TAbMEP Assessment: ICARTT HNO_3 Measurements

1. Introduction

Here we provide the assessment for the nitric acid (HNO_3) measurements during the summer 2004 ICARTT field campaign [*Fehsenfeld et al.*, 2006, *Singh et al*., 2006]. The inter-platform assessment is based upon the three wing-tip-to-wing-tip intercomparison flights conducted during the field campaign. The two DC-8 instruments are compared using all available data from the mission (flights 6 – 20). Recommendations provided here offer TAbMEP assessed uncertainties for each of the measurements and a systematic approach to unifying the ICARTT HNO_3 data for any integrated analysis. These recommendations are directly derived from 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 two aircraft. Table 1 summarizes these techniques and gives references for more information. The two CIMS systems report data integrated for less than 1 second and the MC system has an integration time of ~100 seconds.

Table 1. HNO_3 measurements deployed on aircraft during ICARTT

Aircraft	Instrument	Reference
NASA DC-8	Mist chamber (MC)	*Scheuer et al.* [2010]
NASA DC-8	Chemical ionization mass spectrometer (CIMS)	*Crounse et al.* [2006]
NOAA WP-3D	Chemical ionization mass spectrometer (CIMS)	*Neuman et al.* [2002, 2006]

3. Summary of Results

Table 2 summarizes the assessed 2σ precisions, biases, and uncertainties, along with PI reported uncertainties. More detailed descriptions are provided to illustrate the process for assessment of bias and precision in Sections 4.1 and 4.2 respectively. The assessed 2σ precisions reported in Table 2 are equal to twice the highest adjusted precision value for that instrument listed in Table 5. Table 2 also reports an assessed bias (see Section 4.1 for details) that can be applied to maximize the consistency between the data sets. The assessed bias should be subtracted from the reported data to 'unify' the data sets when conducting an integrated analysis. The assessed bias is derived from intercomparison periods only and may be extrapolated to the entire mission if one assumes instrument performance remained constant throughout the mission. The recommended 2σ uncertainty in Table 2 is the larger of either the uncertainty reported by the PI or the quadrature-sum of the assessed 2σ precision and assessed bias listed in Table 2.

This intercomparison has led to the identification of a problem with the DC-8 CIMS stratospheric data. *The DC-8 CIMS PI has indicated that he will resubmit his data files by removing the stratospheric data and reprocessing the data based on the ICARTT water assessment report. We opt to keep the comparison of stratospheric data in the current version of the assessment to be consistent with the current data archive status. This report will be updated when the revised data is posted in the archive.* It is noted that the DC-8 CIMS PI uncertainty is reported point by point at 90% confidence level. This is slightly different from the others, which are reported as 2σ uncertainty (95% CI).

Table 2. Recommended ICARTT HNO_3 measurement treatment

Aircraft/ Instrument	Reported 2σ Uncertainty	Assessed 2σ Precision	Assessed Bias (pptv)	Recommended 2σ Uncertainty
NASA DC-8 MC	60-70% for < 25 pptv 40% for 25-100 pptv 30% for >100 pptv	44%	$-6.9 – 0.12\ HNO_{3DC\text{-}8MC}$	Quadrature Sum[b]
NASA DC-8 CIMS	Point by point, average: 40%[a]	43%	$2.4 – 0.099\ HNO_{3DC\text{-}8CIMS}$	0 – 255 pptv: Point by point > 255 pptv: Quadrature Sum
NOAA WP-3D CIMS	Precision: 40 pptv Accuracy: 100 pptv + 30%	43%	$-1.8 + 0.13\ HNO_{3WP\text{-}3D}$	0 – 672 pptv: precision: 40 pptv, accuracy: 100 pptv + 30% > 672 pptv: Quadrature Sum

[a] The average encompasses all DC-8 CIMS data not including points below the LOD because these points greatly skewed the average.
[b] There is a small range (11-24 pptv) where the PI uncertainty is larger than the quadrature sum.

Figures 1a – c display the assessed precisions, biases, and recommended uncertainties for the three HNO_3 instruments. For the three instruments (DC-8 MC, DC-8 CIMS, and WP-3D) the uncertainty is driven by the precision.

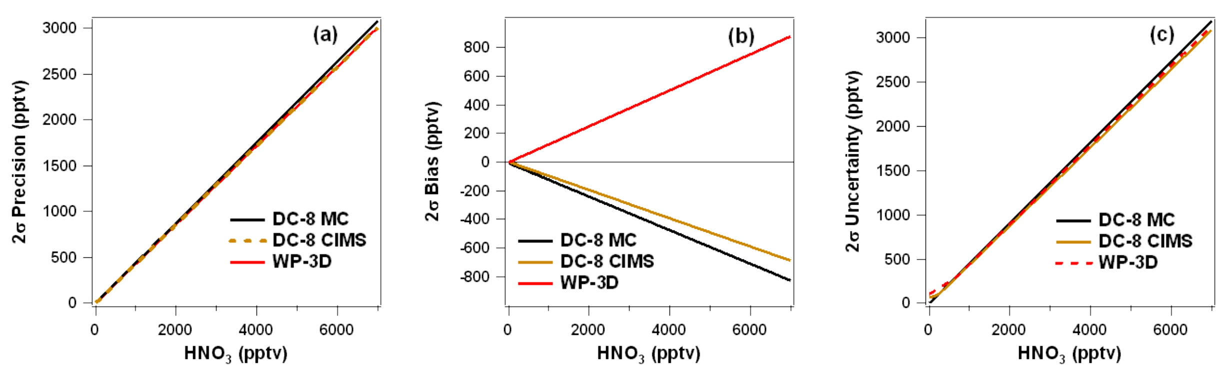

Figure 1. Assessed 2σ precision (panel a), assessed 2σ bias (panel b), and recommended 2σ uncertainty (panel c) for DC-8 MC (black), DC-8 CIMS (gold), and WP-3D (red) as a function of HNO_3 level. Values were calculated based upon data shown in Table 2.

