TAbMEP Assessment: ICARTT Ethyne Measurements

1. Introduction

Here we provide the assessment for the ethyne (C_2H_2) measurements taken from three aircraft platforms during the summer 2004 ICARTT field campaign [*Fehsenfeld et al.*, 2006, *Singh et al.*, 2006]. This assessment is based upon the four wing-tip-to-wing-tip intercomparison flights conducted during the field campaign. Recommendations provided here offer TAbMEP assessed biases for each of the measurements and a systematic approach to unifying the ICARTT ethyne 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 Ethyne Measurements

Three whole air sampler instruments were deployed on three aircraft. Table 1 summarizes these techniques and gives references for more information.

Table 1. Ethyne measurements deployed on aircraft during ICARTT

Aircraft	Instrument	Reference
NASA DC-8	Whole Air Sampler (WAS)	*Colman et al.* [2001]
NOAA WP-3D	Whole Air Sampler (WAS)	Contact PI: eatlas@rsmas.miami.edu
FAAM BAe-146	Whole Air Sampler (WAS)	*Hopkins et al.* [2003]

3. Summary of Results

Table 2 summarizes the assessed biases as well as the PI reported uncertainties for each of the three ethyne measurements involved in the intercomparisons. More detailed descriptions are provided to illustrate the process of the bias assessment in Section 4.1. The TAbMEP-prescribed IEIP procedures cannot be applied to the ICARTT ethyne measurements for precision assessment. This is because the reported data have large time gaps and a small data population (see Section 3.1 of the introduction). The assessed bias reported in Table 2 (see Section 4.1 for details) can be applied to maximize the consistency between the data sets, by subtracting the value from the reported data to 'unify' the data sets. If one assumes instrument performance remained constant throughout the mission, the assessed bias may be extrapolated to the entire mission although it is derived from intercomparison periods only.

Figure 1 illustrates the PI reported uncertainty and the assessed bias from Table 2. It can be seen in the figure that the DC-8 uncertainty is larger than the DC-8 bias for most conditions, whereas for the WP-3D and BAe-146 the bias is larger than the uncertainty for a significant portion of the range shown in Figure 1. Furthermore, it should be noted that there are two comparison points with actual readings from DC-8 while BAe-146 reported points below the LOD (limit of detection). This is not accounted for by the assessed bias given in Table 2 and may suggest large bias under certain circumstances.

Table 2. Recommended ICARTT Ethyne measurement treatment

Aircraft/Instrument	Reported 2σ Uncertainty	Assessed Bias
NASA DC-8 WAS	10%	$-10.1 + 0.0905\ C_2H_{2\ DC\text{-}8}$
NOAA WP-3D WAS	10%	$-28.8 + 0.255\ C_2H_{2\ WP\text{-}3D}$
FAAM BAe-146 WAS	Point by Point, average: 15%[a]	$-6.4 - 0.117\ C_2H_{2\ BAe\text{-}146}$

[a] The average encompasses the entire flight, 24% for the comparison period for the DC-8/BAe-146.

The DC-8 and WP-3D uncertainties reported by PIs are a percentage. This may not be adequate at very low end concentration levels. Ideally, the measurement uncertainty may be better represented in the form of x pptv or y%. Based on the intercomparison data, the TAbMEP analysis cannot provide such assessment. Data users should contact the respective PIs about the proper uncertainties when dealing with the low end of measurements, e.g., < 10 pptv.

