Comparison between DC-8 and ER-2 species measurements in the tropical middle troposphere: NO, NO_y, O_3, CO_2, CH_4, and N_2O

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Recommended Citation

Weinheimer, A. J., et al. (1998), Comparison between DC-8 and ER-2 species measurements in the tropical middle troposphere: NO, NOy, O3, CO2, CH4, and N2O, J. Geophys. Res., 103(D17), 22087–22096, doi:10.1029/98JD01421.

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JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 103, NO. D17, PAGES 22,087–22,096, SEPTEMBER 20, 1998

Comparison between DC-8 and ER-2 species measurements in the tropical middle troposphere: NO, NO_y, O_3, CO_2, CH_4, and N_2O

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Abstract. We compare measurements of six species taken aboard NASA DC-8 and ER-2 aircraft during two flight legs in the tropical middle troposphere near Hawaii. NO, NO_y, O_3, CH_4, and N_2O measurements agree to within the limits set by the known systematic errors. For CO_2, which can be measured with better relative precision than the other five species, differences in measured values from the two platforms are slightly larger than expected if the air masses sampled by the two aircraft were indeed similar in CO_2 composition to better than 0.08%.

1. Introduction

The DC-8 and ER-2 aircraft, operated by NASA Ames Research Center, have been valuable measurement platforms for atmospheric chemistry for many years. While the two have occasionally joined together in a single project to pursue related goals, it is not common for them to fly together in formation to enable a comparison of measurements. During the ER-2 Stratospheric Tracers of Atmospheric Transport (STRAT) mission and the DC-8 Vortex Ozone Transport Experiment (VOTE), the ER-2 flew behind the DC-8 so that ambient air measurements from the two platforms could be compared. A comparison can provide confidence in measurements according to the degree of agreement found and may be valuable in identifying measurement problems.

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Paper number 98JD01421.
0148-0227/98/98JD-01421$09.00

Below we have assembled plots and tables for the comparison of DC-8 and ER-2 measurements of six species: NO, NO_y, O_3, CO_2, CH_4, and N_2O. In most cases there is a plot of each measurement, versus time, at its respective archived resolution, as well as a DC-8/ER-2 comparison plot, versus longitude. For the longitude plots, the data are generally averaged to a common averaging time, both to make the measurements comparable and to reduce noise to facilitate the comparison. These longitude plots allow the structures seen from the two aircraft to be compared over the comparison legs. In addition, tabulated whole-leg means are used to compare the measurements. We focus on whole-leg means, because the data set has a dynamic range too limited to allow a focus on variability. We assess the differences in whole-leg means primarily in light of the specified systematic errors, because the flight legs are long enough that random errors are negligible in most cases. Indeed, for NO, NO_y, O_3, CO_2, and N_2O the random error fails to account for observed differences in means at confidence levels in excess of (usually well in excess of) 99.99%, using standard statistical tests. It is only for CH_4 that differences are not all large with respect to random error. In these cases, however, systematic errors account for the observed differences in all cases.

Measurements of two species could not be included in this comparison: H_2O and CO. Water vapor measurements from the ER-2 instrument [*Weinstock et al.*, 1994] are available for comparison, but the DC-8 diode laser instrument was on its first mission, and an optical feedback problem was discovered (and corrected) after the comparison flight, so those data are not considered sufficiently robust for a comparison. Carbon monoxide measurements from the DC-8 differential absorption CO measurement (DACOM) instrument [*Sachse et al.*, 1991] are available, but the ER-2 aircraft laser infrared absorption spectrometer (ALIAS) [*Webster et al.*, 1994] suffered a laser line shift just before the comparison legs were to start, so no CO comparison is possible. In addition, although an N_2O comparison is included in this paper, the ALIAS N_2O laser also suffered a line shift that compromised data quality, so ALIAS N_2O is not included here, while ALIAS CH_4 is included in the CH_4

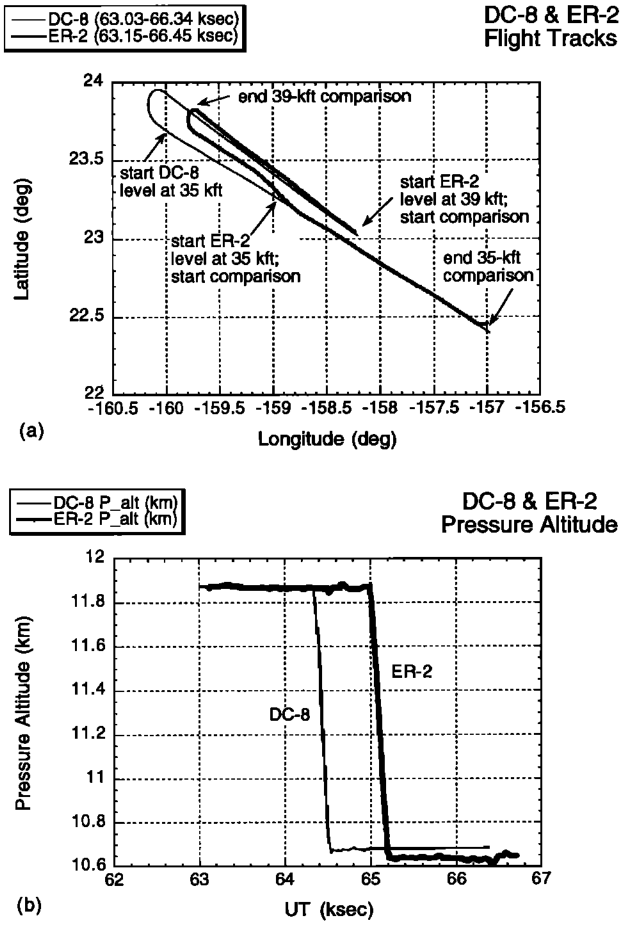


Figure 1. (a) Flight tracks of the DC-8 and ER-2 showing the two comparison legs at 39 kft (11.9 km) and 35 kft (10.7 km). (b) Altitude profiles of the DC-8 and ER-2.

comparison. Also, the airborne chromatograph for atmospheric trace species (ACATS) was unable to provide N_2O data for the comparison, as its calibration gas for N_2O was accidentally diluted.

2. Flight Tracks

On February 8, 1996, two clear-air comparison legs were flown near Hawaii with the DC-8 and ER-2 first at 39 kft (11.9 km), while flying to the northwest, and then at 35 kft (10.7 km), while on a reverse heading (Figure 1). The slower-flying ER-2 followed the DC-8 on these two ~20-min legs and at times sampled the exhaust of the DC-8, as was evident in the NO and NO_y data. To facilitate comparisons, longitude is the chosen coordinate.

Figure 2 shows back trajectories from three points along the aircraft flight tracks during the comparison leg at 35 kft, computed using the Goddard Space Flight Center trajectory model based on National Meteorological Center wind fields. Trajectories at 39 kft are similar, so are not shown. These trajectories suggest that six days prior to sampling, the air was over the equator, just north of New Guinea. The air is indicated to have experienced an overall rise of less than 1 km over the course of the six days (of course, the effects of localized convection are not captured by this trajectory analysis). The air spent a few days slowly drifting northward, just east of the Philippines, then accelerated as it moved eastward toward Hawaii. The analysis of *Jaeglé et al.* [1997] suggests that the air was significantly impacted by deep convection from the boundary layer, which occurred in the western equatorial Pacific five days prior to sampling. The tropical nature of the air is evident in the low NO_y and O_3 mixing ratios [e.g., *Gregory et al.*, 1996] to be shown later. Mixing ratios were broadly similar at the two altitude levels, but mixing ratios of NO, NO_y, and O_3 were slightly higher at 35 kft, while CO_2 and CH_4 were slightly lower there than at 39 kft.