4. Results and Discussion

4.1 Bias Analysis

Section 3.3 in the introduction describes the process used to determine the best estimate bias. Figure 2 shows the time series plots for each of the three WP-3D vs. DC-8 HNO_3 comparisons. There was no DC-8 CIMS data during the comparison period for 08/07/2004. Regression analysis was conducted between the HNO_3 measurements. Figure 3a displays the correlation between DC-8 MC and CIMS data. The DC-8 CIMS data were averaged into the overlapping DC-8 MC measurement time intervals. The WP-3D CIMS measurement is compared with both the DC-8 MC and CIMS systems in Figure 4a and 4b. Similarly, the WP-3D CIMS data were also averaged into the overlapping DC-8 MC measurement time intervals.

Table 3. ICARTT HNO_3 bias estimates

Aircraft/ Instrument	**Linear Relationships (pptv)**	**Best Estimate Bias ($a + b$ HNO_3) (pptv)**
NASA DC-8 MC	$HNO_{3DC\text{-}8MC} = 0.00 + 1.00\ HNO_{3DC\text{-}8MC}$	$-6.9 – 0.12\ HNO_{3DC\text{-}8MC}$
NASA DC-8 CIMS	$HNO_{3DC\text{-}8CIMS} = 8.47 + 1.02\ HNO_{3DC\text{-}8MC}$	$2.4 – 0.099\ HNO_{3DC\text{-}8CIMS}$
NOAA WP-3D CIMS	$HNO_{3WP\text{-}3D} = 5.87 + 1.28\ HNO_{3DC\text{-}8MC}$	$-1.8 + 0.13\ HNO_{3WP\text{-}3D}$
NOAA WP-3D CIMS[a]	$HNO_{3WP\text{-}3D} = 12.1 + 1.39\ HNO_{3DC\text{-}8CIMS}$	N/A
NASA DC-8 CIMS*	$HNO_{3DC\text{-}8CIMS*} = 4.84 + 1.09\ HNO_{3DC\text{-}8MC}$	N/A
NOAA WP-3D CIMS*	$HNO_{3WP\text{-}3D*} = 20.7 + 1.42\ HNO_{3DC\text{-}8MC}$	N/A

[a] This equation was used in the derivation of * equations.
* Derived from regression equations.

The summary of the regression analyses is given in Table 3 along with the best estimate bias which is defined as the difference between the individual measurement and the reference standard for comparison (RSC). Detailed description of RSC and the best estimated bias can be found in the introduction section. For ICARTT HNO_3 measurements, the RSC is constructed using all the available comparison information. Because there were two instruments on the DC-8, the RSC is found by averaging five regressions, three of which are direct from the correlation graphs and two of which come from combining regression equations in order to use all comparisons. The three comparisons from the correlation graphs are: DC-8 MC vs DC-8 MC, DC-8 MC vs DC-8 CIMS, and DC-8 MC vs WP-3D. The WP-3D* is the linear equation derived from the WP-3D vs DC-8 CIMS and DC-8 MC vs DC-8 CIMS equations. Similarly, the DC-8 CIMS* is from the DC-8 CIMS vs WP-3D and WP-3D vs DC-8 MC. The DC-8 MC vs DC-8 MC and DC-8 MC vs DC-8 CIMS direct regression equations were given equal weights of one. The DC-8 MC vs WP-3D direct regression equations and the two derived linear equations were given weights of 0.5 (i.e. [MC + DC8 CIMS + 0.5 WP-3D + 0.5 WP-3D* + 0.5 CIMS*]/3.5). The resulting RSC can be expressed as a function of the DC-8 MC HNO_3 measurement as the following:

$$RSC = 6.914 + 1.117\ HNO_{3DC\text{-}8MC}$$

The RSC is then used to calculate the best estimate bias as described in Section 3.3 of the introduction. It should be noted that the initial choice of the reference instrument (DC-8 MC) is arbitrary, and has no impact on the final recommendations. Table 3 summarizes the assessed measurement bias for each of the three ICARTT HNO_3 measurements. Note that additional decimal places were carried in the calculations to ensure better precision. It is also noted that the intercept in the equations listed in Table 3 should not be viewed as an offset. These linear equations are used to best describe the linear relation between the WP-3D and DC-8 measurements.

The possibility that the DC-8 MC and CIMS comparison was dependent on water was explored by looking at the difference between the two measurements versus water. This dependence is evident in Figure A1. This was further investigated through the analysis of the individual flights. An example of this can be seen in Figure A2 for flight 8 on 07/15/2004. From this Figure, it can be summarized that at low water levels the DC-8 CIMS measurement is larger than the DC-8 MC and at high water levels the DC-8 MC is larger. It is noted that the water vapor at which the difference between CIMS and MC switches sign is variable from flight to flight. Figure 5a – 5c shows how the linear relationship between the two measurements changes based on water level. At diode laser hygrometer (DLH) H_2O below 1000 ppmv the slope (2.02) is significantly larger than the overall comparison (1.02). It is also noted that this group of data has the lowest R^2 value. At higher water levels the linear relationship is much more similar to the overall comparison as shown in Figure 5b and 5c. It can also be seen that the color code suggests that at lower water vapor CIMS tend to be higher than MC while MC tend to be higher at the opposition conditions. The regression line should be considered as a net average for the data group. A summary of the comparison between DC-8 MC and CIMS is given in Table 4 as a function of water vapor mixing ratio. Also given are the best estimate biases. Table 4 highlights the difference between DC-8 MC and CIMS, which is variable and at least partially dependent on water vapor. This is especially relevant considering the fact that low water vapor points remain in the DC-8 CIMS HNO_3 data archive. At the same time, the data user should recognize that the equations provided in Table 4 may improve the data consistency to a certain extent. The limitation can clearly be seen in Figure 9b.

