TAbMEP Assessment: ICARTT $j(NO_2)$ Measurements

1. Introduction

Here we provide the assessment for the photolytic rate coefficient measurements of nitrogen dioxide [$j(NO_2)$]. These measurements were taken from two aircraft platforms during the summer 2004 ICARTT field campaign [*Fehsenfeld et al.*, 2006, *Singh et al*., 2006]. This assessment is based upon three wing-tip-to-wing-tip intercomparison flights conducted during the field campaign. Recommendations provided here offer TAbMEP assessed uncertainties for each of the measurements and a systematic approach to unifying the ICARTT $j(NO_2)$ 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 $j(NO_2)$ Measurements

Two different $j(NO_2)$ instruments were deployed on two aircraft. Table 1 summarizes these techniques and gives references for more information.

Table 1. $j(NO_2)$ measurements deployed on aircraft during ICARTT

Aircraft	Instrument	Reference
NASA DC-8	Scanning Actinic Flux Spectroradiometer (SAFS)	*Shetter and Müller* [1999]
NOAA WP-3D	AFSR Actinic Flux Spectroradiometer (formerly: ZAPHROD)	*Stark et al.* [2007]

3. Summary of Results

Table 2 summarizes the assessed 2σ precisions, biases, and 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 4. 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. 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 assessed 2σ uncertainty 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.

It should be noted here that photolysis rates of $j(NO_2)$ are not directly measurable. The photolysis rate, *J*, is calculated through a function of the compound's absorption cross section σ(λ), the quantum yield Φ(λ), and the actinic flux *I*(λ):

$$J = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda)\, \Phi(\lambda)\, I(\lambda)\, d\lambda \qquad (1)$$

The actinic flux, *I*(λ), is directly observed by the spectrometers onboard both aircraft; while the cross sections and quantum yields are measured in the laboratory. Thus, the uncertainties reported in Table 2 should be viewed as a weighted actinic flux measurement uncertainty over a given range of the solar spectrum and solar zenith angles. Users requesting more information should contact Samuel Hall at halls@ucar.edu for DC-8 or Principal Investigator Harald Stark at harald.stark@noaa.gov for WP-3D for detailed explanations.

Table 2. Recommended ICARTT $j(NO_2)$ measurement treatment

Aircraft/ Instrument	Reported Uncertainty[a]	Assessed 2σ Precision	Assessed Bias (s^{-1})	Assessed 2σ Uncertainty
NASA DC-8 SAFS	11.9%	0.96%	$0.00 + 0.025\ jNO_{2\text{-}DC8}$	Quadrature Sum
NOAA WP-3D AFSR	15%	5.8%	$0.00 - 0.026\ jNO_{2\text{-}WP3D}$	15% [b]

[a] User should see text or consult Samuel Hall at halls@ucar.edu for DC-8 or PI Harald Stark at harald.stark@noaa.gov for WP-3D prior to utilizing this data for explanation of uncertainty values.
[b] This recommendation based on test ranging from 0.0 to 0.02 $j(NO_2)$ (**s^{-1}**).

Figures 1a-1c display the precisions, biases, and recommended uncertainties for the two $j(NO_2)$ instruments. In each case the uncertainty is driven by the precision.

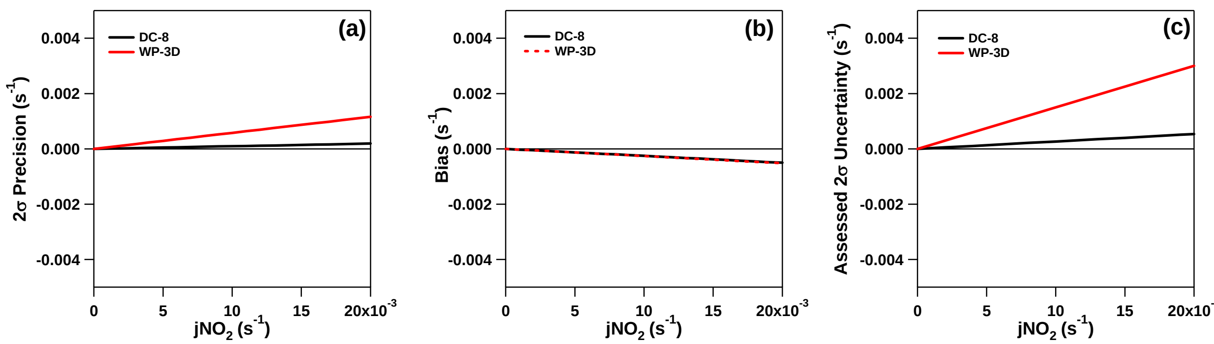

Figure 1. 2σ precision (panel a), bias (panel b), and assessed 2σ uncertainty (panel c) for DC-8 (black) and WP-3D (red) as a function of $j(NO_2)$ level. Values were calculated based upon data shown in Table 2.

