Correlations of Long-Lived Tracers in the Lower Stratosphere using In Situ Observations: Methane Oxidation, Lifetimes, and Mixing Anomalies

G.S. Dutton[1,2], J.W. Elkins[1], D.W. Fahey[3], T. M. Gilpin[1,4], T.J. Baring[1,2,11], G.A. Holcomb[1,2,12], W.C. Kuster[3], R.C. Myers[1], J.H. Butler[1], S.A. Montzka[1], W.T. Sturges[1,2,13], P.C. Novelli[1,2], E.J. Dlugokencky[1], P.S. Bakwin[1], T.M. Thompson[1], T. Swanson[1,2], S.J. Oltmans[1], P.J. Fraser[5,10], L.P. Steele[5,10], K.K. Kelly[3], M. Loewenstein[6], J.R. Podolske[6], C.R. Webster[7], R.D. May[7], L.E. Heidt[4], S.M. Schauffler[4], A.E. Dessler[8], E.M. Weinstock[8], E.J. Hintsa[8], K.A. Boering[8], S.C. Wofsy[8], R.A. Plumb[9], D.W. Waugh[10], K.R. Chan[6]

[1] National Oceanic and Atmospheric Administration (NOAA), Climate Monitoring and Diagnostics Laboratory
[2] Cooperative Institute for Research in Environmental Sciences
[3] NOAA, Aeronomy Laboratory
[4] National Center for Atmospheric Research
[5] CSIRO, Australia
[6] NASA, Ames Research Center
[7] Jet Propulsion Laboratory
[8] Harvard University
[9] Massachusetts Institute of Technology
[10] CRC for Southern Hemisphere Meteorology, Australia
[11] Now at University of Alaska
[12] Now at HPS a division of MKS Instruments Inc., Boulder, CO
[13] Now at the University of East Anglia, UK

Abstract: Correlations between long-lived trace gas molecules are used to examine three separate topics: water production from methane oxidation, stratospheric and atmospheric lifetimes, and evidence of polar air mixing into mid-latitudes. A gas chromatograph (GC) designed for the NASA ER-2 aircraft to measuring CFC-11 (CCl_3F), CFC-113 (CCl_2FCCl_3), and methane (CH_4) is introduced. The Airborne Chromatograph for Atmospheric Trace Species (ACATS) was one of several instruments that participated on the second Airborne Arctic Stratospheric Expedition (AASE-II) and the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE) campaigns. Along with the GC data, measurements of nitrous oxide (N_2O), water vapor (H_2O), and CH_4 in the upper troposphere and lower stratosphere are used in the analysis. A comparison between three H_2O and two CH_4 in situ continuous measurements illustrate the difficulty in accurately calculating the water production from CH_4 oxidation chemistry. The idea of "slope equilibrium" [*Plumb and Ko*, 1992] is used to estimate stratospheric (CH_4) and in some cases atmospheric lifetimes (CFC-113 and N_2O) based on the assumed lifetime of CFC-11. Slope equilibrium is achieved when horizontal mixing along constant isentropic surfaces is much more rapid than advection or chemical processes.

At least one flight during the SPADE campaign (May 7, 1993) encountered air that had not yet reached slope equilibrium. Further evidence dramatically shows that rapid mixing of polar stratospheric air with mid-latitude air occurred as far South as 40˚ N latitude.

Introduction

There have been several aircraft campaigns in the past decade that have helped characterize long-lived tracer correlations in the lower stratosphere. Understanding and expecting such correlations have permitted calculations of the following: average age of air parcels [*Pollock et al.*, 1992], ozone depletion potentials of substitute chlorofluorocarbons (CFCs) [*Pollock et al.*, 1992], chlorine budget estimates [*Kawa et al.*, 1992; *Woodbridge et al.*, 1995], H_2O production from CH_4 oxidation [*Jones et al*., 1986; *Hanson and Robinson*, 1989; *Dessler et al.*, 1994], and atmospheric lifetime estimates [*Plumb and Ko*, 1992]. In this work we use tracer correlation from two aircraft campaigns, SPADE in November 1992 and April-May 1993 and AASE-II from August 1991 through March 1992. Both campaigns used the NASA ER-2 aircraft which has a maximum cruising altitude of 21 km and a range of 2400 km (about 20˚ latitude). In situ measurements of trace gases CFC-11 and CFC-113 during AASE-II were made by a single-channel gas chromatograph (GC). A second channel was added to the existing instrument during the SPADE campaign to measure CH_4. This paper will present three separate results from AASE-II and SPADE trace gas correlations and a comparison of simultaneous measurements of CH_4 and water vapor.