Table 4. ICARTT HNO_3 DC-8 CIMS bias at various water levels

Aircraft/ Instrument	**Range of DLH Water**	**Linear Relationships**	**Best Estimate Bias ($a + b\ HNO_3$) (pptv)**
NASA DC-8 CIMS	$[H_2O] < 1000$ ppmv	$HNO_{3DC\text{-}8CIMS} = -115 + 2.02\ HNO_{3DC\text{-}8MC}$	$-71 + 0.45\ HNO_{3DC\text{-}8CIMS}$
	$1000 \leq [H_2O] \leq 15000$ ppmv	$HNO_{3DC\text{-}8CIMS} = -48.1 + 1.06\ HNO_{3DC\text{-}8MC}$	$-58 – 0.058\ HNO_{3DC\text{-}8CIMS}$
	$[H_2O] > 15000$ ppmv	$HNO_{3DC\text{-}8CIMS} = -154 + 1.05\ HNO_{3DC\text{-}8MC}$	$-171 – 0.063\ HNO_{3DC\text{-}8CIMS}$

The potential effect of fine nitrate interference on the MC measurement is also explored here through examining the dependence of the difference between MC and CIMS values on the fine nitrate measurement by PILs, which is shown in Figure A3. For more information on the PILS measurement contact Rodney Weber at rweber@eas.gatech.edu. There is a definite trend shown and the regression line suggests that the difference between the instruments may be explained by the fine nitrate. At the same time, it should also be noted that there are a significant number of cases that the difference is well beyond the observed fine nitrate level, especially for the part where the fine nitrate is less than 100 pptv. The PILs measurement showed only ~7% of data with values larger than 100 pptv for the entire INTEX-A campaign. Figure A4 shows that the linear relationship at the lowest nitrate levels (under LOD) is similar to the overall linear relationship between DC-8 MC and CIMS shown in Figure 3a. Therefore, it is reasonable to conjecture that the fine nitrate interference should not have a major influence on the difference between the DC-8 MC and DC-8 CIMS systems. This reflects the general low nitrate concentration observed in the DC-8 sampling region.

4.2 Precision Analysis

A detailed description of the precision assessment is given in Section 3.1 of the introduction. The IEIP precision, expected variability, observed variability, and adjusted precision are summarized in Table 5. Based on the results in Table 5, the largest "adjusted precision" value was taken as a conservative precision estimate for each ICARTT HNO_3 instrument and twice that value is listed in Table 2 as the assessed 2σ precision.

Table 5. ICARTT HNO_3 precision (1σ) comparison

Flight	Platform	IEIP Precision	Expected Variability	Observed Variability	Adjusted Precision
07/22	DC-8 MC	15%	16.8%	23.6%	22%
	WP-3D	7.5%			11%
07/31	DC-8 MC	15%	21.2%	15.8%	15%
	WP-3D	15%			15%
08/07	DC-8 MC	15%	19.2%	22.4%	18%
	WP-3D	12%			14.4%

Flight	Platform	IEIP Precision	Expected Variability	Observed Variability	Adjusted Precision
07/22	DC-8 CIMS	7.5%	10.6%	28.9%	21.5%
	WP-3D	7.5%			21.5%
07/31	DC-8 CIMS	7.5%	16.8%	17.3%	8.5%
	WP-3D	15%			17%
08/07	DC-8 CIMS	12%	17.0%	N/A[a]	N/A
	WP-3D	12%			N/A

[a] DC-8 CIMS did not have any measurements during the comparison period.

To minimize the effect of bias in precision assessment, we make corrections for bias before computing the observed variability, as the bias may have a significant impact on the observed variability. Figures 6 – 8 show the magnitude of the bias for each intercomparison. The assessed values of the observed variability are displayed in Figures 10 – 11. The observed variability estimated from the DC-8 MC and DC-8 CIMS comparison, shown in Figure 9a is not used to derive adjusted precision. This is because the observed variability is influenced by the bias related water vapor, which should not be considered as precision issues. Figure 9b shows a smaller spread as the data for water < 1000 ppmv which was corrected using the equation provided in Table 4. This correction has reduced the observed variability by more than 20%, which indicates the observed variability is an inadequate measure of precision. The final analysis results are shown in Table 2, which is based on the intercomparison periods between DC-8 and WP-3D. As all intercomparisons were conducted below 5 km and the water vapor effect on the observed variability is not significant, analysis of the data demonstrates that Table 2 provides a reasonable estimate of the precisions.

As shown in Figure 7 and 8, over 90% of the data falls within the combined recommended uncertainties for both of the DC-8 vs. WP-3D comparisons, which is consistent with the TAbMEP guideline for unified data sets. The DC-8 MC vs. DC-8 CIMS comparison does not meet this guideline most likely due to the aforementioned larger variability at low water levels, even with additional bias correction as shown in Figure 9a and 9b.