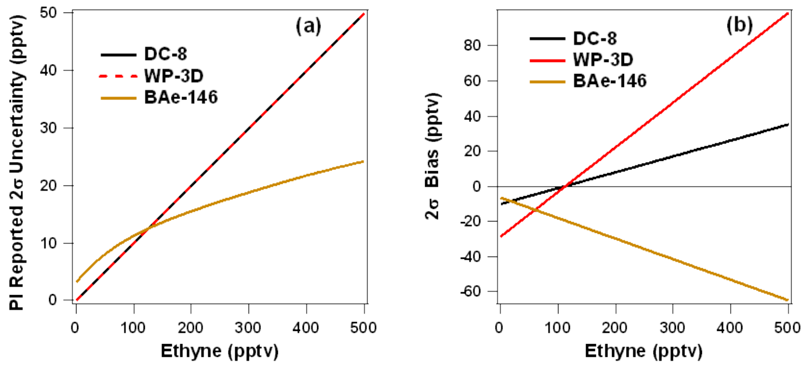

Figure 1. PI reported 2σ uncertainty (panel a) and recommended bias (panel b) for DC-8 (black), WP-3D (red), and BAe-146 (gold) as a function of ethyne level. Values were calculated based upon data shown in Table 2. The BAe-146 PI reported uncertainty was calculated using a function derived from the 60 second merge file.

4. Results and Discussion

4.1 Bias Analysis

Section 3.3 in the introduction describes the process used to determine the best estimate bias. Figures 2 and 4 show the time series plots for the DC-8/WP-3D and DC-8/BAe-146 comparisons. The DC-8 is on average higher than the WP-3D by 5 pptv. Figure 4 clearly shows examples of time periods where the BAe-146 WAS recorded a point below LOD and the DC-8 WAS had a value. The DC-8 is consistently lower on average than BAe-146 by 7 pptv. Figures 5 and 6 show the magnitude of the bias for each intercomparison and Figures 7 and 8 show the corresponding relative residuals.

For two of the three DC-8/WP-3D flights, there are only 3 or 4 overlapping points. It is not statistically significant to show the linear regression individually for these flights. Therefore, linear regression is performed over the data combined from all three DC-8/WP-3D flights shown in Figure 3. The linear relationships listed in Table 3 were derived from the regression equations found in Figures 3 and 4. Note the regression line shown in Figure 4 does not include the points that the BAe-146 reported as under the LOD. For plotting purposes, zero was assigned to the BAe-146 values as the LOD was undefined. The reference standard for comparison (RSC), as defined in the introduction, is constructed by averaging the NASA DC-8 and NOAA WP-3D measurements with equal weights of one. The FAAM BAe-146 was not included in the RSC calculation because the range of comparison is small and the points below the LOD were not assigned any value. The resulting RSC can be expressed as a function of the DC-8 C_2H_2 measurements as the following:

$$RSC_{C2H2} = 10.13 + 0.909\ C_2H_{2\text{-}DC8}$$

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 WAS) is arbitrary, and has no impact on the final recommendations. Table 3 summarizes the assessed measurement bias for each of the three ICARTT ethyne 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 measurements.

The WAS technique for measuring VOCs presents some challenges in analyzing the data. The DC-8 data have an integration time of approximately 60-70 seconds, while the WP-3D data have an integration time between 6-11 seconds. For these measurements to be considered simultaneous and able to used in the regression analysis, the start and stop times of the WP-3D data must fall within the start and stop times of the DC-8 data. In order to maximize the data coverage for statistical analysis, one exception is made to this rule. If the shorter (WP-3D) integration time falls outside the longer integration time by no more than two seconds, the data points are also considered to be simultaneous. BAe-146 integration times range from approximately 30-60 seconds. Since the DC-8 and BAe-146 have similar integration times, the measurements are considered eligible for regression analysis if the midpoint of DC-8 or BAe-146 fall within the start and stop time of the other measurement. Only the PI reported data is used in this assessment, no interpolation is included. It is noted here the integration time difference may potentially be another factor leading to the difference between measurements.