3. Species-by-Species Comparisons

3.1. Nitric Oxide

Nitric oxide was measured with similar chemiluminescence instruments on the DC-8 [*Ridley et al.*, 1994] and the ER-2 [*Fahey et al.*, 1989]. In this method the NO mixing ratio is determined by counting photons emitted from excited NO_2 molecules produced by the reaction of ambient NO with reagent ozone. The signal integration time is 1 s for both instruments. Primary NO calibration standards for both instruments were from the National Institute of Standards and Technology (NIST). Calibration tanks from the two laboratories have been compared in the past but not specifically for these missions.

Plates 1a and 1b show the 1-s NO time series measured from the two aircraft, with points from the comparison legs in different colors. The spikes to greater than 200 parts per trillion by volume (pptv) are due to the sampling of aircraft exhaust, and those 1-s points are not included in the 60-s averages (Plate 1c) used in comparing the measurements of background air. Points were excluded on the basis of NO and NO_y being high; the same set of points were excluded for both. Black points are not included in the averages, either because they do not occur during the longitude overlap at a given altitude or because they are exhaust. Fresh exhaust plumes are small-scale features with large gradients, and we do not expect the aircraft to sample similar enough air in such circumstances. The ER-2 probably sampled the DC-8 exhaust but may have also sampled the exhaust of other aircraft as well, as the DC-8 (in front of the ER-2) apparently sampled other aircraft exhaust. For the ER-2, 29 points (1 s) were deleted at 39 kft and 51 points at 35 kft. For the DC-8, 6 points at 35 kft were deleted. Aircraft exhaust is a much stronger source of NO and NO_y than of other species, relative to respective ambient

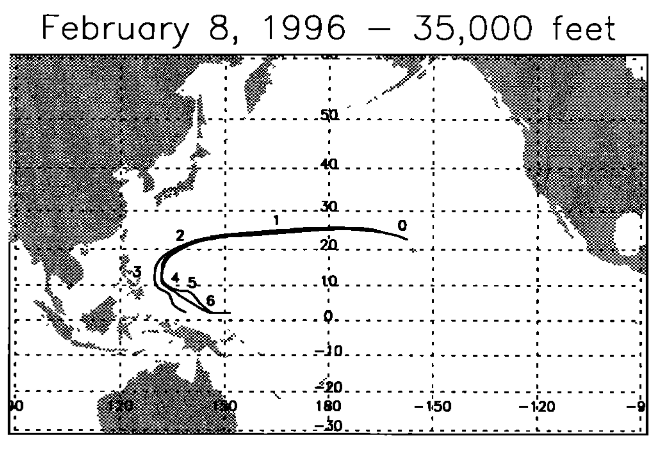


Figure 2. Air parcel back trajectories for air sampled during the 35-kft comparison leg near Hawaii.

Table 1. For NO: Comparison-Leg Means, ±1 Standard Deviation, and Their Differences (1-s Data With Exhaust Spikes Excluded)

Altitude	DC-8 NO ± 1 s.d., pptv	ER-2 NO ± 1 s.d., pptv	(ER-2) minus (DC-8), pptv	Sum of Systematic Errors, pptv
39 kft	12.0 ± 18.6	6.1 ± 7.1	-5.9	20
35 kft	19.3 ± 16.3	13.3 ± 6.6	-6.0	20
(39 kft) minus (35 kft)	-7.3	-7.2	0.1	

levels, so this exclusion of data is not necessary for the other species to follow.

For the chemiluminescence detection technique, both systematic and random errors are latitude, altitude, and mixing ratio dependent; the errors discussed below are relevant to the current measurements. The portion of the random error that is latitude and altitude dependent is due to cosmic ray interference in the photomultiplier tubes. Cosmic rays induce multiple-count events in the detectors that cause an increase in the width of the count distribution beyond that expected from Poisson statistics, thereby causing the distribution to be non-Poissonian [*McFarland et al.*, 1986]. As is evident in the time series plots of 1-s mixing ratios (Plates 1a and 1b have the same vertical scale), the DC-8 time series is noisier than that for the ER-2. The DC-8 standard deviations are larger by a factor of 2.5 (Table 1). This suggests that the DC-8 instrument is more susceptible to interference from cosmic rays, but differences in instrument sensitivity also contribute. The factor, by which the standard deviation of the counting rate on the DC-8 exceeded the Poissonian value, was 2.2, while that for the ER-2 was 1.7. A significant contributor to the systematic error is what is termed the "instrument artifact." This is a correction to the measurement of instrument background, and it can be difficult to control and quantify under some ambient conditions. It is measured via the introduction of synthetic air into the inlet. Its error dominates the total systematic error in a case such as this with low NO mixing ratios.

For the DC-8 during the time period of the comparison the 1-s errors (1?) are a random error of ±16 pptv and a systematic error of ±16 pptv. (Errors for all instruments are summarized in Table 2.) For 60-s averages the random error becomes ±2.0 pptv. The DC-8 systematic error is dominated by the error in the artifact. For the DC-8 the artifact correction increased apparent NO mixing ratios by 32 pptv, and its contribution to the systematic error is estimated to be one-half the magnitude of the correction, ±16 pptv. This level of artifact is much larger than normally tolerated. Since the Tropical Ozone Transport Experiment (TOTE)/VOTE flights were mostly at night, background NO measurements were not critical, and this was not addressed during the mission. For this flight, the ER-2 systematic error (1?) includes an error of ±6% of the measured mixing ratio due to calibration factors (±(0.4-0.8) pptv at the mean levels observed) and ±3 pptv from background correction. The random error for these 1-s measurements is ±7 pptv. The total error (obtained by simple addition of the random and systematic errors) for the 60-s average data is approximately ±5 pptv. Artifact correction throughout both legs of the comparison reduced the apparent NO signal by 5 pptv.

The amount of NO was very low and at or near detection limits (errors are comparable to measured values). Plate 1c compares the 60-s averages, and Table 1 gives averages over the two legs. ER-2 values are 6 pptv lower than DC-8 values, on average, at both levels. Both saw higher NO at 35 kft than at 39 kft, and by the same amount of 7 pptv. The average values agree to within the combined (via simple addition) systematic errors.