4. Results and Discussion

4.1 Bias Analysis

Section 3.3 in the Introduction describes the process used to determine the best estimate bias. The linear relationships listed in Table 3 were derived from the regression equation found in Figure 3. In the case of nitrogen dioxide photolysis, the regression equation for the NOAA WP-3D, is manipulated algebraically to be expressed as a function of $j(NO_2)_{\text{-}DC8}$ shown in Table 3. The reference standard for comparison (RSC) is constructed by averaging the NOAA WP-3D and NASA DC-8. The resulting RSC can be expressed as a function of the DC-8 $j(NO_2)$ measurement as the following:

$$RSC_{jNO2} = 0.00 + 0.975\ jNO_{2\text{-}DC8}$$

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 SAFS) is arbitrary, and has no impact on the final recommendations. Table 3 summarizes the assessed measurement bias for each of the two ICARTT $j(NO_2)$ measurements.

Table 3. ICARTT j(NO_2) bias estimates

Aircraft/ Instrument	Linear Relationships [a]	Best Estimate Bias (a + b jNO_2) (s^{-1})
NASA DC-8 SAFS	$jNO_{2\text{-DC8}} = 0.00 + 1.00\ jNO_{2\text{-DC8}}$	$0.00 + 0.025\ jNO_{2\text{-DC8}}$
NOAA WP-3D AFSR	$jNO_{2\text{-WP3D}} = 0.00 + 0.95\ jNO_{2\text{-DC8}}$	$0.00 - 0.026\ jNO_{2\text{-WP3D}}$

[a]Derived from Fig. 3.

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 the adjusted precision are summarized in Table 4. Based on the results presented in Table 4, the largest "adjusted precision" value is taken as a conservative precision estimate for each ICARTT j(NO_2) instrument and twice that value is listed in Table 2 as the assessed 2σ precision.

To minimize the effect of bias, we make corrections for bias before computing the observed variability, as the bias may have a significant impact on the observed variability. Figure 4 shows the magnitude of the bias for each intercomparison. The assessed values of the observed variability are displayed in Figure 5. The final analysis results are shown in Table 2.

Table 4. ICARTT j(NO_2) precision (1σ) comparisons

Flight	Platform	IEIP Precision	Expected Variability	Observed Variability	Adjusted Precision
07/22	DC-8	0.07%	0.46%	3.00%	0.45%
	WP-3D	0.45%			2.90%
07/31	DC-8	0.45%	1.40%	1.00%	0.45%
	WP-3D	1.30%			1.30%
08/07	DC-8	0.05%	0.21%	2.00%	0.48%
	WP-3D	0.20%			1.90%