Table 3. ICARTT Ethyne bias estimates

Aircraft/ Instrument	**Linear Relationships**	**Best Estimate Bias ($a + b\ C_2H_2$) (pptv)**
NASA DC-8 WAS	$C_2H_{2\ DC\text{-}8} = 0.00 + 1.000\ C_2H_{2\ DC\text{-}8}$	$-10.13 + 0.0905\ C_2H_{2\ DC\text{-}8}$
NASA WP-3D WAS	$C_2H_{2\ WP\text{-}3D} = 20.5 + 0.819\ C_2H_{2\ DC\text{-}8}$	$-28.77 + 0.255\ C_2H_{2\ WP\text{-}3D}$
FAAM BAe-146 WAS	$C_2H_{2\ BAe\text{-}146} = -4.08 + 1.50\ C_2H_{2\ DC\text{-}8}$	$-6.415 – 0.117\ C_2H_{2\ BAe\text{-}146}$

As a part of ICARTT intercomparison standard exchange exercises, University of California, Irvine (UCI) prepared the common VOC samples that were sent to University of Miami (Miami), University of New Hampshire (UNH), and University of York (York) for their lab analyses. Some of these same institutions had instruments on the following planes during ICARTT: UCI on the DC-8, Miami on the WP-3D, and York on the BAe-146. The comparison incorporated 9 species, which included ethyne. We believe that the inclusion of this comparison result will help the readers better understand the airborne intercomparison analysis. The difference in this lab comparison between the DC-8 and WP-3D instruments was 3 pptv, WP-3D being higher, at a DC-8 instrument reading of 532 pptv. From the same lab comparison, the difference between the DC-8 and BAe-146 was 0.25 pptv, BAe-146 being higher. Comparing the ICARTT flights to this lab comparison shows different relationships for both the DC-8/WP-3D and DC-8/BAe-146 intercomparisons (see Figures 5 – 6). The average lab comparison level of 533 pptv is much higher than the average level seen during the intercomparison flights which have an average of level of 131 pptv for the DC-8/WP-3D flights and 23 pptv for the DC-8/BAe-146 flight. This difference between intercomparisons does not seem unreasonable, considering that instrument performance can vary depending on calibration and environmental factors, and the time intervals were not the same for all instruments.

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, and adjusted precision could not be calculated for ethyne because of the small number of points and large time gaps between measurements.

