5.2. AIRBORNE PROJECTS

5.2.1. AIRBORNE CHROMATOGRAPH FOR ATMOSPHERIC TRACE SPECIES (ACATS-IV)

Overview

Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV) is a four-channel gas chromatograph designed to measure atmospheric trace gases in the upper troposphere and lower stratosphere onboard the NASA high-altitude ER-2 aircraft [*Elkins et al*., 1996]. ACATS-IV measures six chlorinated trace gases (CFC-12, CFC-11, CFC-113, $CHCl_3$, CH_3CCl_3, CCl_4) in addition to halon-1211, N_2O, CH_4, H_2, and SF_6. ACATS-IV has been part of the ER-2 payload for studies of stratospheric transport and ozone depletion since 1994, and in 1997 participated in the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) study. The principal objective of POLARIS was to determine the roles of photochemistry and transport in summertime decreases of stratospheric ozone over the arctic. Nineteen instruments onboard the NASA high-altitude ER-2 aircraft made in situ measurements of trace gases, radicals, aerosols, radiation, and meteorology in the upper troposphere and lower stratosphere of the northern hemisphere during spring, early summer, and late summer. The edge of the arctic polar vortex was penetrated during one flight in late April, and fragments of the eroding vortex were sampled during several other flights in May and June. The observed 35% decrease of the ozone column above Fairbanks, Alaska, was largely attributed to photochemistry, predominantly catalytic reactions between O_3 and NO in air parcels continuously exposed to sunlight for up to 10 days. ACATS-IV data from POLARIS were incorporated in several publications that appeared during 1999 [e.g., *Hurst et al*., 1999; *Romashkin et al*., 1999; *Sen et al*., 1999; *Toon et al*., 1999].

Hydrogen Budget

The total hydrogen budget of the northern hemisphere lower stratosphere was recently evaluated for closure from in situ measurements of H_2O, CH_4, and H_2 onboard the NASA ER-2 aircraft during POLARIS and the 1995-1996 Stratospheric Tracers of Atmospheric Transport (STRAT) mission [*Hurst et al.,* 1999]. Budget closure requires that measured abundance relationships between these principal hydrogen reservoirs corroborate theoretical hydrogen partitioning predicted by reactions that oxidize CH_4 to H_2O and H_2, and oxidize H_2 to H_2O. A simple evaluation of these reactions predicts that H_2O production (ΔH_2O) should equal two times CH_4 loss ($-2 \bullet \Delta CH_4$) plus the net change in H_2 (ΔH_2). ACATS-IV measurements revealed that H_2 mixing ratios are relatively constant in the lower stratosphere (Figure 5.24). From the measured $\Delta H_2/\Delta CH_4 = -0.027 \pm 0.003$ (Figure 5.24), the ratio of H_2O production to CH_4 destruction ($\Delta H_2O/\Delta CH_4$) was predicted to be -1.973 ± 0.003 [*Hurst et al*., 1999].

This predicted relationship was compared to the slope of the anticorrelation between H_2O and CH_4 mixing ratios measured in the lower stratosphere during STRAT and POLARIS. H_2O was measured during both campaigns by the Harvard University Lyman-α hygrometer [*Hintsa et al*., 1999] and also by the Jet Propulsion Laboratory (JPL) tunable diode laser (TDL) hygrometer during POLARIS. CH_4 was measured by ACATS-IV and a JPL TDL spectrometer. The anticorrelation between H_2O and CH_4 in the lower stratosphere was found to be tight and linear for air masses with mean ages greater than 3.8 years (Figure 5.25). In younger air masses large variations in H_2O mixing ratios degrade the compactness of the anticorrelation. These variations result from the seasonal cycle of temperature near the tropical tropopause, the entry point for most stratospheric air masses. Air masses passing through the tropical tropopause are regularly imprinted with an H_2O mixing ratio dictated by the lowest temperature they encounter [e.g., *Mote et al*., 1996]. As young air masses age in the stratosphere, they gradually lose their H_2O imprint as they mix with air masses of different H_2O content.