3.2. NO_y

The NO_y instruments on the two aircraft were identical to their respective NO counterparts, with the exception that in each case the sampled air was first passed through a gold catalytic converter to reduce NO_y species to NO [*Fahey et al.*, 1989; *Ridley et al.*, 1994]. Although the operational parameters for the two NO_y instruments were similar, two significant differences in the catalyst systems are worth noting. First, the ER-2 instrument had a valve upstream of the converter that allowed the catalyst to operate at a constant pressure of 35 torr, while the DC-8 instrument catalyst functioned at near ambient pressure. Second, in the DC-8 instrument, a continuous flow of water vapor was injected into the sample flow (adding 500 ppmv H_2O to the flow)

Table 2. Random and Systematic Errors for Different Instruments

Species	Instrument	Random Errors	Systematic Errors
NO	DC-8	±16 pptv at 1 s	±16 pptv
NO	ER-2	±7 pptv at 1 s	±4 pptv
NO_y	DC-8	±12 pptv at 1 s	±21 pptv
NO_y	ER-2	±10 pptv at 1 s	±20 pptv
O_3	DC-8	±0.2 ppbv at 1 s	±1.0 ppbv
O_3	ER-2	±2 ppbv at 1 s	±0.6 ppbv
CO_2	DC-8	±0.042 ppmv at 5 s	±0.1 ppmv wrt NOAA CMDL std.
CO_2	ER-2	±0.03 ppmv at 10 s, short term	±0.1 ppmv wrt SIO/WMO std.
		±0.05 ppmv at 10 s, long term	+0.15 ppmv wrt NOAA CMDL
			±0.1 ppmv wrt NOAA CMDL, when adjusted
CH_4	DC-8	±0.5 ppbv at 20 s	±2 ppbv wrt NOAA CMDL std.
CH_4	ER-2/ACATS	±26 ppbv	±(<34) ppbv wrt NOAA CMDL std.
CH_4	ER-2/ALIAS	±86 ppbv at 3 s	±86 ppbv wrt NOAA CMDL std.
CH_4	ER-2/WAS	±4 ppbv	±5 ppbv wrt NOAA CMDL std.
N_2O	DC-8	±0.1 ppbv at 20 s	±0.3 ppbv wrt NOAA CMDL std.
N_2O	ER-2/ATLAS	±3 ppbv accuracy at 1 s	

Please see text for details. Those errors (or portions thereof) which are reported as percentages (as reflected in the text) have been converted here to mixing ratios for the sake of uniformity. Some systematic errors are specified with respect to (wrt) certain standards (std.), as described more fully in the text. All errors are 1σ values.

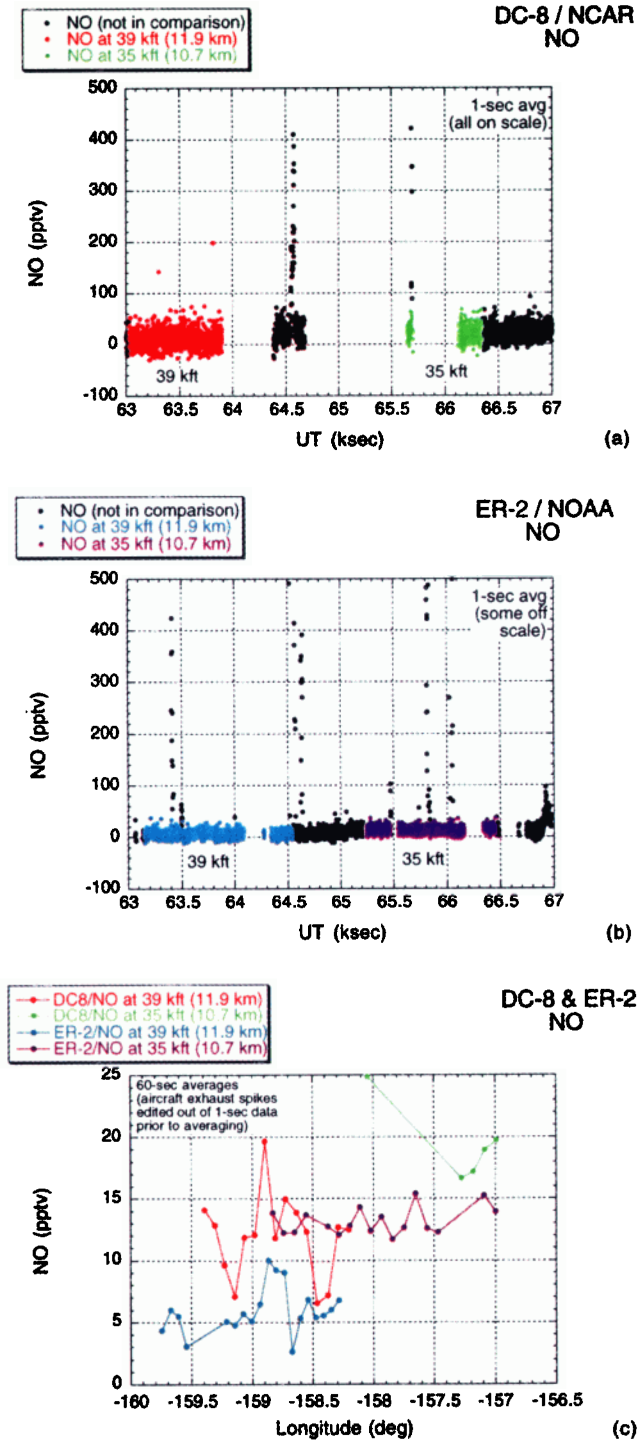


Plate 1. (a) DC-8 NO time series of 1-s values covering the 39- and 35-kft legs. Points in black are not included in the calculation of means and standard deviations, thus excluding the samples of aircraft exhaust. (b) As in Plate 1a but for the ER-2. (c) NO as a function of longitude for the 39- and 35-kft legs for the DC-8 and the ER-2.

upstream of the converter in order to minimize the conversion of HCN to NO [*Fahey et al.*, 1985]. The potential error introduced by HCN interference is discussed below.

Plates 2a and 2b show the two NO_y time series. As for NO, it was necessary to exclude some aircraft exhaust samples from both the ER-2 and the DC-8 1-s time series prior to computing the 60-s averages used in comparing the measurements of background air. The same points were excluded for NO_y as for NO. The NO_y mixing ratios are very low and not far above detection limits. Plate 2c compares the 60-s averages, and Table 3 gives averages over the two legs. ER-2 values are lower than DC-8 values, on average, at both levels: by 6 pptv at 39 kft and by 13 pptv at 35