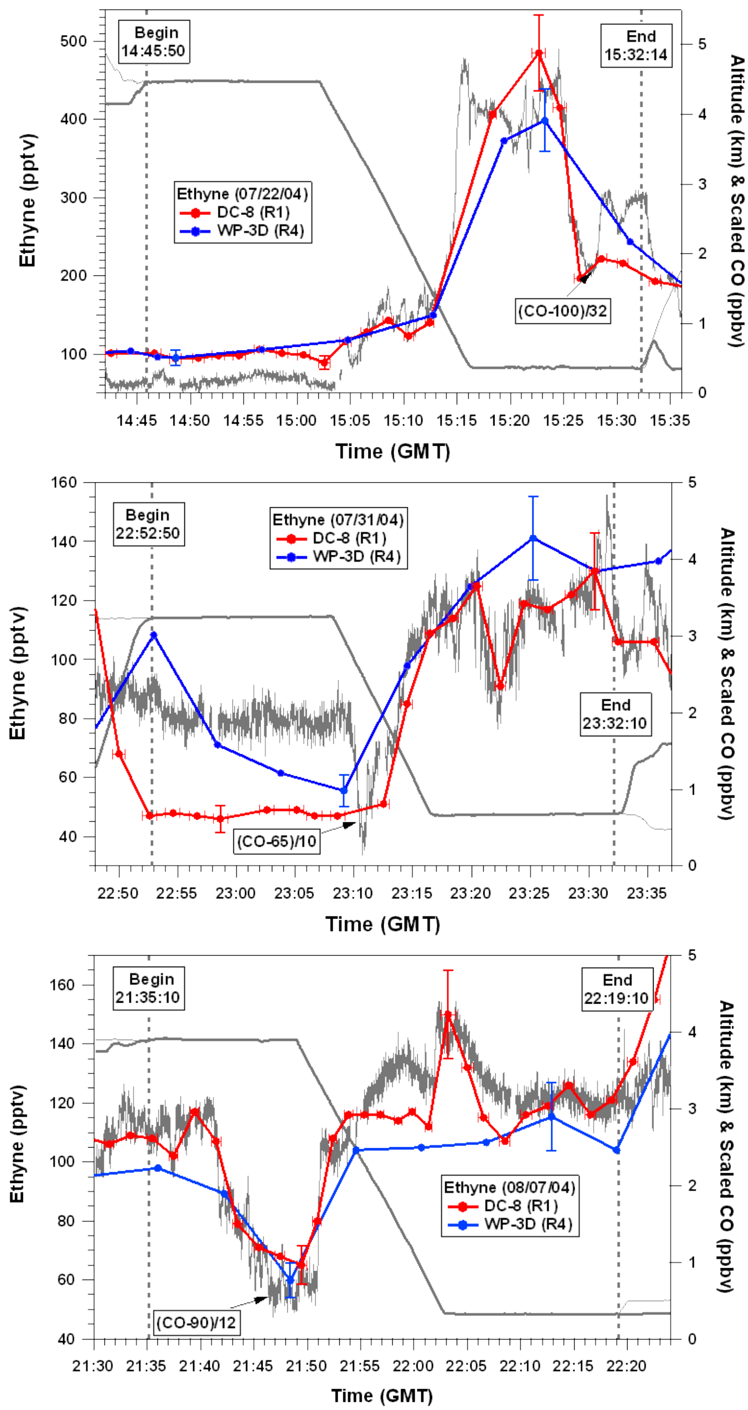

Figure 2. Time series of ethyne measurements and aircraft altitudes from two aircraft on the three intercomparison flights between the NASA DC-8 and the NOAA WP-3D. Error bars represent the PI reported uncertainty. In parenthesis next to the plane is the data version number.

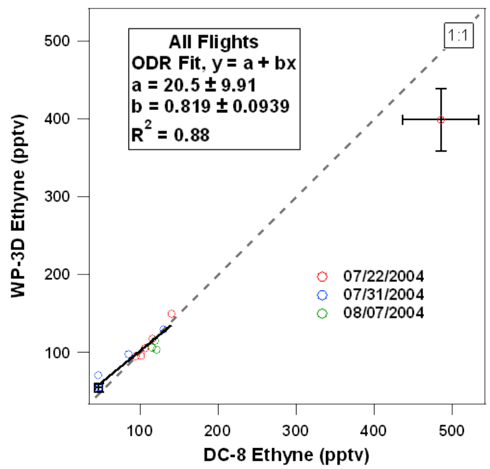

Figure 3. Combined correlation for the ethyne measurements on NASA DC-8 and the NOAA WP-3D for 7/22, 7/31, and 8/07 2004. Error bars represent the PI reported uncertainty. One influential point was not included in the regression analysis.

