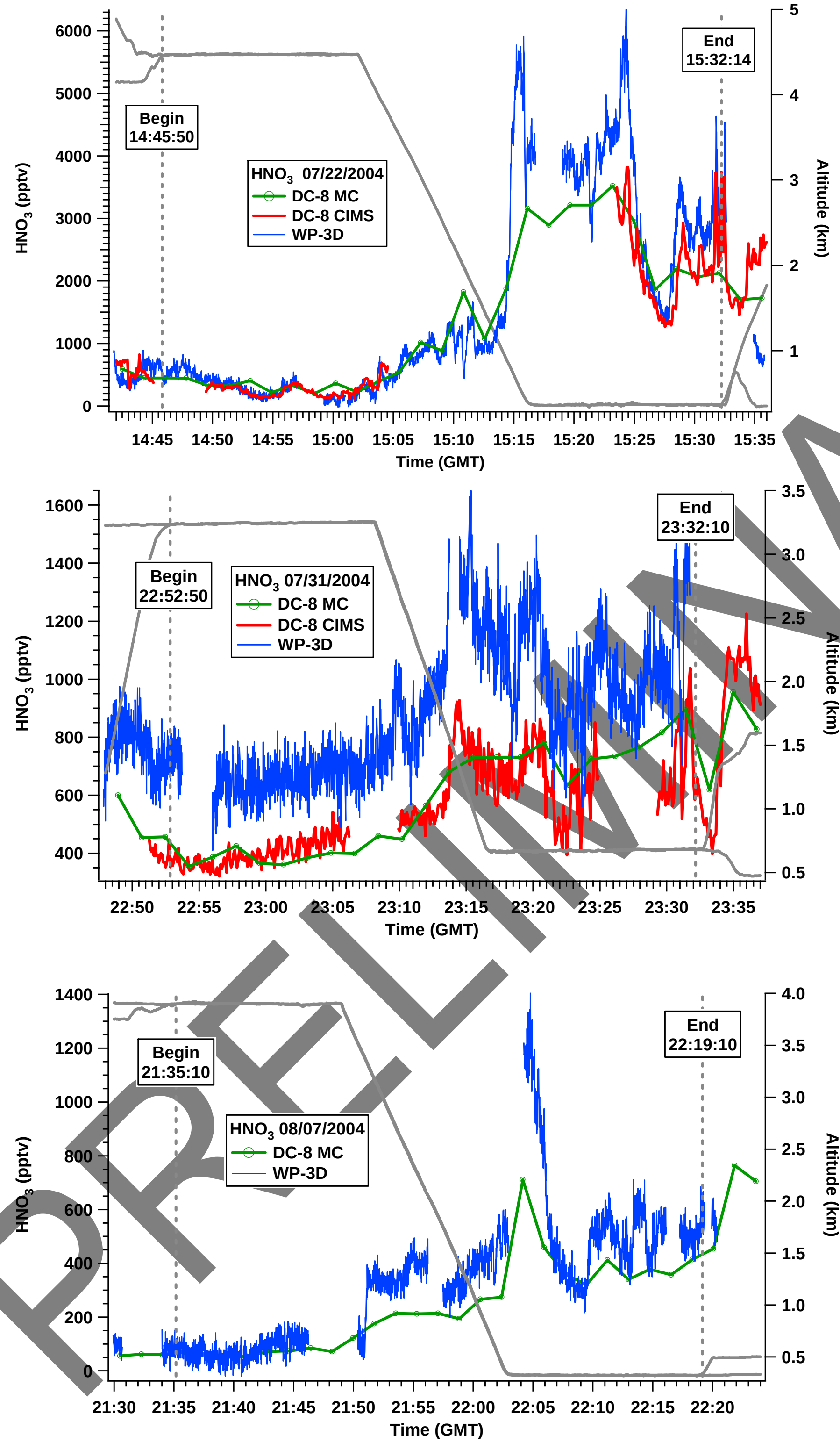

Figure A1: Time series of HNO_3 measurements and aircraft altitudes from two aircraft on the three intercomparison flights between the NASA DC-8 and the NOAA WP-3D.