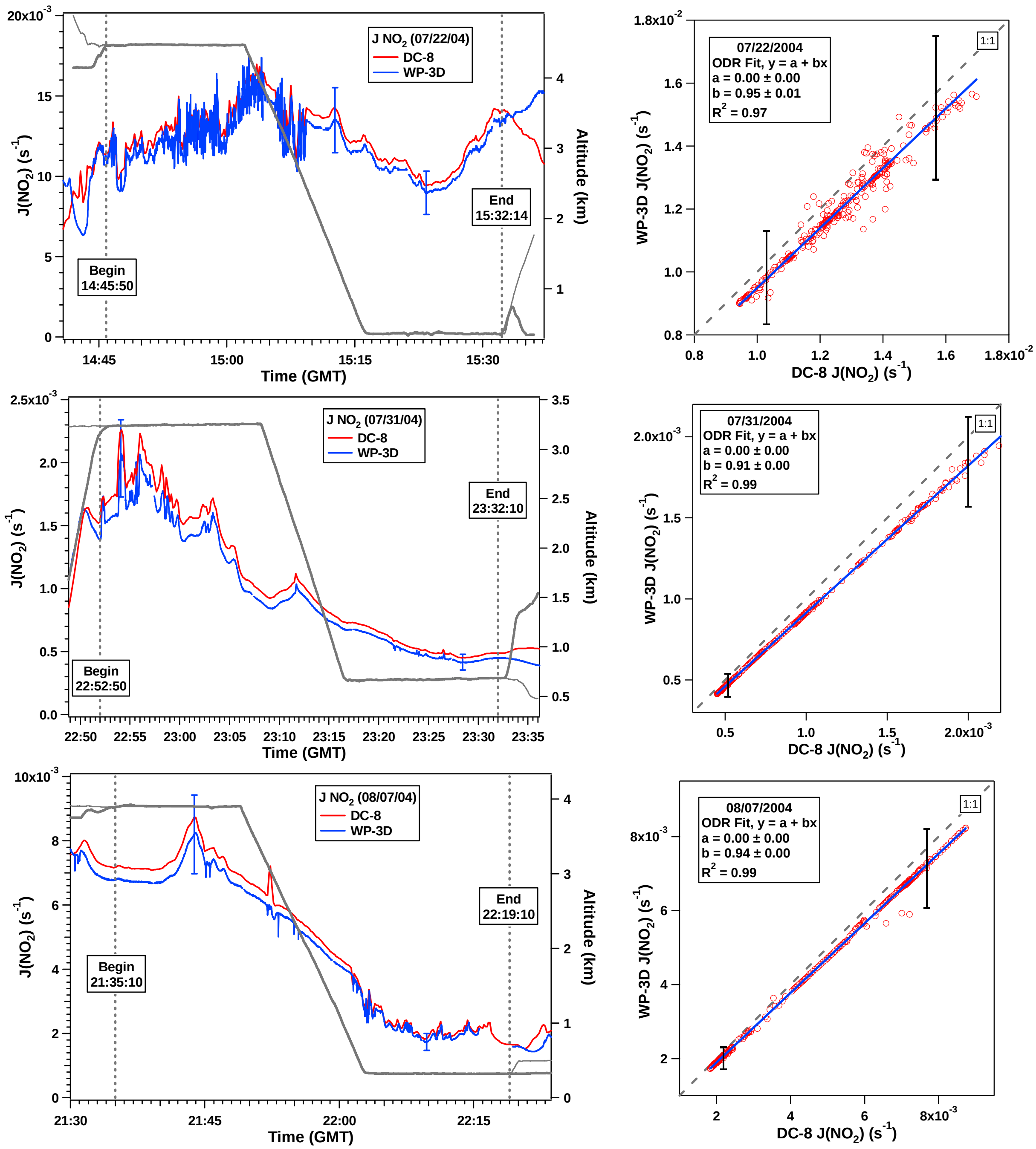

Figure 2. (left panels) Time series of j(NO_2) measurements and aircraft altitudes from two aircraft on the three intercomparison flights between the NASA DC-8 and the NOAA WP-3D. (right panels) Correlations between the j(NO_2) measurements on the two aircraft. Error bars shown depict the reported measurement uncertainties.

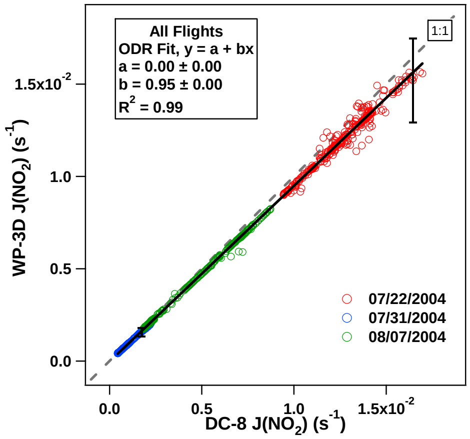

Figure 3. Correlation between the j(NO_2) measurements on the DC-8 and WP-3D for 7/22, 7/31, and 8/7 2004. Error bars shown depict the reported measurement uncertainties.