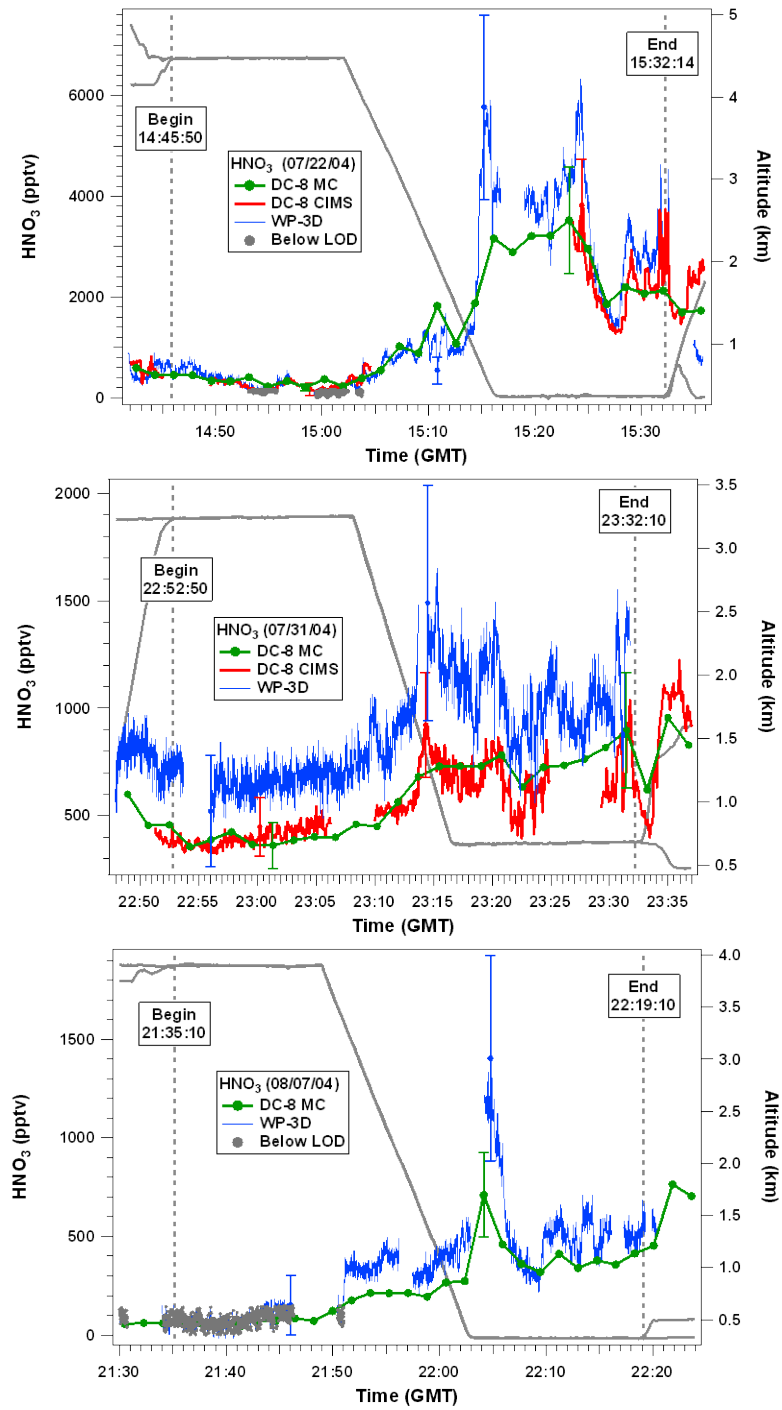

Figure 2. Time series of HNO_3 measurements and aircraft altitudes from two aircraft on the three intercomparison flights between the NASA DC-8 and the NOAA WP-3D. Error bars represent the PI reported uncertainty.

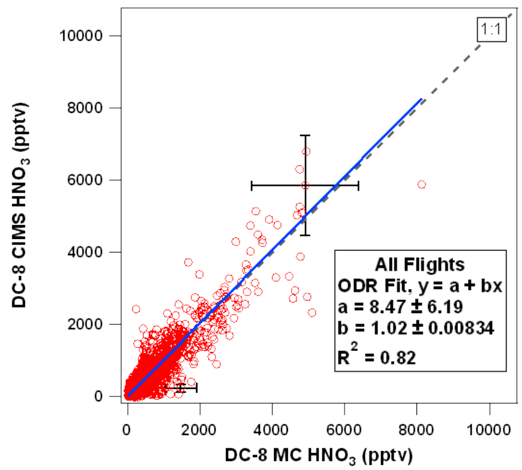

Figure 3. Correlation of DC-8 MC and CIMS HNO_3 measurements for all ICARTT flights. Data was taken from the UNHMC merge file.

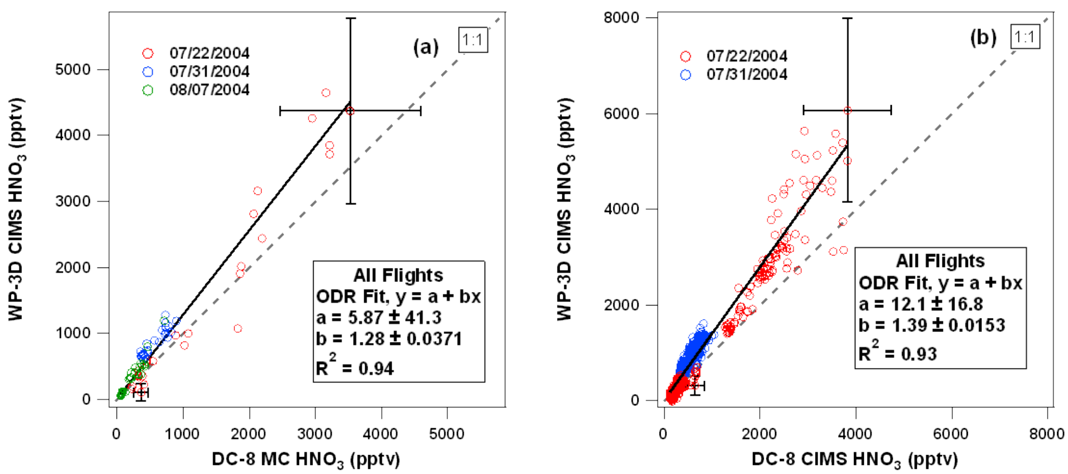

Figure 4. Combined correlation for the HNO_3 measurements on the NASA DC-8 and the NOAA WP-3D for 7/22, 7/31, and 8/07 2004. (left panel) DC-8 MC and (right panel) DC-8 CIMS. Error bars represent the PI reported uncertainty.