In the first section, we address differences in three H_2O measurements and two CH_4 measurements, review stratospheric CH_4 chemistry leading to water vapor production, and the variability in H_2O production calculated using the different measurements. Secondly, we will present stratospheric (CH_4) and atmospheric (N_2O and CFC-113) lifetime estimates based on the CFC-11 assumed lifetime. In a similar calculation we estimate CO_2 growth rate given CFC-11 and CO_2 lifetimes and compare it two measured tropospheric growth. Finally, we focus on the May 7, 1993 flight during the SPADE campaign in which isentropic mixing between polar and mid-latitude air begins as the vortex starts to break apart. Such mixing has not been observed in prior aircraft campaigns and may have implications for trace gas distributions in the mid-latitudes.

Experimental Methods

The Airborne Chromatograph for Atmospheric Trace Species (ACATS), was designed and built cooperatively by the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) and the NOAA Aeronomy Laboratory (AL). The original ACATS instrument used during AASE-II was a single-channel GC with an electron capture detector (ECD) designed to measure two halocarbons, CFC-11 and CFC-113, every 120 seconds. The instrument remained unchanged for the November 1992 deployment of SPADE; but a second GC/ECD channel was added for CH_4 measurements during the second phase of SPADE (April and May 1993). During SPADE, both GC channels sampled air every 180 seconds because of the longer time required for separation of CH_4 from air. ACATS occupied a rectangular space (45.7 cm wide $\times$ 86.4 cm long $\times$ 20.3 cm tall) inside the AL reactive nitrogen package (NOy) and the two instruments were mounted together inside the equipment bay (Q-bay) of the ER-2. To help reduce space and weight, the two instruments shared a pump motor, cylinder rack, and a data acquisition system. A 6.4 mm diameter, stainless steel, L-shaped tube was used for the GC's sample air inlet. The tube extended 20 cm away from the fuselage in order to sample outside of the aircraft's boundary layer (Figure 1). ACATS is the predecessor of ACATS-IV, a four channel airborne GC [*Elkins et al.*, 1996], that flew during the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) campaign in 1994.

Typical ER-2 flight speeds of 200 m s^{-1} (0.8 mach) require fast sampling rates to obtain data with adequate spatial resolution. The faster sampling rates were made possible by a 12-port, 2-position gas sample valve from Valco Instruments, Inc. (Houston, TX). The gas sample valve diverts (GSV) or heart-cuts oxygen in the sample away from the ECD prior to routing the separated peaks to the detector. In addition to the GSV, each channel contains two gas chromatographic separation columns, a pre-column and a main column, and an ECD from Shimadzu Corp. (Tokyo, Japan). Upon injection of the sample into the GC, the gas sample valve position is switched and the carrier gas sweeps the sample (5 cm^3 and 15 cm^3 for the halocarbon and CH_4 channels respectively) into the pre-column and subsequently through the main analytical separation column.

Both channels share a clean supply of ultra-high purity nitrogen (99.999% N_2) carrier gas from General Air Gas Co. (Boulder, CO). Though the gas is the highest grade commercially available, it can still have up to 10 parts per million by mole fraction (ppm, 10^{-6} mol mol^{-1}) of contaminants. The N_2 was scrubbed, in flight, through a 30 cm^3 zirconium getter (Supelco, PA) controlled at 350˚C, 50 cm^3 hopcalite trap (manganese dioxide and copper oxide mixture) at 40˚C, and followed by a 50 cm^3 molecular sieve trap at 40˚C.

The GC/ECD measurement technique for CH_4 was adapted from the work of *Phillips et al.* [1979]. The ECD technique is better suited for aircraft applications than conventional GC/FID (flame ionization detector) methods because there is no flammable gases and the ECD is inherently more stable under harsh environments. An ECD can be "sensitized" to CH_4 by doping the carrier gas leading into the detector with mixing ratios of 15-50 ppm of nitrous oxide. Pure N_2O was delivered at about 10^{-3} cm^3 min^{-1} directly into the ECD through a small piece of stainless steel crimped capillary tubing, yielding ~20 ppm of N_2O in the N_2 carrier gas.