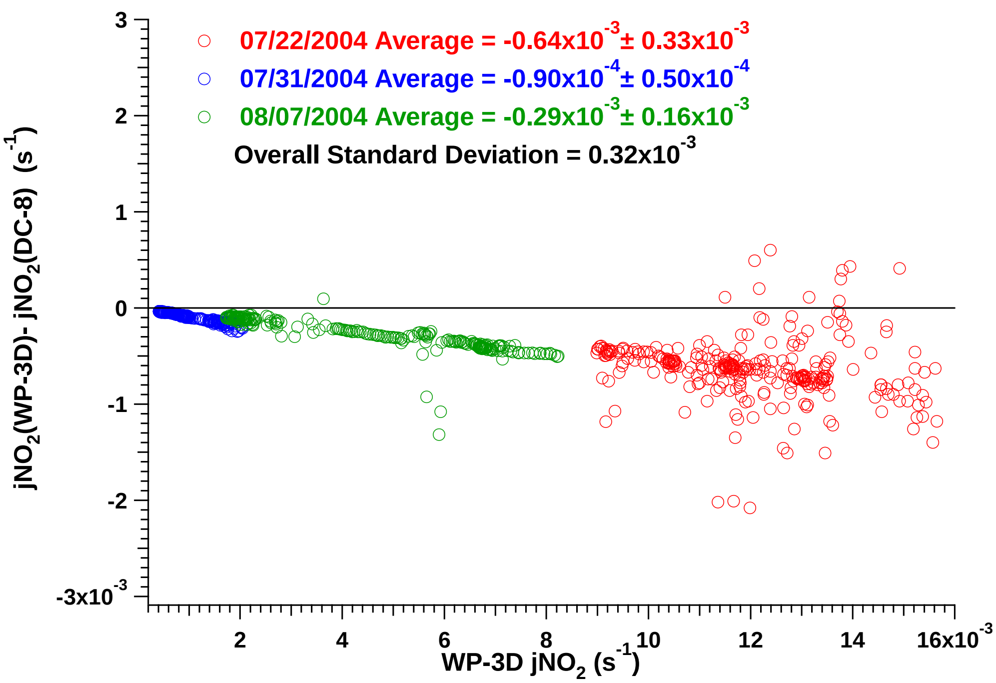

Figure 4. Difference between j(NO_2) measurements from the three DC-8/WP-3D intercomparison flights as a function of the WP-3D j(NO_2).

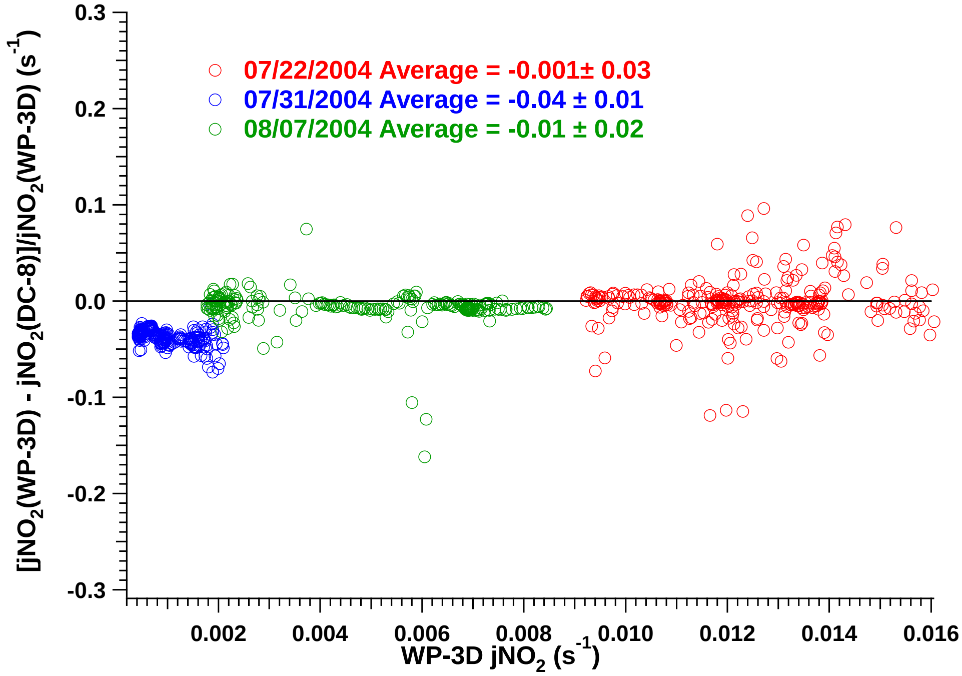

Figure 5. Relative difference between j(NO_2) measurements from the three DC-8/WP-3D intercomparison flights as a function of the WP-3D j(NO_2). A correction was made to account for bias.

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.

Shetter, R. E. and M. Müller (1999), Photolysis frequency measurements on the NASA DC-8 during the PEM-Tropics Mission using actinic flux spectroradiometry: Instrumentation description and results, *J. Geophys. Res.*, *104*, 5647-5661.

Singh, H. B., et al. (2006), Overview of the summer 2004 Intercontinental Chemical Transport Experiment-North America (INTEX-A), *J. Geophys. Res., 111*, D24S01, doi:10.1029/2006JD007905.

Stark, H., et al. (2007), Atmospheric in-Situ Measurement of Nitrate Radical (NO3) and Other Photolysis Rates Using Spectro- and Filter Radiometry, *J. Geophys. Res.,112*, D10S04, doi:10.1029/2006JD007578.