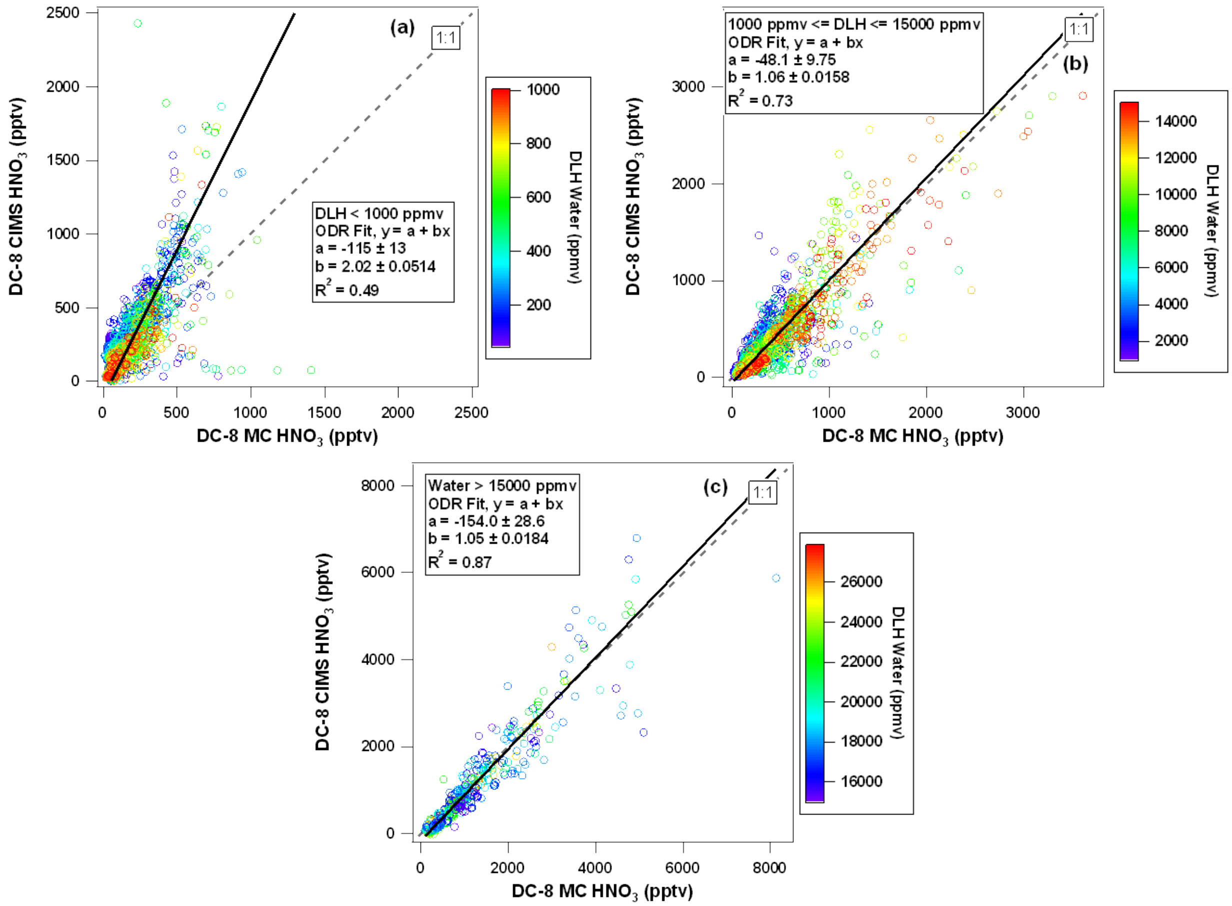

Figure 5. Correlation of DC-8 MC and CIMS HNO_3 measurements at different ranges of DLH H_2O: (top left panel) water < 1000 ppmv, (top right panel) water between 1000 and 15000 ppmv, and (bottom panel) water > 15000 ppmv. The correlations are colored by DLH H_2O level.

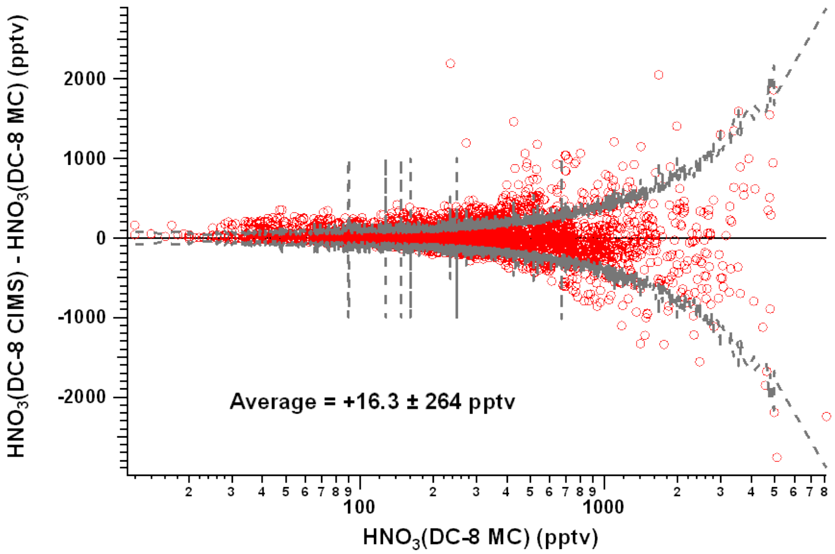

Figure 6. Difference between HNO_3 measurements from DC-8 MC and CIMS for all flights as a function of DC-8 MC HNO_3. The dashed lines indicate the range of results expected from the reported 2σ measurement uncertainties.