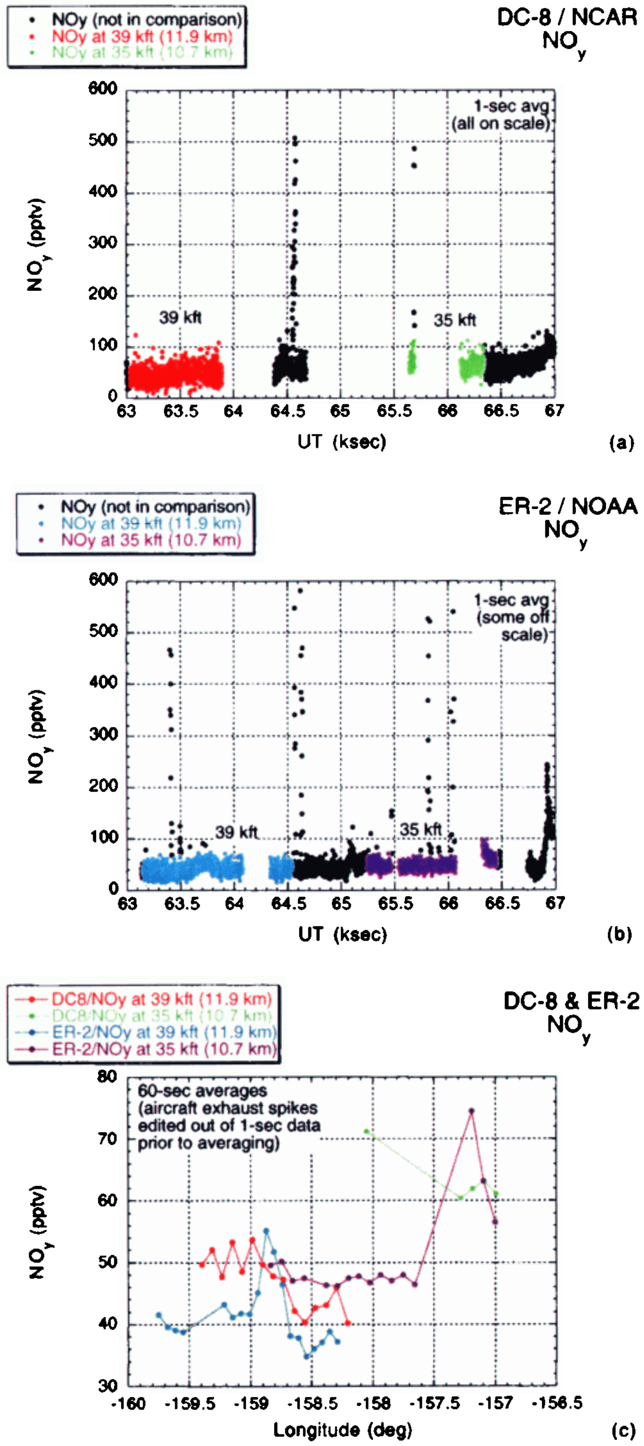


Plate 2. (a) DC-8 NO_y time series of 1-s values covering the 39- and 35-kft legs. Points in red are not included in the calculation of means and standard deviations, thus excluding the samples of aircraft exhaust. (b) As in Plate 2a but for the ER-2. (c) NO_y as a function of longitude for the 39- and 35-kft legs for the DC-8 and the ER-2.

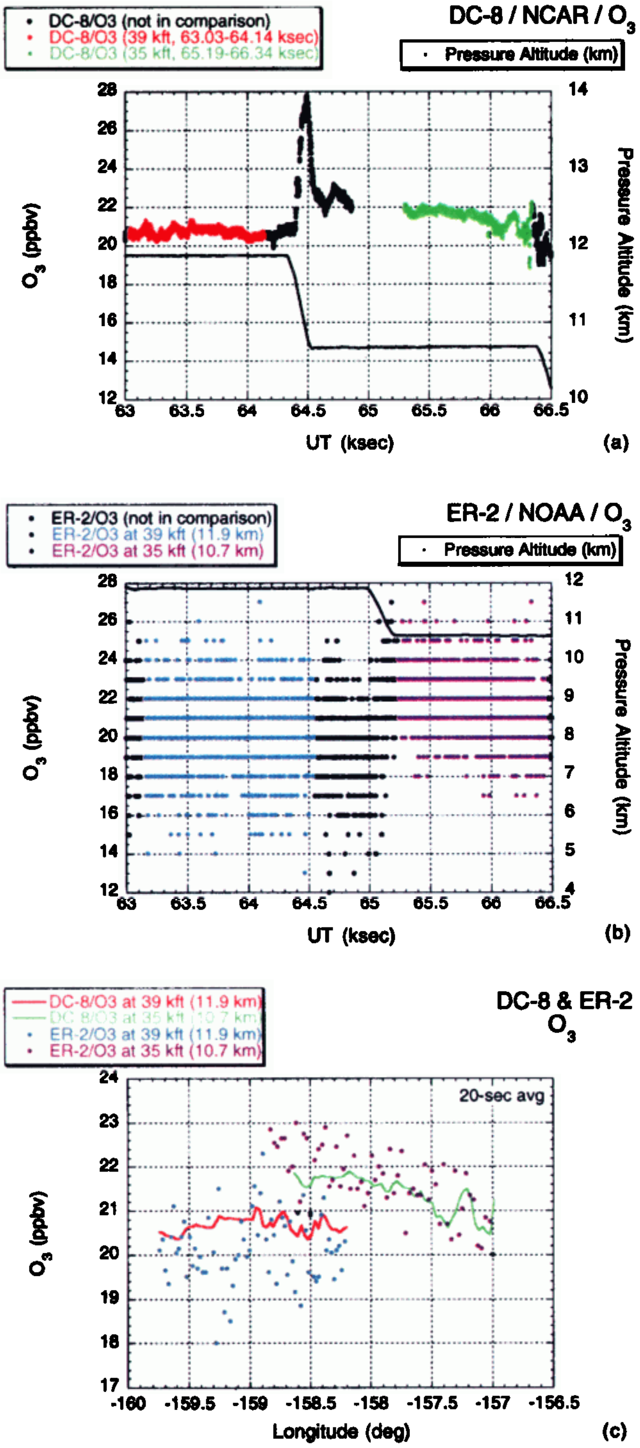


Plate 3. (a) DC-8 O_3 time series of 1-s values covering the 39- and 35-kft legs. (b) ER-2 O_3 time series of 1-s values covering the 39- and 35-kft legs. (c) O_3 as a function of longitude for the 39- and 35-kft legs for the DC-8 and the ER-2.

kft. Both see higher NO_y at 35 kft than at 39 kft (as for NO). The average values agree to within the combined systematic errors.

For the DC-8 during this time period the 1-s errors (1?) are a random error of ±12 pptv and a systematic error of ±21 pptv. For 60-s averages the random error is ±1.6 pptv. For the DC-8 the artifact correction increased apparent NO_y mixing ratios by 42 pptv, and its contribution to the systematic error is estimated to be one-half the magnitude of the correction, ±21 pptv. For this flight, the ER-2 systematic error (1?) includes an error of ±6% of the measured mixing ratio due to calibration factors (~3 pptv at the mean levels observed) and ±17 pptv from background correction. The random error for these 1-s measurements is ±10 pptv. The total error for the 60-s average data is approximately ±21 pptv. Artifact correction throughout both legs of the comparison reduced the ER-2 apparent NO_y signal by 21 pptv. As was the case for the NO measurements, the DC-8 NO_y is