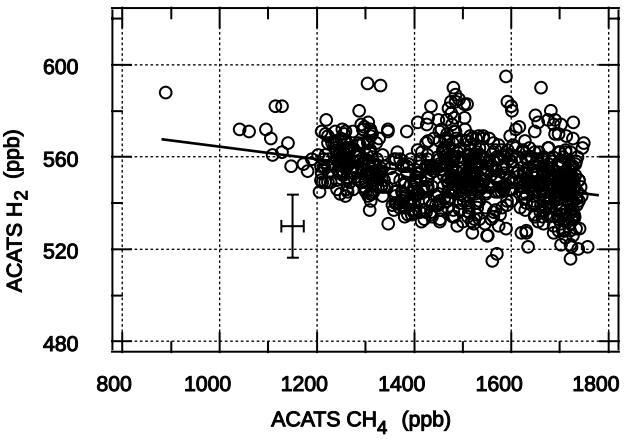

Fig. 5.24. H_2 and CH_4 measured by ACATS-IV in the lower stratosphere between 3°S and 60°N latitude during STRAT (1995-1996). The solid line is an ODR fit to the data with a slope of -0.027 ± 0.003, indicating that H_2 production slightly exceeds H_2 destruction in the strtosphere. The crossed error bars represent the average random errors (1σ) of the measurements.

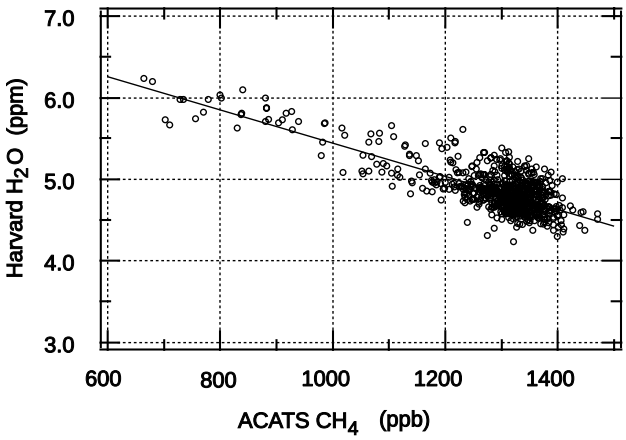

Fig. 5.25. A tight, linear anticorrelation between Harvard H_2O and ACATS-IV CH_4 was observed in the lower stratosphere during STRAT (1995-1996) and POLARIS (1997). The solid line is an ODR fit to the data with a slope of -2.01 ± 0.16. Data for air masses with mean ages <3.8 years were omitted from this analysis.

Data from each unique combination of H_2O and CH_4 instruments were fit with an orthogonal distance regression (ODR). Data for air masses with mean ages <3.8 year (or alternately CH_4 >1450 ppb) were excluded from the fits. For all instrument combinations the mean slope ($\Delta H_2O/\Delta CH_4$) was -2.15 ± 0.18 (1σ). The mean slope using only ACATS-IV CH_4 data, -2.02 ± 0.17, is in excellent agreement with the predicted $\Delta H_2O/\Delta CH_4 = -1.973$. The annual mean mixing ratio of H_2O in air masses entering the stratosphere was estimated from the slope and intercept values from each ODR and a CH_4 mixing ratio of 1.7 ppm (the annual mean CH_4 mixing ratio entering the stratosphere). The result, 4.0 ± 0.4 ppm H_2O, agrees well with the 3.8 ± 0.3 ppm H_2O deduced from a recent re-evaluation of radiosonde temperature data near the tropical tropopause [*Dessler*, 1998].