During the SPADE mission, two different column packing combinations were used on the CH_4 channel. Originally, a pre-column 3-m long by 3.2-mm outside diameter (o.d.) stainless steel tube was packed with Porapak Q (a porous polymer) and preconditioned at 230˚C with 20-30 cm^3 min^{-1} N_2 flow for about 8 hours. The main column, 3-m long by 3.2-mm o.d., was packed with molecular sieve 5A and preconditioned at 350˚C with 20-30 cm^3 min^{-1} N_2 flow for about 8 hours. Unfortunately, Porapak Q produced carbon monoxide (CO) at temperatures above 50˚C. At 100˚C, mixing ratios in excess of 500 parts per billion by mole fraction (ppb, 10^{-9} mol mol^{-1}) of CO were found which overwhelmed the neighboring CH_4 peak. We subsequently switched to a pre-column 3-m long by 3.2-mm o.d. packed with silica gel and a 3-m long by 4.8-mm o.d. molecular sieve 5A analytical column both preconditioned at 350˚C with 20-30 cm^3 min^{-1} N_2 flow. There was no detectable CO (<26 ppb detection limit) being produced from the later configuration. The halocarbon channel used a 1-m by 3.2-mm o.d. pre-column and a 2-m long by 3.2-mm o.d. analytical column of which both were packed with 10% OV-101 (Analabs, MA) and preconditioned at 170˚C with 20-30 cm^3 min^{-1} N_2 flow for about 8 hours.

All columns were used isothermal and controlled by Omega CN9000A controllers (Omega Engineering, Inc., Stamford, CT). The CH_4 pre-column ran at 50˚C with a backflush flow of 100 cm^3 min^{-1} maintained by a differential pressure flow controller (Model VCD-1000, Porter

Instruments, PA). The CH_4 main column had constant carrier gas flow of 60 cm^3 min^{-1} controlled by a Tylan mass flow controller (Model FC-260, Tylan Corp., CA) and ran isothermal at 105˚C.

The precision of GC/ECD measurements are predominately affected by the ECD sensitivity, several techniques were used to maintain constant detector response. The ECD's housing was purged with about 3 cm^3 min^{-1} flow of scrubbed N_2. The purge flow helped minimize any contamination resulting from minute leaks in the detector seal. Slight fluctuations in the ECD current can cause dramatic changes in baseline response and peak sensitivity, thus the ECDs were operated at a constant current, 1 nano-amp (nA) for the halocarbon channel and 1.5 nA for the CH_4 channel. ACATS ECDs were pressure controlled at 93 kPa with a MKS valve, pressure transducer (SPT300 series, SPAN Inc., Plano, TX), and a PID (proportional, integral, and differential) controller made by MKS. The temperatures of the ECDs on the CFC and CH_4 channels were controlled with an Omega CN9000A controller isothermal at 350˚C and 360˚C, respectively.

Every fifth sample injection was a multi-component standard with 600 ppb of CH_4, 57 parts per trillion by mole fraction (ppt, 10^{-12} mol mol^{-1}) of CFC-113, and 130 ppt of CFC-11. This yielded a single-point calibration every 15 minutes during a flight. Laboratory analysis of CH_4 standards from the CMDL Carbon Cycle Group showed that the calibration curve was linear but had a large positive intercept of ~400 ppb because of interference from the oxygen peak. Though linear, the single-point ACATS standard of 600 ppb was not sufficient to establish the calibration curve for CH_4 over the range of tropospheric to stratospheric values. Values of CH_4 measured by ACATS in the troposphere were calibrated by using a correlation of CH_4 versus CFC-11 measured at the CMDL cooperative air sampling site, Niwot Ridge (NWR), Colorado (40.05˚N, 105.59˚W, altitude 3472 m). The station resides in the mid-troposphere at nearly the same latitude as Moffett Field, California (37˚ 23' N, 122˚ 4' W, altitude 30 m) where the SPADE campaigns were conducted. NWR tropospheric data was not needed to calibrate CFC-11 and CFC-113 because the curvature of the calibrations was characterized in the laboratory and had near zero intercepts. The calibration scales for CFC-11 and CFC-113 were established by comparing the instrumental response to the gravimetric standards prepared by similar techniques to those described in *Novelli et al.*, [1991]. The stability of gravimetric CFC-11 standards is described in *Elkins et al.*, [1993] and can be applied to CFC-113 and CH_4 standards. A new CH_4 scale is used based on in house gravimetric standards. This scale is about 0.9% higher that the original NOAA/CMDL CH_4 scale that was based off of ???? standards [*reference?*].