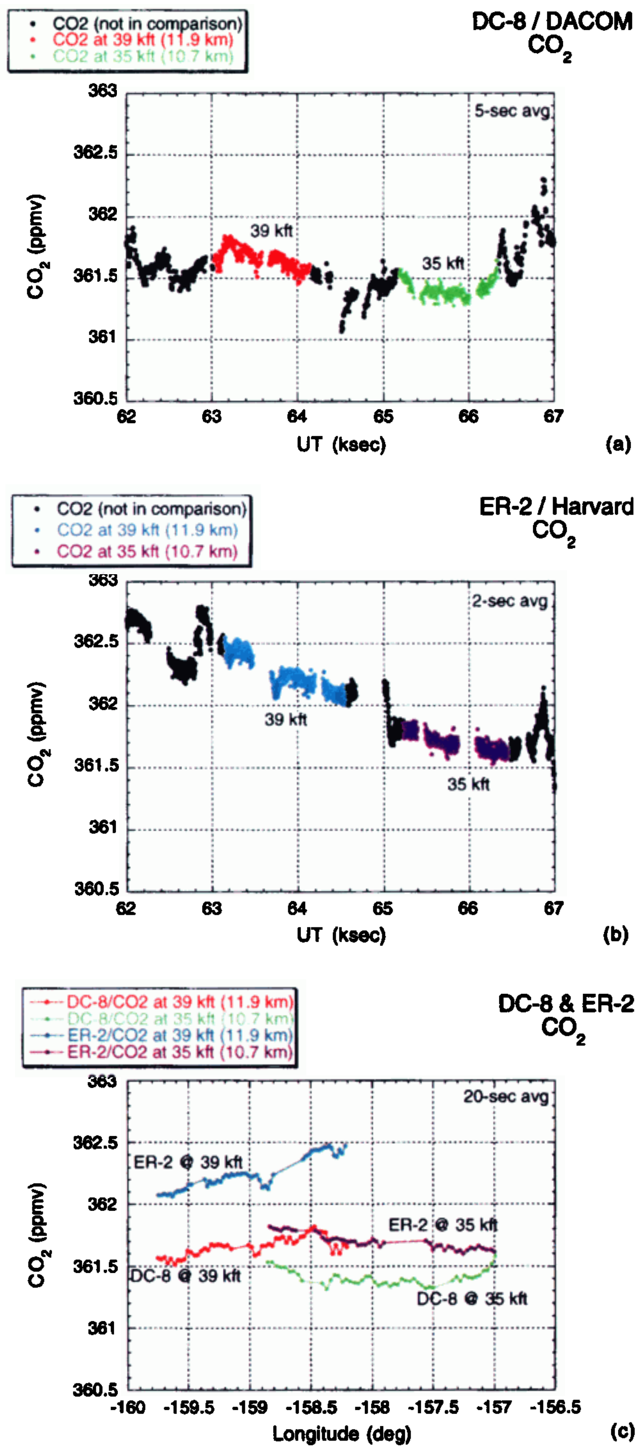


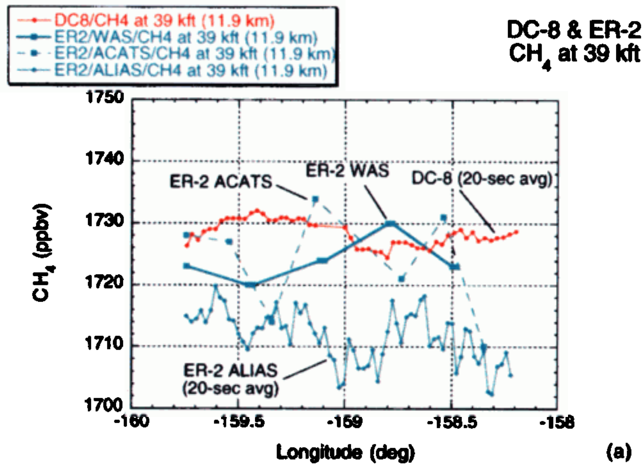
Plate 4. (a) DC-8 CO_2 time series of 5-s averages covering the 39- and 35-kft legs. (b) ER-2 CO_2 time series of 2-s averages covering the 39- and 35-kft legs. (c) CO_2 as a function of longitude for the 39- and 35-kft legs for the DC-8 and the ER-2.

Table 3. For NO_y: Comparison-Leg Means, ±1 Standard Deviation, and Their Differences (1-s Data With Exhaust Spikes Excluded)

Altitude	DC-8 NO_y ± 1 s.d., pptv	ER-2 NO_y ± 1 s.d., pptv	(ER-2) minus (DC-8), pptv	Sum of Systematic Errors, pptv
39 kft	47.3 ± 15.2	41.5 ± 10.5	-5.8	41
35 kft	63.6 ± 13.8	50.4 ± 10.7	-13.2	41
(39 kft) minus (35 kft)	-16.3	-8.9	7.4	

noisier than the ER-2 NO_y, although the difference is not so great as for NO. The DC-8 standard deviations are larger by a factor of about 1.4 (Table 3). The factor by which the standard deviation of the counting rate exceeds the Poissonian value is 2.3 for the DC-8, while that for the ER-2 is 1.6.

An additional source of error, not included in the above error estimates, is the interference due to HCN. It was measured for both instruments. For the DC-8 the HCN conversion efficiency was measured during its next flight on February 13, 1996 and found to be 2% (with 500 ppmv H_2O added to the sample flow, as was the condition during the comparison legs). The conversion efficiency did not change much from flight to flight, and 2% is typical of VOTE. If we assume a canonical middle-tropospheric HCN mixing ratio of 200 pptv [*Cicerone and Zelner*, 1983], the interference due to HCN conversion for the DC-8 instrument is 4



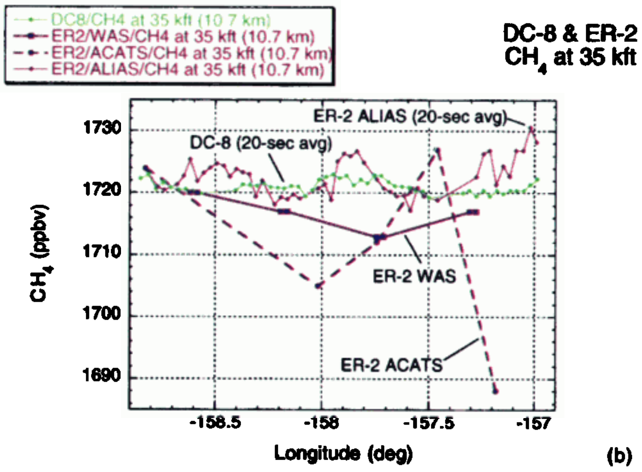
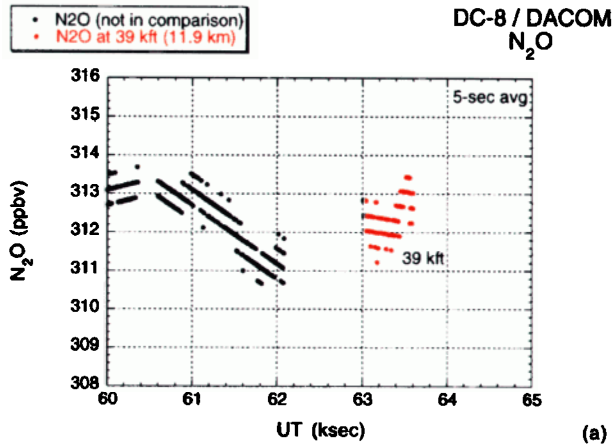
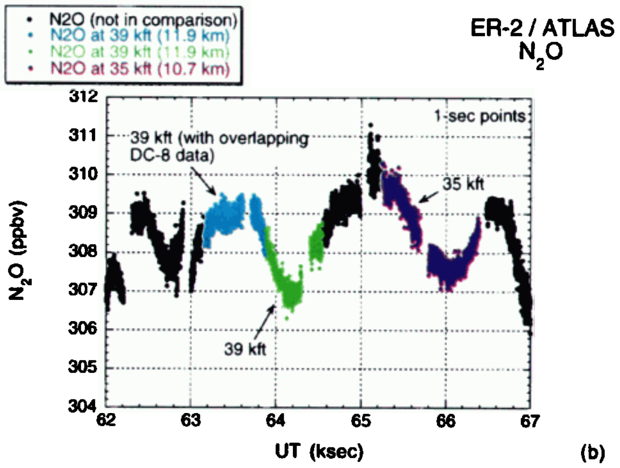


Plate 5. (a) CH_4 at 39 kft as a function of longitude. DC-8 and ALIAS values are 20-s averages, ER-2 WAS values are for cans which fill in 20-30 s, and ER-2 ACATS values represent 5-s samples of ambient air. (b) As in Plate 5a, except at 35 kft.