Tracer Correlations

Measurements of CH_3CCl_3 and CFC-11 in the lower stratosphere during POLARIS revealed significant differences in the CH_3CCl_3-CFC-11 correlation between spring and summer, 1997 [*Romashkin et al.*, 1999]. These differences were associated with the rapid decrease of tropospheric CH_3CCl_3 that began in 1992 (see sections 5.1.2, 5.1.3) and the fact that the mean ages of the air masses observed during spring and summer differed by up to 1 year.

Before the CH_3CCl_3-CFC-11 correlations could be used to gain insight into stratospheric transport, the influences of the large tropospheric CH_3CCl_3 trend on the lower stratospheric CH_3CCl_3 distribution had to be minimized. Initially, the CH_3CCl_3 mixing ratio in each air mass sampled by ACATS-IV was normalized to the CH_3CCl_3 mixing ratio in air masses that entered the stratosphere on January 1, 1997. The normalization was based on the well-documented trend of tropospheric CH_3CCl_3 (Figure 5.9) and the mean ages of stratospheric air masses calculated from ACATS-IV measurements of SF_6.

This normalization procedure, based solely on mean age, is inexact because an air mass is better characterized by a spectrum of ages [*Hall and Plumb*, 1994]. Two methods were used to quantify the effect of age spectra width on the initial normalization. In the first method, the stratospheric entry mixing ratio of CH_3CCl_3 was expressed as the mean tropospheric mixing ratio of CH_3CCl_3 over ±1.25-year intervals, the estimated width of the age spectrum [*Volk et al.*, 1997]. For the second method, a 10-year-wide age spectrum (Green's) function based on a one-dimensional diffusive model (equation 21 of *Hall and Plumb* [1994] with diffusion coefficient $K = 1.5\ m^2\ s^{-1}$) was used to weight the CH_3CCl_3 tropospheric trend. The model-derived, weighted trend was used in combination with mean ages from ACATS-IV because the model underpredicts mean ages by a factor of two or more. The two normalization methods were similar in their influences on lower stratospheric CH_3CCl_3 mixing ratios.

Correlations between normalized CH_3CCl_3 and CFC-11 mixing ratios (Figure 5.26c) exhibit greater curvature than the raw correlations (Figure 5.26b). The induced curvature reveals straight lines of data between different parts of the correlation, evidence that air has mixed between the polar vortex and the midlatitudes (lines α and β on Figure 5.26c). These mixing lines were not visible in the linear, un-normalized correlations (Figure 5.26b). The study confirms that stratospheric correlations between trace gases can be significantly altered by a strong tropospheric trend in one of the gases.