Results

There were 23 successful flights during the AASE-II campaign in which CFC-11 and CFC-113 were measured with 5% and 7% accuracy, respectively [*Woodbridge et al.*, 1995]. During SPADE, ACATS provided measurements of CFC-11 on ten flights (November 9 and 12, 1992; April 30, May 1, 3, 6, 7, 12, 14, and 18, 1993) of CFC-113 on nine flights (November 12, 1992; April 30, May 1, 3, 6, 7, 12, 14, and 18, 1993), and CH_4 on eight flights (April 30, May 1, 3, 6, 7, 12, 14, and 18, 1993). ACATS measured CFC-11, CFC-113, and CH_4 during SPADE with 3%, 5%, and 7% accuracy, respectively. All dates from here on will be referred to in the YYMMDD format.

Nitrous oxide measurements during AASE-II and SPADE were made by the ATLAS instrument using a tunable diode laser (TDL) with an instrumental precision of 5% [*Loewenstein et al.*, 1990, 1993]. In addition to the SPADE ACATS CH_4 measurement, CH_4 was measured using the ALIAS TDL instrument with a stated accuracy of 5-10% [*Webster et al.*, 1994] depending on the flight. AASE-II CH_4 was provide by in-flight flask samples from the Whole Air Sampler (WAS) [*Schauffler et al.,* 1993]. Water vapor was measured by three instruments during SPADE, two on the ER-2 and the third, a frost-point hygrometer from NOAA/CMDL [*Oltmans*, 1985] flew on a balloon platform. The ER-2 H_2O instruments, NOAA/AL [*Kelly et al.*, 1989] and Harvard University [*Weinstock et al.*, 1994], used Lyman-α/OH fluorescence techniques both of which have 7% stated accuracy. The NOAA/AL H_2O instrument also flew during AASE-II. Data sampling frequency for the TDL instruments and the Lyman-α hygrometers ranged from 0.3 to 1.0 Hz. To reduce the data for ease in comparison to the less frequent data, ACATS (once every 180 seconds) and the frost-point hygrometer, the data was binned into 10 second median bins.

CH_4 Comparison

The SPADE campaign provided a unique opportunity to compare simultaneous in situ measurements from different instruments, ACATS and ALIAS, using independent measurement techniques. Obviously, a "tight" or good comparison between the two data would allow unambiguous correlations with other tracers and would justify using the more frequent 1/3-Hz ALIAS data. Unfortunately, there is poor agreement between the two measurements. There were four flights in which both instruments made coincident measurements: 930430, 930503, 930506, and 930507. A linear orthogonal-difference-regression (ODR) fit [*Numerical Recipes*, 19XX], which uses the uncertainties (mean accuracies are shown in Figure 2) in both variables, was used instead of a least-squares fit.

$$\text{ALIAS } CH_4 = (0.89 \pm 0.03) * \text{ACATS } CH_4 + (0.00 \pm 0.04) \text{ ppm}$$

The fit uncertainties (1 standard deviation) were also calculated with the ODR algorithm and are purely statistical, thus do not incorporate any foreseen systematic uncertainties in either data. The slope discrepancy from the 1:1 line is strikingly large and clearly not accounted for by the instrumental uncertainties. There is on average a 12% systematic offset between both instruments. In Spring of 1993, a mid-latitude Northern hemisphere site, Niwot Ridge (NWR), measured a mean CH_4 mixing ratio of 1.72 ± 0.06 ppm (large solid circle on the 1:1 line in Figure 2), ACATS's tropospheric measurements are comparable but ALIAS is considerably lower with a mean tropospheric mixing ratio of 1.52 ppm. It is no surprise that the ACATS tropospheric measurements are similar to NWR values because tropospheric measurements were used in the calibration of CH_4. There are also several ACATS values much greater than 1.72 ppm, which probably came from terrestrial pollution sources near the San Francisco Bay area. Plotting ACATS CH_4 versus CO_2 (future correlations will be expressed with a colon, i.e. CH_4:CO_2) shows that most of the high CH_4 measurements are coincident with high, polluted CO_2 measurements (plot not shown).