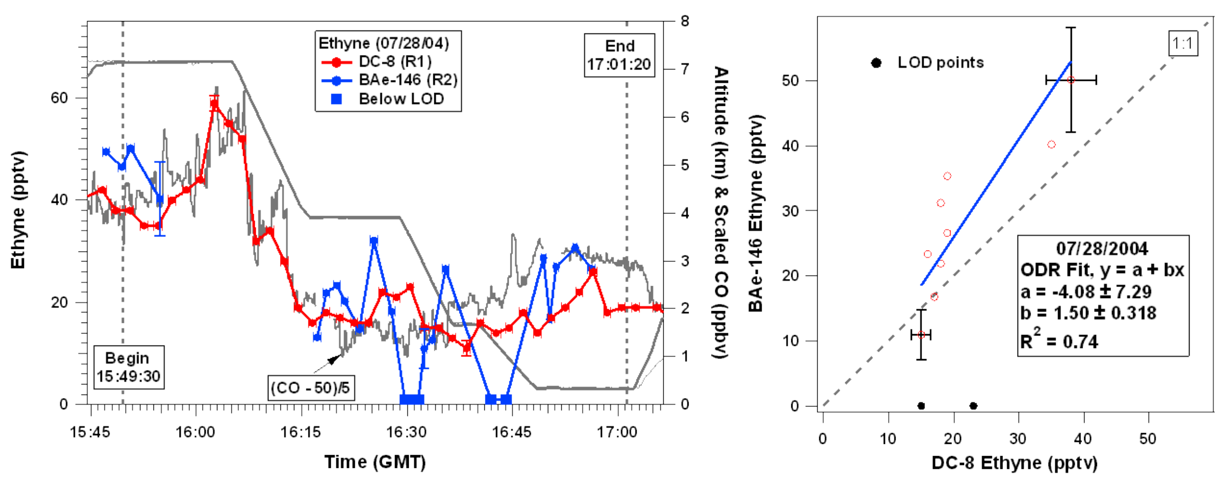

Figure 4. (left panel) Time series of ethyne measurements and aircraft altitudes from the intercomparison flight between the NASA DC-8 and the FAAM BAe-146. In parenthesis next to the plane is the data version number. (right panel) Correlation between the ethyne measurements on the two aircraft. LOD points are not included in calculating the regression equation. Error bars represent the PI reported uncertainty.

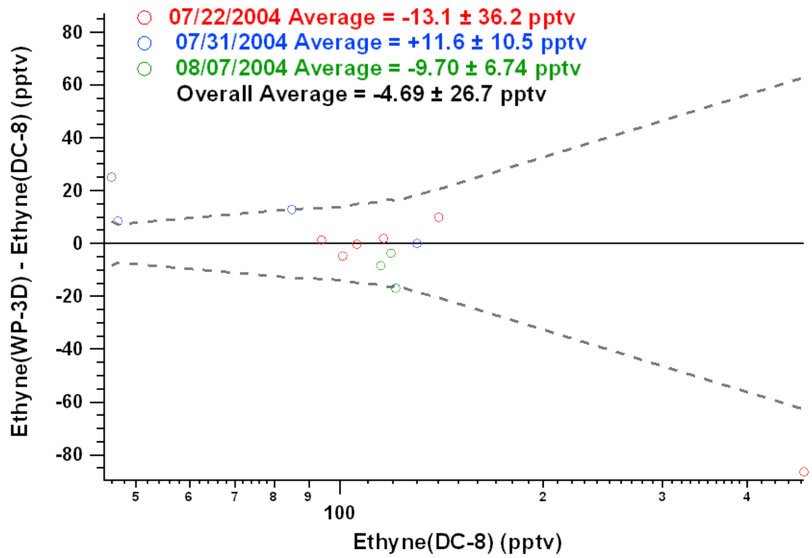

Figure 5. Difference between ethyne measurements from the three DC-8/WP-3D intercomparison flights as a function of the DC-8 ethyne. The dashed lines indicate the range of the results expected from the reported measurement uncertainties.

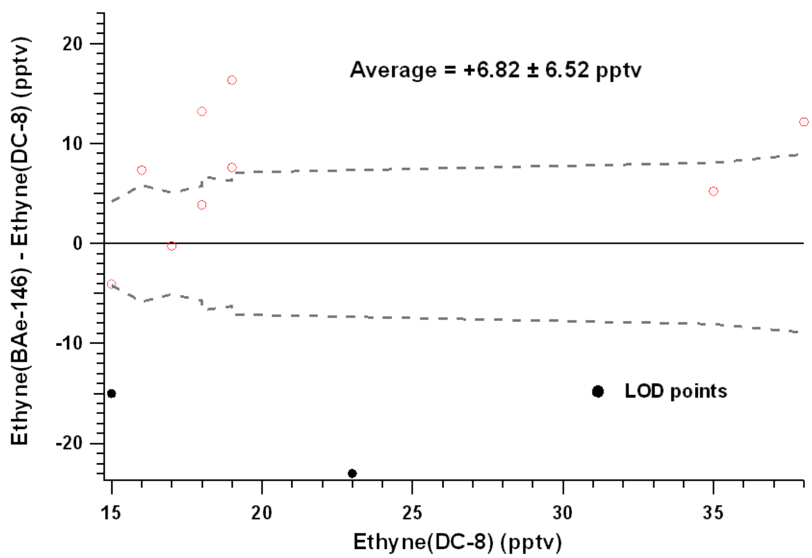

Figure 6. Difference between ethyne measurements from the DC-8/BAe-146 intercomparison flights as a function of the DC-8 ethyne. The LOD points are not included in the average. The dashed lines indicate the range of the results expected from the reported measurement uncertainties.