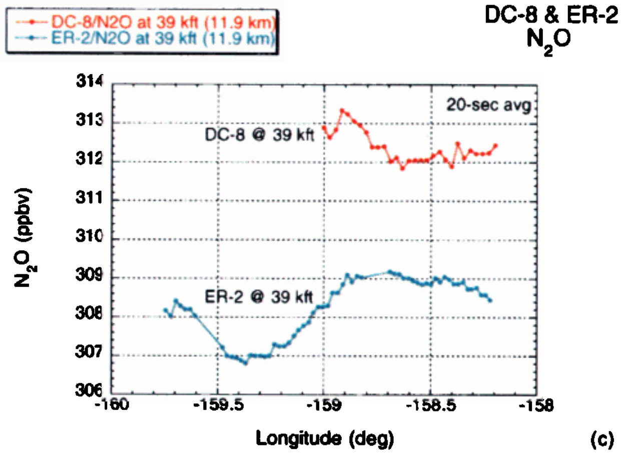


Plate 6. (a) DC-8 N_2O time series of 5-s values at 39 kft (no data for 35 kft). (b) ER-2/ATLAS N_2O time series of 1-s values at 39 and 35 kft. (c) N_2O as a function of longitude at 39 kft for the DC-8 and ER-2/ATLAS.

Table 4. For O_3: Comparison-Leg Means, ±1 Standard Deviation, and Their Differences (1-s Data)

Altitude	DC-8 O_3± 1 s.d., ppbv	ER-2 O_3± 1 s.d., ppbv	(ER-2) minus (DC-8), ppbv	Sum of Systematic Errors, ppbv
39 kft	20.7±0.2	20.2±2.0	-0.5	1.6
35 kft	21.4±0.5	21.7±1.7	+0.3	1.6
(39 kft) minus (35 kft)	-0.7	-1.5	-0.8	

pptv. Since this error is less than 10% of the lowest measured NO_y mixing ratio and a small fraction of the stated instrument error, a correction for HCN interference is not incorporated into the DC-8 data set.

For the ER-2 instrument, preflight and postflight tests of the HCN conversion efficiency in dry synthetic air showed a 10% conversion, or approximately 20 pptv equivalent NO_y (assuming 200 pptv HCN as above). Extensive tests of the ER-2 catalyst system indicate that HCN conversion under ambient conditions should be equal to or less than that found in dry synthetic air (S. G. Donnelly et al., in preparation, 1998). The error due to HCN conversion in the ER-2 instrument is a more significant problem due to the higher conversion efficiency of HCN, with the potential HCN error being as high as 40 to 50% of the measured values. The difference in HCN conversion efficiencies should result in a positive bias in the ER-2 data of 16 pptv relative to the DC-8 data. However, the 60-s averages shown in Plate 2c as well as the averages over each flight leg listed in Table 3 show that ER-2 values are lower than the DC-8 values. Although the data support the argument that the in situ HCN conversion efficiency in the ER-2 catalyst is less than that measured in the laboratory, the data are insufficient to make a conclusive statement to this effect. Because the in situ HCN conversion efficiency is not fully characterized and because HCN is not separately measured on the ER-2 (or DC-8), a correction for HCN interference is also not incorporated into the ER-2 NO_y data set.

3.3. Ozone

Ozone was measured on the DC-8 using a chemiluminescence technique [*Ridley et al.*, 1992] and on the ER-2 using ultraviolet absorption [*Proffitt and McLaughlin*, 1983]. The DC-8 chemiluminescence instrument was calibrated every few flights against a commercial calibrator based on ultraviolet absorption (Thermo Electron Instruments, model 49PS, Hopkinton, Massachusetts). A nearly linear, second-order polynomial was fit to the calibration points. The ER-2 instrument employed an absolute calibration dependent on the absorption cross section of O_3 as well as on measurements of temperature, pressure, and absorption path length.

Plates 3a and 3b show the time series, and Plate 3c compares the data as a function of longitude. Ozone was fairly uniform over the two levels. The ER-2 saw a smooth transition between the two levels, while the DC-8 saw a 6 ppbv pulse toward the end of its descent to 35 kft. The respective descents occurred about 130 km apart, so if this apparent layer of enhanced O_3 was not horizontally extensive, this would explain why the descent profiles are different.

For the DC-8 during this time period the 1-s errors (1?) are a random error of ±0.2 ppbv and a systematic error of ±1.0 ppbv. For the ER-2, the 1-s random error (1?) of $\pm 1.5 \times 10^{10}$ cm^{-3} in the O_3 concentration [*Proffitt and McLaughlin*, 1983] corresponds to ±2.3 ppbv at 39 kft and ±2.0 ppbv at 35 kft, and indeed these are near the standard deviations of the 1-s time series, 2.0 and 1.7 ppbv. The reported systematic error of ±3% corresponds to ±0.6 ppbv at these levels near 20 ppbv. At these very low (and uniform) mixing ratios, the higher precision of the DC-8 chemiluminescence instrument is apparent. The larger random error for the ER-2 absorption instrument is often a much smaller percentage of ambient O_3 than it is here, as the ER-2 often flies in the stratosphere where O_3 mixing ratios can be larger by a factor of 100 or more.

Table 4 shows the mean values over the two legs. The ER-2 and DC-8 values are very close to one another at each level, on average, with the DC-8 higher by 0.5 ppbv at 39 kft and the ER-2 higher by 0.3 ppbv at 35 kft. Both saw lower O_3 at 39 kft than at 35 kft. This agreement of the means at each flight level to 0.5 ppbv or less is better than could be expected on the basis of the combined errors.

3.4. Carbon Dioxide

Carbon dioxide (CO_2) was measured using nondispersive infrared absorption sensors on both the DC-8 [*Anderson et al.*, 1996] and the ER-2 [*Boering et al.*, 1994]. The DC-8 data were acquired at 20 Hz and archived as 5-s averages. The ER-2 data were archived at 2-s intervals, median-filtered from a 4-Hz acquisition rate. For the DC-8 the 5-s errors (1?) are a random error of ±0.042 ppmv and an instrumental systematic error of ±0.1 ppmv. On the DC-8, in-flight calibrations were performed every 10 min using National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) standards, and there is a systematic error of ±0.1 ppmv with respect to NOAA CMDL standards. (That is, the measurements are referred to such a standard, and even if the standard were perfect, the measurement would have a systematic error of ±0.1 ppmv due to instrumental systematic errors.) For the ER-2, in-flight calibrations were performed every 10 min using

Table 5. For CO_2: Comparison-Leg Means, ±1 Standard Deviation, and Their Differences (5-s Data for DC-8, 2-s Data for ER-2)

Altitude	DC-8 CO_2 ± 1 s.d., ppmv	ER-2 CO_2 ± 1 s.d., ppmv	(ER-2) - (DC-8), ppmv	(ER-2) - (DC-8), ppmv, Adjusted*	Sum of Systematic Errors, Adjusted,* ppmv
39 kft	361.66±0.08	362.25±0.14	0.59	0.44	0.2
35 kft	361.41±0.07	361.70±0.07	0.29	0.14	0.2
(39 kft) minus (35 kft)	0.25	0.55	0.30	0.30	

*In column 5 the differences, ER-2 minus DC-8, are adjusted downward by 0.15 ppmv to account for the offset in the CO_2 scales for ER-2/ Harvard (on SIO/WMO scale) and for DC-8/DACOM (on the NOAA/CMDL scale); the difference of the differences is not affected.