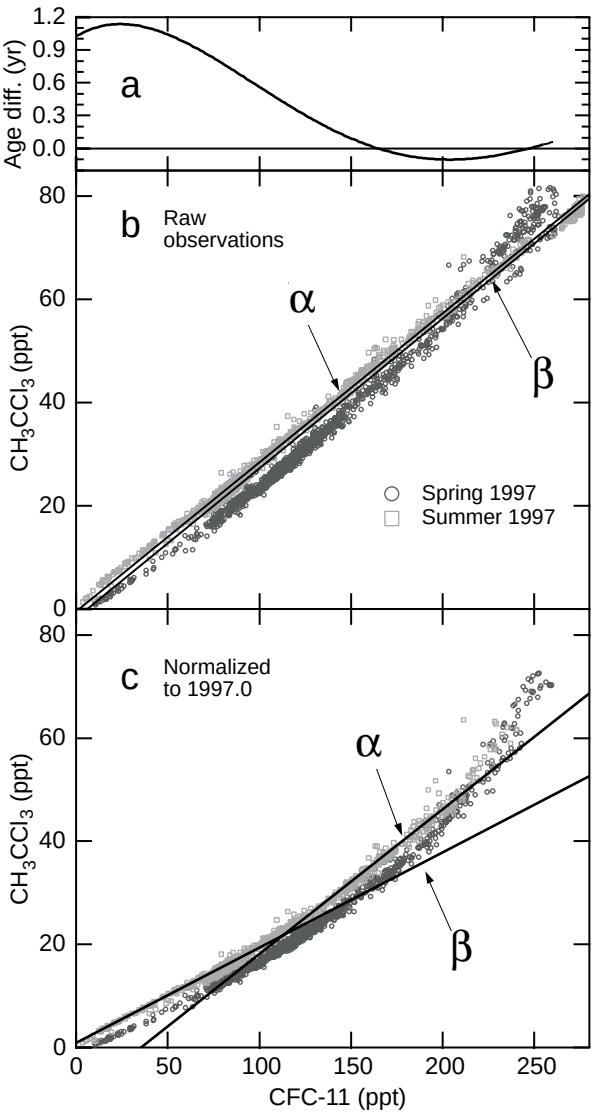

Fig. 5.26. Results from CH_3CCl_3 and CFC-11 measurements made during the POLARIS campaign (1997): (a) differences between the SF_6-based mean ages of air masses sampled by ACATS-IV (summer-spring), (b) correlations between CH_3CCl_3 and CFC-11 during spring and summer, and (c) same correlations as (b) with the effects of the tropospheric CH_3CCl_3 trend removed using 10-year-wide age spectrum, normalized to January 1, 1997. Solid lines in (b) and (c) are least squares fits to the following data subsets: α, 100 ppt<CFC-11<225 ppt measured on June 26, 1997; β, 0 ppt<CFC-11<125 ppt measured on June 29, 1997.

Total Inorganic Chlorine

Sen et al. [1999] compared two methods of determining the total inorganic chlorine content (Cl_y) of air masses sampled in the arctic stratosphere during POLARIS. In the first method, Cl_y was calculated as the difference between the total chlorine content (Cl_{tot}) of an air mass when it entered the stratosphere and the total organic chlorine content (CCl_y) of the same air mass at the time it was sampled by the ER-2. CCl_y was determined from ACATS-IV in situ measurements of chlorinated source gases

near 20 km altitude (lower stratosphere) during the ER-2 flight of April 26, 1997. Cl_{tot} values for the sampled air masses were compiled from time series of source gas mixing ratios measured at the Earth's surface in flasks and at NOAA observatories [*Woodbridge et al*., 1995; *Montzka et al*., 1996a]. The date of stratospheric entry of each sampled air mass was determined from its mean age calculated from ACATS-IV SF_6 data. Cl_y was also calculated as the sum of remotely sensed solar occultation Fourier transform infrared (FTIR) measurements of HCl, $ClONO_2$, and HOCl by the JPL MkIV interferometer and estimates of ClO from a photochemical model. The MkIV observations were made during a balloon flight on May 8, 1997. These two methods of estimating Cl_y agree to within 10% (Figure 5.27), adding confidence to both the in situ and remotely sensed data and suggesting that the photochemical model estimates of ClO are realistic for the sunlit lower stratosphere.

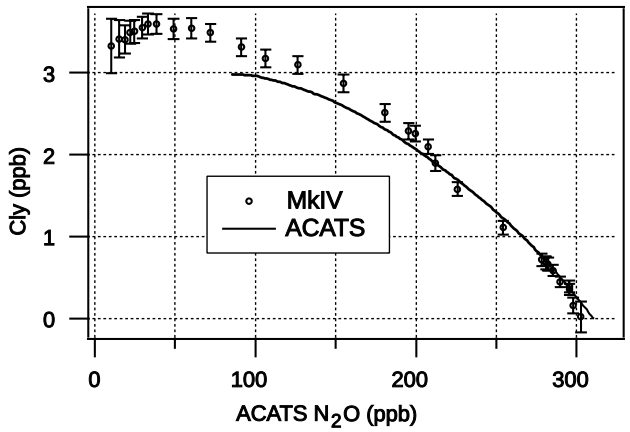

Fig. 5.27. Two independent methods were used to determine the total inorganic chlorine content (Cl_y) of stratospheric air masses during POLARIS (1997). One method (solid line) utilized CMDL surface measurements of chlorinated source gases and ACATS-IV (1997) measurements of organic chlorine compounds in the lower stratosphere. The other method (open circles) combined MkIV measurements of HCl, $ClONO_2$, and HOCl and modeled estimates of ClO. The two methods agree to within 10%.