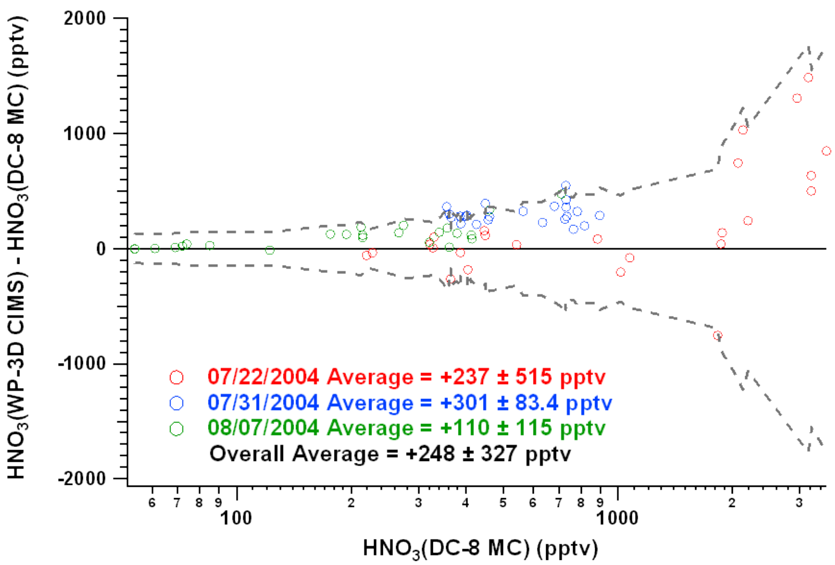

Figure 7. Difference between HNO_3 measurements from the three DC-8 MC and WP-3D intercomparison flights as a function of DC-8 MC HNO_3. The dashed lines indicate the range of results expected from the reported 2σ measurement uncertainties.

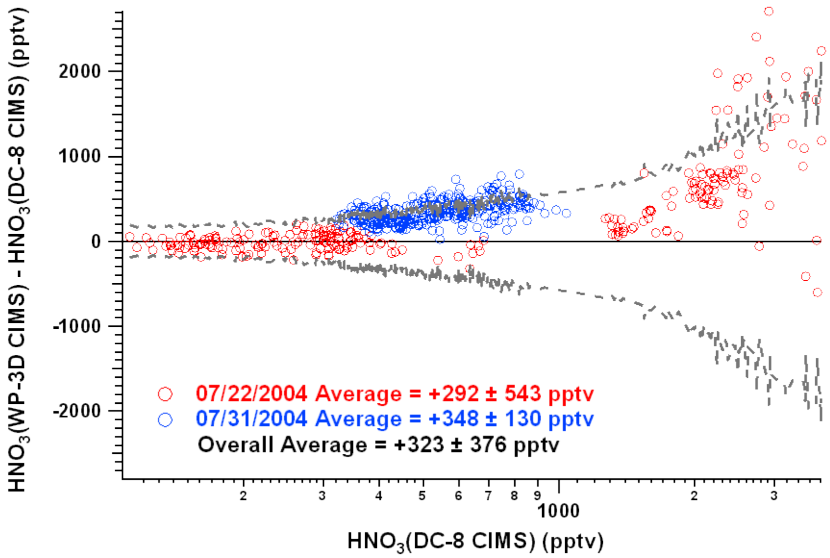

Figure 8. Difference between the HNO_3 measurements from the two DC-8 CIMS and WP-3D intercomparison flights as a function of DC-8 CIMS HNO_3. The dashed lines indicate the range of results expected from the reported 2σ measurement uncertainties.

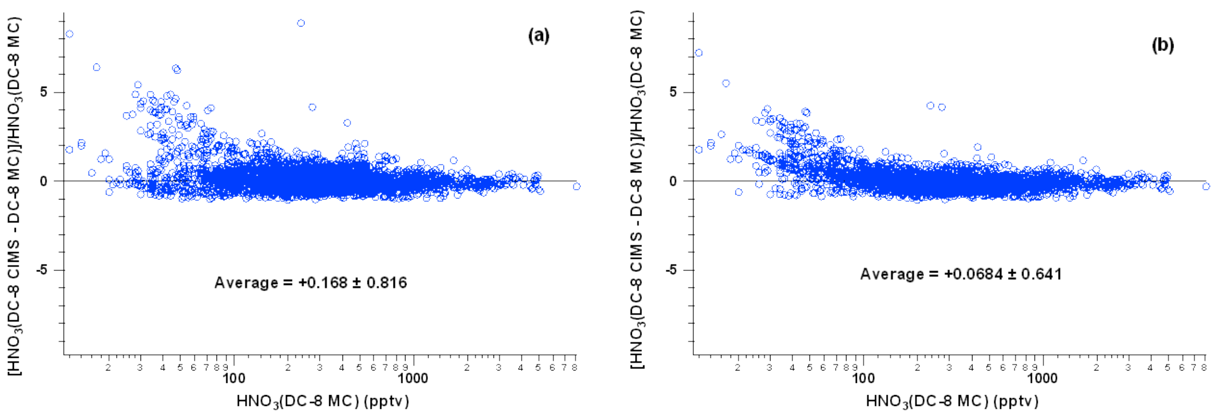

Figure 9. Relative difference between HNO_3 measurements from DC-8 MC and CIMS for all flights as a function of DC-8 MC HNO_3. (left panel) A correction was made to account for bias. (right panel) Two corrections were used, one for water < 1000 ppmv, and the general correction to account for bias.