The systematic difference between the two instruments can not solely be caused by calibration problems during flight, but may point to problems prior to the ER-2 take-off. The ALIAS instrument is calibrated prior to and after each flight, but not during a flight; where as, ACATS injects a calibrated gas sample every 15 minutes throughout a flight. If both ACATS and ALIAS calibrations were accurate prior to take-off, thus in agreement with each other, we would expect the correlation of the CH_4 ascent data between the two instruments to be 1:1. As a flight progresses the CH_4 correlation would deviate form the 1:1 correlation if one instrument's response, relative to its calibration, slowly changed. Similarly, if there was a pressure or temperature dependence that effected the instrument's response, we would predict good agreement in the troposphere and through the tropopause but worsening agreement at higher altitudes or lower concentrations. Neither of these deviations appear in the CH_4 correlation plot, rather a constant percentage offset between each instrument is shown, which may indicate contamination or a calibration problem prior to take-off. The systematic offset does not manifest in laboratory intercomparisons where the measurements of calibrated standards are within the instrumental and calibration uncertainties.

Previous laboratory intercomparisons may not have been a good assessment of "in-flight" conditions and flight preparation techniques. A better intercomparison experiment would be to prepare both instruments for a flight and then run a calibrated gas mixture in a temperature and pressure controlled environment. Such an experiment could determine any instrument calibration changes caused by preparing the instruments for a flight. Without further laboratory intercomparisons to better simulate pre-flight and in-flight conditions, we cannot resolve the systematic difference between ACATS and ALIAS. It is difficult to choose the most accurate CH_4 data, but based on tropospheric comparisons and in-flight calibrations, ACATS CH_4 is arguably more accurate.

H_2O Comparison

During the SPADE campaign, there were three independent water vapor measurements, two by in situ Lyman-α hygrometers aboard the ER-2 (NOAA/AL and Harvard instruments) and one by a balloon borne frost point hygrometer (from NOAA/CMDL). The ER-2 was based out of Moffett Field, California (37° 23' N, 122° 4' W) and the balloon was launched at the nearby location of Crow's Landing, California (37° 23' N, 121° 4' W). A direct comparison between the AL and Harvard ER-2 instruments can easily be made; but the comparison with the CMDL frost point hygrometer is more difficult due to temporal and spatial differences. The CMDL instrument measured several vertical profiles up to 29 km, while the majority of the ER-2 measurements were between 15-21 km, thus reducing the number of comparable data. Nonetheless, we compare the three water vapor measurements for the flight of 930507, when the ER-2 H_2O instruments and the CMDL frost point hygrometer measured water at the same latitude and between 1-5 degrees of longitude of each other (Figures 3 and 4). The ER-2 and the balloon were launched within an hour of each other but the ascent of the balloon measurements were generally excluded. Using the descent data, the temporal difference between the ER-2 and balloon measurements, at the same altitude and closest location, can be up to 4 hours. The aircraft made 7 passes over the coast of Northern California, in a "racetrack" type path.

The most striking discrepancy between the three H_2O measurements is the systematic differences between the measurements (Figure 4). The CMDL data is about 1 ppm lower than the AL measurement, where as, the Harvard data is about 0.8 ppm greater than the AL measurement (Figure 4b). On closer inspection, the difference between the two ER-2 instruments, NOAA/AL minus Harvard H_2O, are quite dependent upon altitude. In the troposphere below about 12 km (150 mbar) the difference can be as large as 100 ppm. However, above 12 km the difference can be expressed as a function of pressure. *** Add function *** These offsets are fairly constant over all altitudes and flights indicating some intrinsic problem, such as contamination, or a calibration scale problem relative to each instrument. As with the constant percentage offset between the CH_4 measurements, a constant offset can indicate a background level of contamination.

Upper atmospheric H_2O measurements are extremely difficult when the instrument has to pass through wet tropospheric air that can have, on the order of, 1000 times more H_2O. To minimize ascent contamination problems associated with the balloon's surface out-gassing, generally, only descent data was used. The CMDL balloon instrument's inlet is made solely from stainless steel. Though the ER-2 instruments do not have to contend with out-gassing from the platform itself because the inlets are outside of the ER-2s boundary layer. The instruments may have out-gassing from their inlet lines, themselves, which are longer and, in the case of the AL hygrometer, have portions of Teflon tubing. Laboratory intercomparisons of the three instruments have not resolved the in-flight differences; and have demonstrated good agreement between the CMDL and AL instruments and an improved comparison (better than 1 ppm) with the Harvard instrument [*Vömel,* priv. comm., *Vömel et al.*, in preparation]. The improved laboratory comparisons also point to in-flight contamination problems, but would clearly have to be evident on at least two instruments and in different proportions. With the given uncertainties with each instrument, it is difficult to choose the most accurate H_2O measurement.