Intercomparison of Trace Gas Measurements

ACATS-IV measurements of CFC-11, CFC-12, CFC-113, CCl_4, and SF_6 during POLARIS were compared to remotely sensed solar occultation FTIR measurements by the JPL MkIV interferometer on a balloon floating at 38 km altitude [*Toon et al*., 1999]. Both sets of tracer data were correlated with N_2O to account for the different dynamical histories of air masses sampled several days apart by the two instruments. Differences were less than 2% for both CFC-11 and CFC-12, well within the experimental uncertainties of the MkIV measurements. CFC-113 and CCl_4 data agreed to within experimental uncertainties (11-15%) between 13 and 21 km altitude, but the MkIV mixing ratios of both gases increased anomalously below 13 km. The anomalous increases were not observed for other long-lived tracers and were attributed to interfering absorption lines in the spectral regions used to quantify these gases. ACATS-IV SF_6 mixing ratios were on average 0.5 ppt (14%) lower than the MkIV values. This bias is surprising given that there was no discernable bias between SF_6 data from ACATS-IV and the Atmospheric Trace Molecule Spectroscopy (ATMOS) FTIR instrument aboard the space shuttle during 1993 and 1994 [*Chang et al*., 1996; *Michelson et al*., 1999]. The reason for this discrepancy has not yet been determined.

Instrument Modifications for TIES and SOLVE

ACATS-IV was modified twice during the second half of 1999 in preparation for the 2000 Stratospheric Aerosol and Gas Experiment-III (SAGE) Ozone Loss and Validation Experiment (SOLVE) in Kiruna, Sweden. The first modifications were made for the 1999 Tracer Intercomparison Experiment for SOLVE (TIES) mission, a side-by-side intercomparison of coincident measurements by the three in situ N_2O and CH_4 instruments selected for the SOLVE ER-2 payload. TIES was conducted at NASA Dryden, Edwards Air Force Base, California, during September-October 1999. The mission was a critical evaluation of N_2O and CH_4 measurements by the JPL TDL spectrometer and a new, lightweight, compact TDL spectrometer that will replace a heavy, large TDL spectrometer that provided high quality N_2O data aboard the ER-2 for many years. ACATS-IV was modified to include a new, rapid chromatography channel to measure N_2O and SF_6 every 70 seconds. The new channel was operated in parallel with the "old" 250-s N_2O and SF_6 channel during TIES, and the coincident data were in excellent agreement. ACATS-IV measurements of N_2O and CH_4 were used to assess the reliability of higher-frequency measurements by the TDL instruments. The assessment demonstrated that the quality of TDL N_2O data was, at times, inadequate for the upcoming SOLVE mission, and that further refinements of the spectrometers and their retrieval algorithms were necessary.

ACATS-IV was again modified after the TIES mission by replacing the "old" N_2O and SF_6 channel with a new, rapid chromatographic channel to measure CFC-12 and halon-1211 every 70 seconds. This channel was thoroughly tested in the laboratory for artifacts, flown during SOLVE test flights in December 1999 and then adopted as part of the final instrument configuration for SOLVE. The two modifications to ACATS-IV enabled 70-s measurements of N_2O, SF_6, CFC-12, and halon-1211, 140-s measurements of CFC-11, CFC-113, $CHCl_3$, CH_3CCl_3, CCl_4, CH_4, and H_2, and improved the precision of SF_6 and halon-1211 measurements to about ±1% during SOLVE.