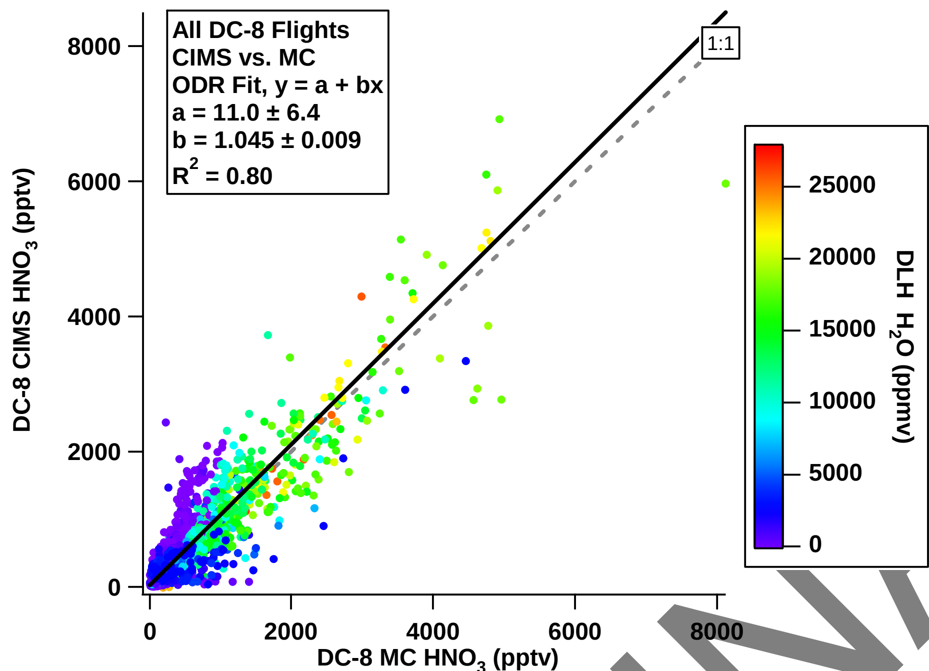

Figure A2: Correlation of HNO_3 measurements for DC-8 MC and DC-8 CIMS for all intercomparison flights.

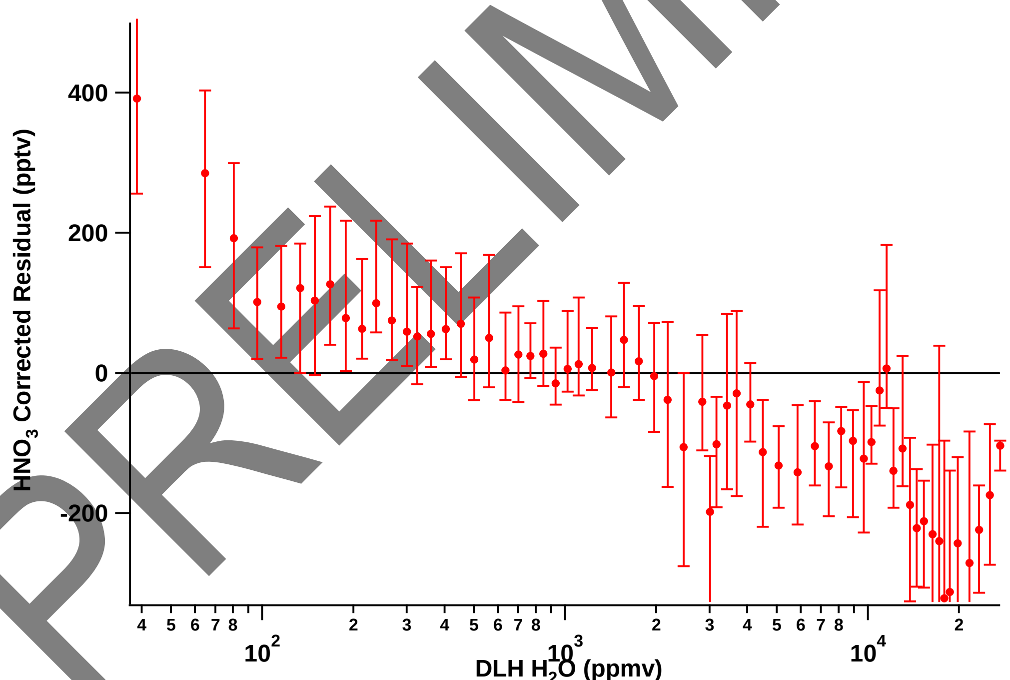

Figure A3: Trend between HNO_3 corrected residual and DC-8 DLH.