H_2O Production from CH_4 Oxidation

There are several motivations for measuring stratospheric methane and water vapor. Both gases are greenhouse gases and have long lifetimes in the lower stratosphere. Apart from the tropospheric intrusions of H_2O, methane oxidation is the dominate source for upper atmospheric water. To quantitatively estimate the amount of water entering from the troposphere, an understanding of the stratospheric H_2O sources is imperative.

The methane chemistry discussed below will focus on the chemistry from the tropopause through the lower stratosphere because the ER-2's altitude never exceeds 21 km. For a more thorough discussion of upper atmospheric methane chemistry see for example, *Le Texier et al.*, 1988 or *Brasseur and Solomon.*, 1984. Methane is primarily destroyed via oxidation by the hydroxyl radical (OH):

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad (1)$$

Reactions with atomic chlorine, excited oxygen $O(^1D)$, and photolysis are negligible in the lower stratosphere. The resulting methyl radical (CH_3) reacts rapidly with molecular oxygen:

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (2)$$

to produce the methyl peroxy radical (CH_3O_2). The methyl peroxy radical can react with NO, HO_2 or itself:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{3a}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \tag{3b}$$

$$CH_3O_2 + CH_3O_2 \rightarrow 2\ CH_3O + OH \tag{3c}$$

where reaction 3a is the most common. The methoxy (CH_3O) molecule of reaction (3a and 3c) is then rapidly destroyed by molecular oxygen:

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{4}$$

The methyl hydrogen peroxide (CH_3OOH) of reaction 3b reacts with OH:

$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O \tag{5}$$

and forms methyl peroxy radical that is destroyed via the reaction scheme 3. So that the net result of all the methyl peroxy reactions is the formation of formaldehyde (CH_2O). Formaldehyde is destroyed via similar reactions as CH_4 where the dominate reactions are:

$$CH_2O + OH \rightarrow CHO + H_2O \tag{6a}$$

$$CH_2O + h\nu \rightarrow CHO + H \tag{6b}$$

$$CH_2O + h\nu \rightarrow CO + H_2 \tag{6c}$$

The unstable radical CHO reacts with O_2 or is photolyzed to form CO and hydrogen radicals:

$$CHO + h\nu \rightarrow CO + H \tag{7a}$$

$$CHO + O_2 \rightarrow CO + HO_2 \tag{7b}$$

The ultimate fraction of water produced from methane is determined by the destruction mechanisms of formaldehyde. If the photolysis contribution is negligible, then for every CH_4 molecule, two H_2O molecules are produced. If the OH-formaldehyde reaction efficiency decreases, the number of H_2O molecules produced decreases and molecular hydrogen and hydrogen radicals increase. Note, the CO production from formaldehyde remains constant despite the destruction scheme, but the H_2O, H_2, and odd hydrogen (such as H, OH, and HO_2) partitioning changes. The remaining odd hydrogen is short lived and has a multitude of reaction paths that can lead to H_2O and H_2 production. [*Brasseur and Solomon*., 1986] Therefore, the destruction of methane produces water vapor and molecular hydrogen such that the sum:

$$\alpha\,[CH_4] + \beta\,[H_2] + [H_2O] \approx \text{constant} \qquad (8)$$

is approximately constant with altitude above the tropospheric effects (where [] is used to denote mixing ratios and α and β are constants) with two caveats:

1) Any remaining odd hydrogen is negligible.

2) The intermediate reactions occur rapidly such that mixing processes do not effect the partitioning.

Equation 8 is only constant with altitude at heights where tropospheric effects, such as seasonality, are thoroughly damped out. The extent to which tropospheric signals affect lower stratospheric distributions of trace gases is not well know, thus making H_2O production estimates difficult in the lower stratosphere.