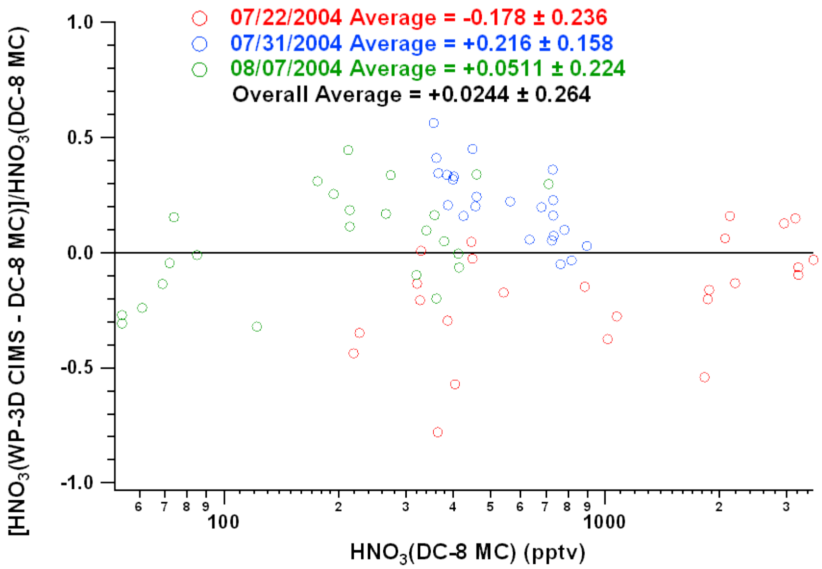

Figure 10. Relative difference between HNO_3 measurements for the three DC-8 MC and WP-3D intercomparison flights as a function of DC-8 MC HNO_3. A correction was made to account for bias.

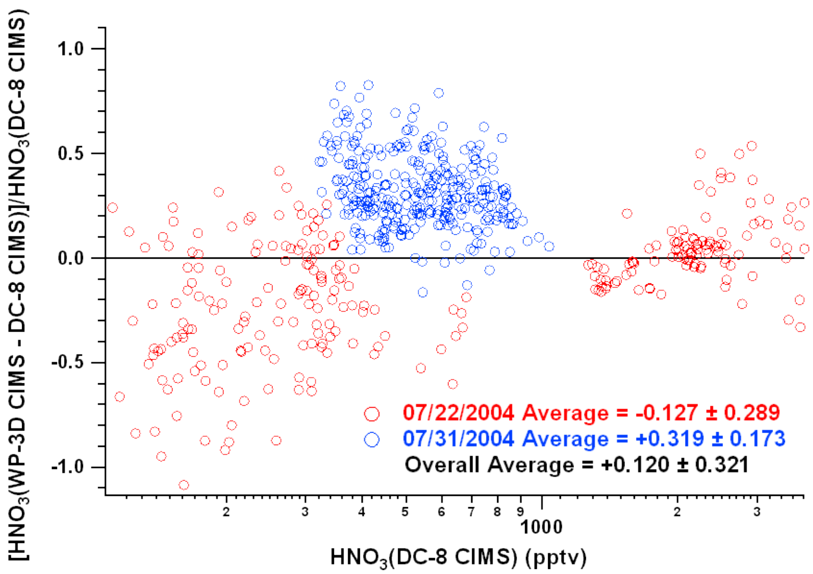

Figure 11. Relative difference between HNO_3 measurements for the two DC-8 CIMS and WP-3D intercomparison flights as a function of DC-8 CIMS HNO_3. A correction was made to account for bias.

Appendix

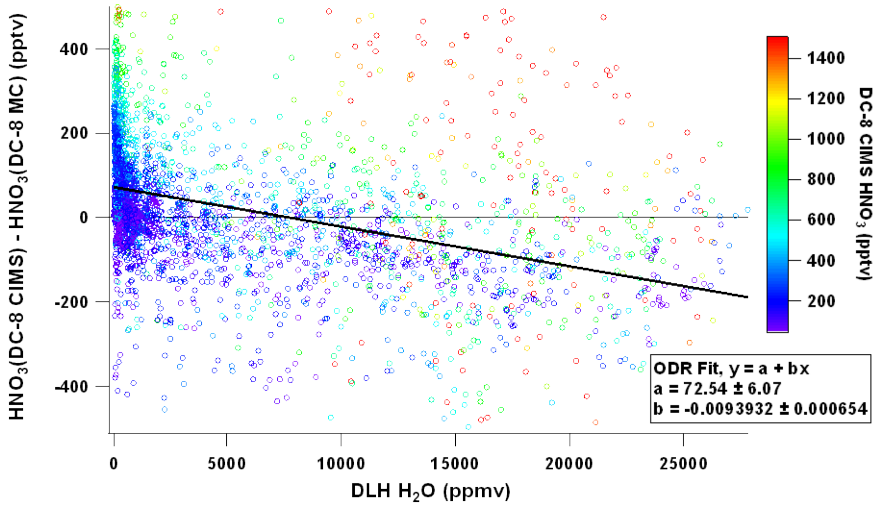

Figure A1. Difference between HNO_3 measurements from DC-8 MC and CIMS for all flights as a function of DLH H_2O and colored by DC-8 CIMS HNO_3. Some data points are not shown because the plot is zoomed in to accentuate the relationship between the residual and DLH at low HNO_3 levels.