Table 6a. For CH_4: Comparison-Leg Means, ±1 Standard Deviation, and Altitude Differences

Altitude	DC-8 CH_4 ± 1 s.d., ppbv	ACATS CH_4 ± 1 s.d., ppbv	ALIAS CH_4 ± 1 s.d., ppbv	WAS CH_4 ± 1 s.d., ppbv
39 kft	1728.4 ± 2.2	1722.8 ± 9.5	1711.8 ± 4.6	1724.3 ± 4.2
35 kft	1721.1 ± 1.5	1711.2 ± 15.7	1722.7 ± 3.4	1716.8 ± 2.9
(39 kft) minus (35 kft)	7.3	11.6	-10.9	7.5

standards directly traceable to the Scripps Institution of Oceanography/World Meteorological Organization (SIO/WMO) scale, with an accuracy of ± 0.1 ppmv. A recent blind comparison among 20 CO_2 laboratories worldwide showed that reported ER-2 values are 0.15 ppmv higher than NOAA CMDL values. (Results from the direct comparison between NOAA CMDL and SIO/WMO standards are not yet available.) For the ER-2, the short-term precision of a 10-s average is better than ±0.03 ppmv, and the long-term precision (i.e., flight to flight and year to year) of 10-s averages is ±0.05 ppmv, as determined by a long-term surveillance standard analyzed every 2 hours in flight [*Boering et al.*, 1994]. Installation of the ER-2 instrument into a superpod for the January-February 1996 STRAT deployment, however, may have resulted in a slightly worsened precision for data collected in the first half hour of these early superpod flights due to a significantly different thermal environment than that of an ER-2 spearpod in which the instrument had flown since 1992. The calibrations over 10-min intervals during the first half hour showed some irregularities, with a maximum added uncertainty of 0.15 ppm (up to 63,600 s for this flight on February 8, 1996).

Plates 4a and 4b show the CO_2 time series for the two instruments, and Plate 4c compares the measurements at the two flight levels. The data in the figures have not been adjusted for the reported difference of 0.15 ppmv in the different CO_2 scales used by Harvard and NOAA CMDL (used by DC-8/DACOM). Table 5 gives means over the comparison legs. The ER-2 means (without adjustment) are higher than those for the DC-8, by 0.59 ppmv at 39 kft and by 0.29 ppmv at 35 kft. Taking into account the comparison of NOAA CMDL versus ER-2 standards, the ER-2 data are higher than the DC-8 data by 0.44 ppmv at 39 kft and by 0.14 ppmv at 35 kft. The similarity (DC-8 to ER-2) of the shapes of the longitude plots over much of each level supports the validity of the comparison, because it suggests there is similarity of the air masses. Indeed, similar differences (~0.4 ppmv at 39 kft and ~0.2 ppmv at 35 kft, after scale adjustment by 0.15 ppmv) appear as a function of longitude, without averaging over the legs, except at the eastern ends of both legs where the shapes diverge. The adjusted difference of 0.14 ppmv in reported CO_2 mixing ratios from the two instruments at 35 kft is within that expected based on the systematic errors (relative to the respective standards) of ±0.1 ppmv for both the DC-8 and the ER-2. The adjusted difference at 39 kft of 0.44 ppmv is larger than expected, based on these systematic errors. A standard statistical Z test shows that random errors also do not account for the difference (at a confidence level greatly in excess of 99.99%, as Z = 108).

Since the differences (DC-8 versus ER-2) in means at the two flight levels are themselves different from one another (0.44 versus 0.14 ppmv), this implies that the two aircraft do not agree on the CO_2 mixing ratio difference between 39 and 35 kft. This is borne out by examination of the altitude differences shown as a function of longitude (Plate 4c). It is also reflected in the means. Both see higher CO_2 at 39 kft than at 35 kft, but for the DC-8, the difference is 0.25 ppmv, while for the ER-2, it is 0.55 ppmv, using flight-leg averages. The difference in these differences of 0.30 ppmv is beyond that expected based on the estimated systematic errors, of course assuming the aircraft are sampling similar air. However, a discrepancy of 0.30 ppmv between the reported values of the difference in CO_2 between the two legs is equivalent to a relative difference in absolute CO_2 mixing ratios of only 0.08%. Because, on the one hand, it is possible to measure CO_2 more precisely than any of the other species in this comparison and, on the other hand, CO_2 is not as variable as other species, it is difficult to discern whether this discrepancy is due to real but quite small differences in air mass composition or whether the difference is attributable to larger than expected errors in the measurements of one or both of the instruments of approximately 0.2 ppmv. For example, the standard deviation of the ER-2 data on the 39 kft leg is twice that of either DC-8 leg or of the 35 kft ER-2 leg and could reflect either a detectable air mass difference sampled by the two aircraft at this altitude or increased calibration uncertainty for the ER-2 instrument in the new superpod environment up to 63,600 s. When data obtained before 63,600 s are excluded, the standard deviation drops to 0.07 ppmv, but the difference of the difference is 0.22 ppmv, still larger than expected if the air masses were identical. Thus whether these differences are attributable to the air masses sampled or to the measurements remains ambiguous.

3.5. Methane

Methane (CH_4) was measured during the comparison legs by three instruments aboard the ER-2. The airborne chromatograph for atmospheric trace species (ACATS) employed an in situ gas chromatograph (GC) with an electron capture detector [*Elkins et al.*, 1996]. For CH_4 ACATS had an ambient-air sample integration time of about 5 s. The aircraft laser infrared absorption spectrometer (ALIAS) employed a tunable diode laser spectrometer to measure CH_4 on a 3-s time base [*Webster et al.*, 1994]. The whole air sampler (WAS) pressurized ambient air for 20-30 s into cans whose contents were later analyzed on the ground using gas chromatography with flame ionization detection. On the DC-8, CH_4 was measured using a tunable diode laser as part of the DACOM package [*Sachse et al.*, 1991], and data were archived with an averaging period of 5 s.

For ACATS the precision is ±1.5% (±26 ppbv at 1720 ppbv), and the systematic error is less than ±2% (<34 ppbv at 1720 ppbv). In-flight calibrations were performed using secondary

Table 6b. For CH_4: Differences Among Instruments of Comparison-Leg Means

Altitude	(ACATS) - (DC-8), ppbv	Sum of Systematic Errors, ppbv, DC-8 and ACATS	(ALIAS) - (DC-8), ppbv	Sum of Systematic Errors, ppbv, DC-8 and ALIAS	(WAS) - (DC-8), ppbv	Sum of Systematic Errors, ppbv DC-8 and WAS
39 kft	-5.6	36	-16.6	88	-4.1	7
35 kft	-9.9	36	+1.6	88	-4.3	7

Table 7. For N_2O: Comparison-Leg Means, ±1 Standard Deviation, and Their Differences (5-s Data for DC-8, 1-s Data for ER-2)

Altitude	DC-8 N_2O ± 1 s.d., ppbv	ER-2 N_2O ± 1 s.d., ppbv	(ER-2) - (DC-8), ppbv	Sum of Systematic Errors,* ppbv
39 kft	312.4 ± 0.5	308.8 ± 0.3 ppbv	-3.6	4.8

ER-2 data are averaged over only that portion of the leg for which there are DC-8 data.