There have been few measurements of H_2 in the stratosphere and no in situ continuous measurements prior to SPADE. The few previous flask measurements [*Ehhalt and Heidt*, 1973, *Ehhalt and Tonnissen*, 1980, *Pollock et al.*, 1980] have given some indication that H_2 is virtually constant (as compared to CH_4 and H_2O variations) from the upper troposphere through most of the stratosphere with a mixing ratio of about 0.5 ppm. If we assume H_2 is constant, thus conserved, in the stratosphere then the β $[H_2]$ term of equation. 8 can be combined into the constant, thus simplifying to:

$$\alpha\,[CH_4] + [H_2O] \approx \text{constant} \qquad (9)$$

or differentiating,

$$\alpha\,\Delta[CH_4] \approx -\,\Delta[H_2O] \qquad (10)$$

where Δ denotes change in the mixing ratio (similar treatment as *Hansen and Robinson,* 1989 and *Jones et al.*, 1986). Thus, using the outlined arguments and chemistry above, an H_2O:CH_4 correlation should give a slope of $-\alpha$ with α quantifying the number of H_2O molecules produced from one CH_4 molecule.

Table 1 summarizes how measurement differences of CH_4 and, to a much greater extent, H_2O affect the H_2O production slope, $-\alpha$. To complicate matters, seasonal fluctuations in H_2O that are transported into the lower stratosphere can cause the slope to oscillate on an annual cycle (*Mote et al.*, 1995 and *Hintsa et al.*, 1994). It is hard to determine the extent to which tropospheric fluctuations effect the SPADE H_2O data thus, it is difficult to filter out such disturbances. To exclude tropospheric effects, CH_4 data below the 430 K Θ surface was filtered out.

It is clear that no conclusions about H_2O production can be made without understanding the systematic problems and uncertainties in the CH_4 measurements and more importantly the H_2O data. Recent improvements with the ER-2 CH_4 and H_2O instruments for the 1994 ASHOE/MAESA campaign may help in quantifying α.

Lifetime Calculations of CFC-113, CH_4, and N_2O

The quantitative formalism for calculating stratospheric lifetimes from trace gas correlations was developed in *Plumb and Ko* [1992] in their "global diffuser" model. They argued that compact long-lived tracer correlations arise because quasi-horizontal mixing time scales are more rapid than source and sink mechanisms. Two trace species are said to be in "slope equilibrium" if their mixing ratio is constant along a shared insentropic surface. In terms of general global mixing, quasi-horizontal mixing dominates all other forms of mixing, such as, vertical advection and diffusion. Though, a simplified picture of global dynamics, *Plumb and Ko* hold that any measured upper atmospheric tracer correlation at a given location is representative of correlations globally. Though, recent work has shown that tropic tracer correlations can be different than mid-latitude and polar correlations [*Murphy et al.*, 1993]. Where mixing in the tropics can be dominated by vertical advection rather than quasi-horizontal movement [*Plumb*, 1995]. *Volk et al.*, 1996, has recently estimated mid-latitude to tropics exchange rates and has examples of trace gas correlations in the tropics. For our purpose, the global diffuser model is adequate for the mid-latitude and polar campaigns of AASE-II and SPADE.

Vertical transport in the global diffuser model can be express in terms of flux through the constant mixing surface. If two molecules are in slope equilibrium and have long lifetimes relative to vertical advection time scales, then the ratio of fluxes is simply the slope of species in a tracer correlation at the constant mixing surface.

$$\frac{F_1}{F_2} = \frac{\partial\sigma_1}{\partial\sigma_2} = m \tag{11}$$

Where the flux, F, is expressed as mass per unit time, $\partial\sigma$ is the change in mixing ratio, and the numbered subscripts symbolize each trace species. The quantity $\partial\sigma_1/\partial\sigma_2$ is the slope, m, of the correlation $\sigma_1 : \sigma_2$ where σ_1 is the dependent variable and σ_2 is the independent variable. Since we are interested in stratospheric lifetimes, the constant mixing surface chosen will be the tropopause. The flux can be expressed as the change in loading due to growth minus the sink (S) above the constant mixing surface, or simply, the burden above the surface.

$$F_1 = \frac{\partial q_1'}{\partial t} - S_1 \tag{12}$$

Where q' is the mass above a constant mixing surface. From here on there are analogous equations for the second specie. The change in loading above the constant mixing surface can be approximated in terms of global growth rate (r) scaled by the mass above the constant mixing surface.

$$\frac{\partial q_1'}{\partial t} \approx -r_1 q_1' \tag{13}$$

The sink can be expressed in terms of total atmospheric mass of the specie (q) divided by its atmospheric lifetime (τ) if there is no tropospheric sink. If there is a tropospheric sink (e.g. CH_4), then τ is used to represent stratospheric lifetime.