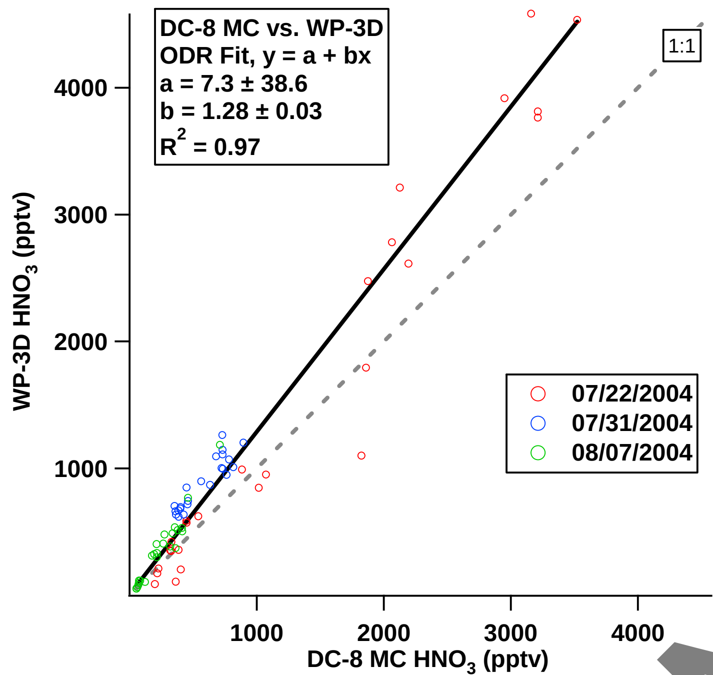

Figure A4: Correlation between the HNO_3 measurements for the DC-8 MC and WP-3D CIMS for all three intercomparison days.

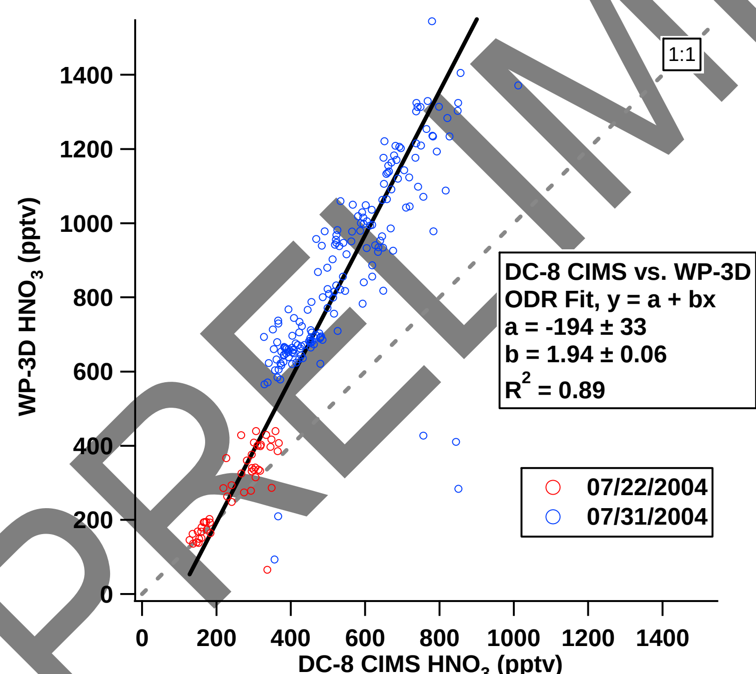

Figure A5: Correlation between the HNO_3 measurements for the DC-8 CIMS and WP-3D CIMS for both intercomparison days.