*This includes, for the DC-8, the 0.3 ppbv instrumental systematic error and 1.5 ppbv (1σ) for the calibration tank, and for the ER-2, the 3 ppbv 1-Hz accuracy.

standards that were calibrated against gravimetric standards on a laboratory GC at NOAA CMDL. For ALIAS the precision is ±5% (±86 ppbv), and the accuracy, relative to NOAA CMDL standards, is ±5% (±86 ppbv). For WAS the precision, based on replicate analyses, is ±4 ppbv (1?). The systematic error is likely small (<5 ppbv), as the WAS reference standard was NIST-certified (±1%) and compared well (within ±5 ppbv) with a tank calibrated by NOAA CMDL. For DACOM the precision (1?) for a 20-s average is ±0.5 ppbv, and the systematic error is comprised on an instrumental systematic uncertainty of ±2 ppbv (1??? and an uncertainty of ±1% (±17 ppbv, 2?) for the NOAA CMDL calibration standard that was used.

Plates 5a and 5b show the CH_4 comparisons at 39 and 35 kft, and Tables 6a and 6b summarize the means over the comparison legs. The relatively small standard deviations for the DACOM instrument (Table 6a) suggest that much of the scatter seen by the other instruments, especially ACATS, is a reflection of the precision. These small standard deviations also indicate that in spite of the sparse sampling of the ACATS and WAS instruments, their means are nonetheless meaningful (albeit perhaps with significant instrumental random error). All three instruments see higher CH_4 at 39 kft, on average. Both ACATS and WAS CH_4 are lower than DC-8 CH_4, on average, at each level. Also, ACATS is lower, on average, than WAS at each level, while ALIAS is higher than the DC-8 at 35 kft and lower at 39 kft. The differences among the single-flight-level means, however, are not large in comparison to the estimated errors (Table 6b): (1) For DACOM versus ACATS the differences in means are 5-10 ppbv, and even given only the 26 ppbv ACATS precision, this difference is within expectations, even allowing for a reduction in this by a factor of (7)0.5=2.6 (seven samples at 39 kft), from 26 ppbv down to 10 ppbv (ACATS systematic error also enters here, but the 34 ppbv may be an overestimate.) (2) For DACOM versus ALIAS the differences of 1-17 ppbv are well within expectations. (3) For DACOM versus WAS the differences of 4 ppbv are within expectations, given systematic errors of ±2 ppbv for DACOM (without including the uncertainty in the standard) and ±5 ppbv for WAS. Additionally, the three differences in means, between 39 and 35 kft, indicate agreement, all three being in the range of 7-12 ppbv.

3.6. Nitrous Oxide

Nitrous oxide (N_2O) was measured on the DC-8 by the DACOM instrument [*Sachse et al.*, 1991], and data were archived with an averaging period of 5 s. Data are available for only the first half of the 39-kft leg, and no data are recoverable for the 35-kft leg. N_2O was measured at 1 Hz on the ER-2 by the airborne tunable laser absorption spectrometer (ATLAS) [*Keim et al.*, 1997].

For DACOM the precision for a 20-s average is ±0.1 ppbv (1?), and the instrumental systematic error (not including the contribution from the reference gas) is ±0.3 ppbv (1?). DACOM's calibration tank is calibrated against NOAA CMDL standard reference gases which are accurate to ±1%, or ±3 ppbv (2?). The ATLAS 1? accuracy at 1 Hz is ±1% (±3 ppbv at 310 ppbv), and the in-flight calibrations are based on a laboratory calibration using a NIST standard.

Plates 6a and 6b show the individual N_2O time series, and Plate 6c compares the different instruments as a function of longitude. Table 7 summarizes the means. For the early portion of the 39-kft leg where the measurements overlap, the ER-2/ATLAS values are, on average, 3.6 ppbv less than those from the DC-8. Such a difference is consistent with the total systematic errors of ~2 ppbv (1 ?) for the DC-8 and 3 ppbv for the ER-2.

4. Summary

In a comparison such as the present one, an important bottom-line question is this: Is the level of agreement consistent with what is expected on the basis of estimated measurement errors? For these data it is necessary to consider only systematic errors, because these are sufficient to account for the observed differences in all cases but one. This one case is CO_2 at 39 kft for which random error also fails to account for the difference. For the six species, we summarize the results of the comparison as follows:

1. For NO the differences in means, at both 39 and 35 kft, are 6 pptv and are well within the combined systematic errors (16 pptv for DC-8, 5 pptv for ER-2) and therefore within the total errors. The low mixing ratios encountered do not provide a critical test of the dynamic range of these instruments. However, because artifact and other baseline corrections account for the majority of the error in low signal conditions, this comparison indicates that these background effects have been adequately addressed for each instrument. Also, it is noted that the random error on the DC-8 instrument is larger than for the ER-2.

2. For NO_y the differences in means, at 39 and 35 kft, are 6 and 13 pptv and are well within the combined systematic errors (21 pptv for DC-8, 20 pptv for ER-2). As with NO, the good agreement at such low mixing ratios indicates that background issues are being adequately addressed for each instrument. The low NO_y mixing ratios and good agreement between the two instruments also indicate a limited error due to HCN conversion. Again, the DC-8 random error is greater than for the ER-2.

3. For O_3 differences in means have magnitudes of 0.3-0.5 ppbv and are within the combined systematic errors (1.0 ppbv for DC-8, 0.6 ppbv for ER-2). Also, it is noted that the random error on the ER-2 ultraviolet absorption instrument is larger than for the DC-8 chemiluminescence instrument.

4. For CO_2 the ER-2 values are higher on average by 0.14 ppmv for the 35-kft leg and by 0.44 ppmv for the 39-kft leg (taking into account a direct ground-based comparison between Harvard ER-2 and NOAA CMDL CO_2 standards). The difference

at 39 kft of 0.44 ppmv is larger than that expected based on systematic errors (relative to the respective calibration standards) of ± 0.1 ppmv for both the DC-8 and the ER-2. There is also a discrepancy of 0.30 ppmv as to the mixing ratio difference between the two flight levels, on average, and this exceeds expectations based on reported errors. However, given the higher precision of the CO_2 measurements relative to the measurements of the other species in this comparison, the degree of similarity of the air sampled by the two aircraft may be more critical here (the degree of variability of CO_2 must also be considered).

5. For CH_4 differences in means of 1-17 ppbv are well within expectations given the systematic errors (Table 6b).

6. For N_2O the difference, at 39 kft, of 3-4 ppbv between the DC-8 and the ER-2 ATLAS is within the combined systematic errors (2 ppbv for the DC-8 and 3 ppbv for the ER-2).

Of course, one caveat may always be invoked in a cross-platform comparison: given that there are two platforms, there is always the possibility of a difference in the air actually sampled. A future comparison would benefit from more extensive flight together. This would allow a more thorough look at differences that may arise, as for CO_2 in this case, to see whether consistent differences are seen for a large number of legs flown under a variety of conditions. The fact that only two legs were flown is a limitation for the present study. Flying through air with greater ranges in species abundances would also be of value. This would provide a different sort of test, especially for species such as NO and NO_y whose abundances were very close to their detection limits in the present study.

Acknowledgments. The NASA Upper Atmosphere Research Program supported the STRAT and VOTE campaigns. The success of such projects owes much to the efforts of the dedicated DC-8 and ER-2 flight crews, ground crews, and mission management. We also acknowledge the support of the NASA Subsonic Assessment Program and the NOAA Climate and Global Change Program. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under sponsorship of the National Science Foundation.

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(Received December 23, 1997; revised April 17, 1998; accepted April 22, 1998.)