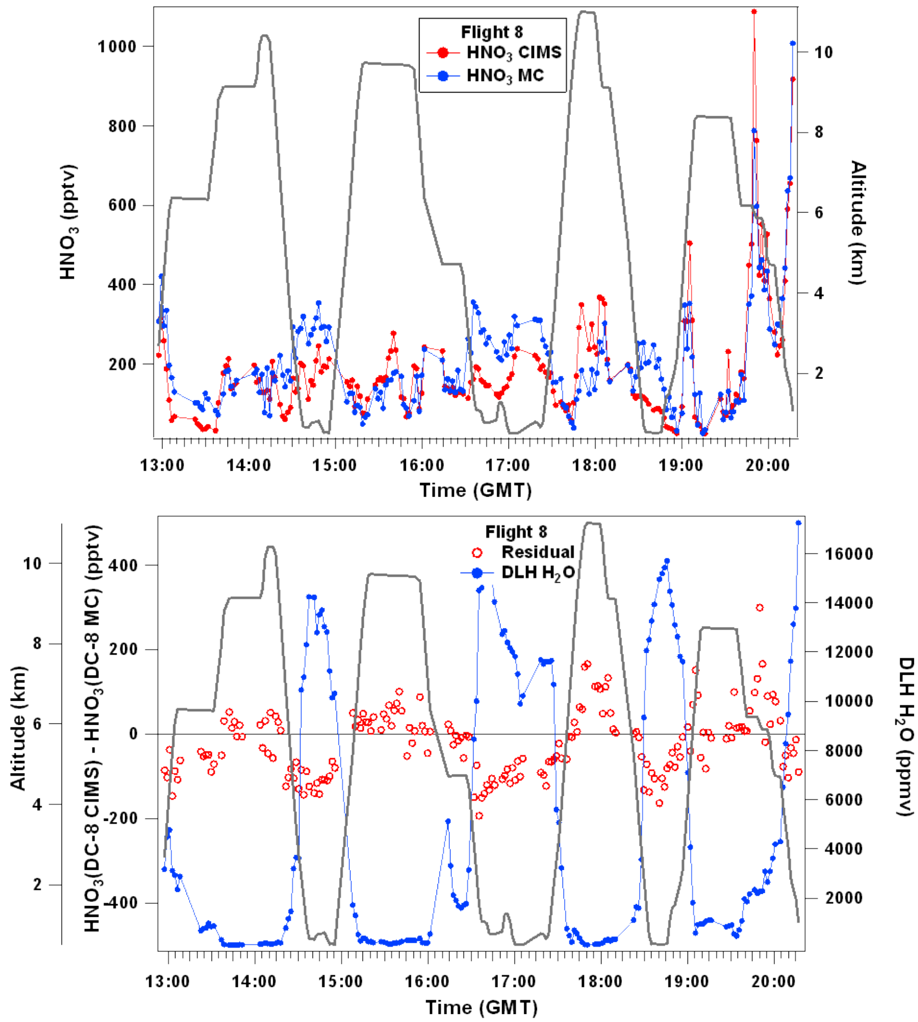

Figure A2. (top panel) Time series plot of HNO_3 measurements and aircraft altitudes from the DC-8 aircraft on flight 8 (07/15/04). (bottom panel) Time series plot of difference between DC-8 MC and CIMS, altitude, and DLH H_2O for flight 8 (07/15/04).

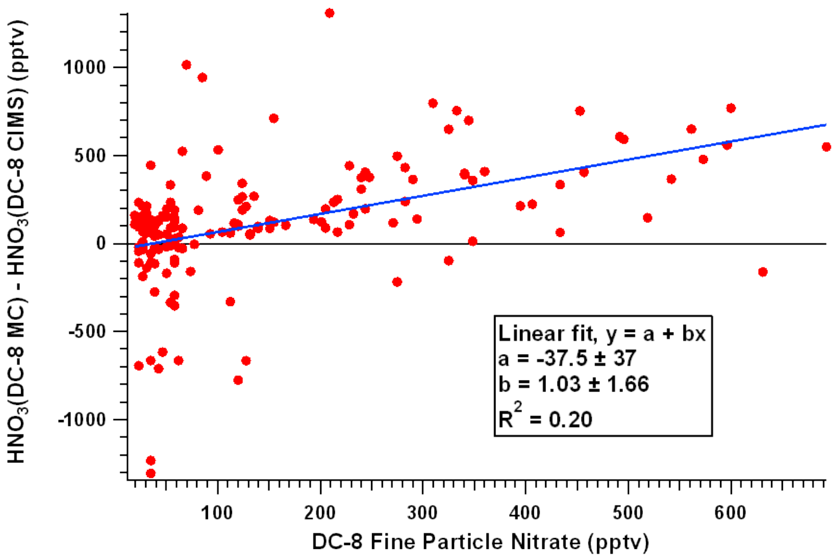

Figure A3. Difference between DC-8 HNO_3 measurements (MC – CIMS) as a function of fine nitrate.

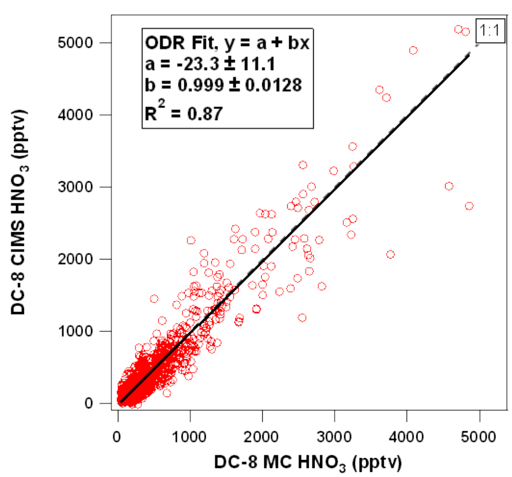

Figure A4. Correlation of DC-8 MC and CIMS HNO_3 measurements for all available fine nitrate below LOD, i.e., minimum fine nitrate interference.

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