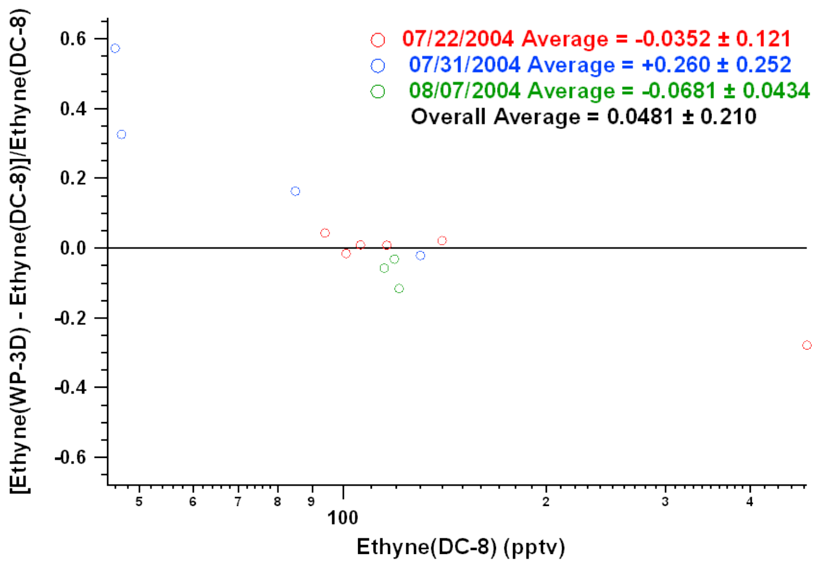

Figure 7. Relative difference between ethyne measurements from the three DC-8/WP-3D intercomparison flights as a function of DC-8 ethyne. A correction was made to account for bias.

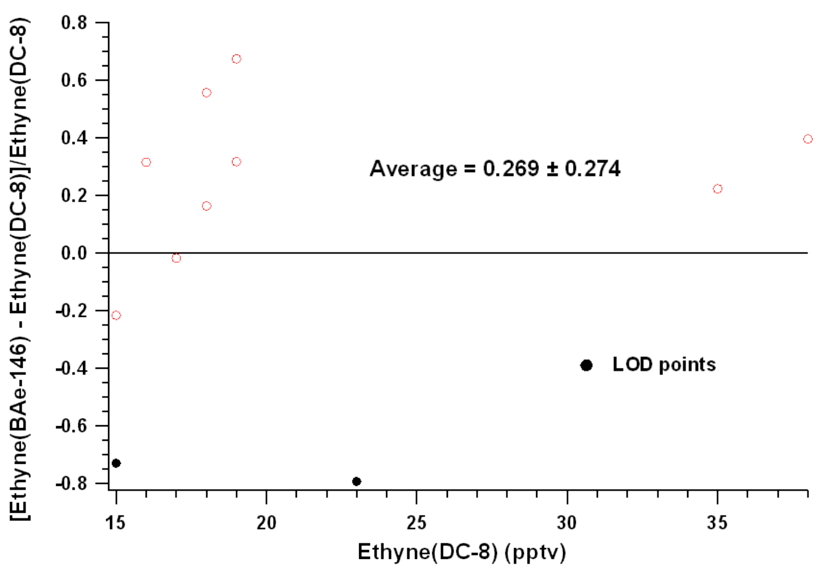

Figure 8. Relative difference between ethyne measurements from the DC-8/BAe-146 intercomparison flight as a function of DC-8 ethyne. The LOD points are not included in the average. A correction was made to account for bias.

References

Colman, J.J., et al. (2001), Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B, *Anal. Chem* ., 73, 3723-3731.

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.

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