$$S_1 = \frac{q_1}{\tau_1} \tag{14}$$

Thus, equation 12 becomes:

$$F_1 \approx -r_1 q_1' - \frac{q_1}{\tau_1} \tag{15}$$

The total atmospheric mass of a specie (q) is the sum of upper atmospheric mass (q') and the tropospheric mass (q^{trop}). Unfortunately, it is difficult to measure q' without having vertical profiles that extend much higher than the chosen mixing surface or, in our case, the tropopause. To remove the q' dependence from equation 15 we introduce the f-factor term (f) [*Butler et al.*, 1992]. The f-factor is the ratio of the fraction of the specie in the troposphere to the fraction of the troposphere to the atmosphere. Standard f-factor calculations use vertical profiles from several latitudes, thus provide a globally averaged f-factor. An f-factor can be between 1.0, well mixed troposphere with no upper atmosphere contribution, to about 1.2, equal concentration in the troposphere and upper atmosphere (this also implies no growth). Solving for the upper atmospheric mass in terms of f-factor gives:

$$q_1' = q_1^{trop}\left(\frac{1}{f_1 M} - 1\right) \tag{16}$$

Where M is the fraction of troposphere to the atmosphere, we have used 0.828 [*Warneck*, 1988]. Replacing q' in equation 15 yields a flux dependent on the tropospheric mass of the specie:

$$F_1 \approx -q_1^{trop}\left[r_1\left(\frac{1}{f_1 M} - 1\right) + \frac{1}{f_1 M \tau_1}\right] \tag{17}$$

Before extending the growth rate influenced flux calculation to the Plumb and Ko relationship and lifetime estimate, some important generalizations can be made. For the growth rate term to be a significant contribution to the flux calculation, the inequality

$$\frac{1}{r_1} >> \tau_1(1 - f_1 M) \tag{18a}$$

$$0 \le (1 - f_1 M) \le 0.17 \tag{18b}$$

should be met. Equation 18b is the theoretical limit derived from the bounds of f-factors. If the inequality is not reached, we can simplify the flux equation to the growth rate independent flux equation in terms of f-factor. In general, almost all natural and most anthropogenic species do not satisfy inequality 18a, thus removing the need for accurate estimates for growth when estimating stratospheric lifetimes. Some exceptions are the CFC replacement compounds such as HCFC-22 ($CHClF_2$) or extremely long-lived molecules such as perflourcarbons (CF_4, C_2F_6, etc.) or SF_6. For a species with about 0.5% growth rate, its lifetime would need to be about 120 years for a 10% effect on the flux estimate. Equation 18a scales linearly so a specie with about 4% growth would need a lifetime on the order of 15 years for a 10% effect.

Substituting the flux equation 17 into the ratio of flux relationship 11 and solving for the lifetime of the dependent species (τ_1) we get:

$$\frac{1}{\tau_1} \approx f_1 m M \frac{\sigma_2^{trop}}{\sigma_1^{trop}}\left[r_2\left(\frac{1}{f_2 M}-1\right)+\frac{1}{f_2 M \tau_2}\right] - f_1 r_1 M\left(\frac{1}{f_1 M}-1\right) \quad (19)$$

Where the ratio of tropospheric masses can be simplified to the ratio of tropospheric mixing ratios, $\sigma_2^{trop}/\sigma_1^{trop}$. Equation 19 is the instantaneous lifetime of a specie that has a non-negligible growth rate. Likewise, the independent specie (with subscript 2) used in the correlation $\sigma_1 : \sigma_2$ also has non-negligible growth. In practice, to reduce the uncertainty in the lifetime estimate, the independent specie should have a negligible growth rate such that inequality 18a is meet, have a well know lifetime, and have a compact linear correlation with the dependent specie. In our study, the dominate uncertainty (greater than 90%) in the lifetime estimates is due to the uncertainty in the assumed lifetime of the independent specie. We chose CFC-11 as the independent specie because of its relative small uncertainty in its lifetime 55 ± 8 years [*Elkins et al.,* 1993]. The uncertainty of CFC-11's lifetime is smaller than other long lived tracers such as N_2O and CH_4, because it is completely anthropogenic and the global emission estimates are fairly accurate [*Fisher and Midgley*, 1994]. Once again, if both species satisfy inequality 18a then the lifetime equation can be simplified in terms of f-factor to the steady state lifetime equation in *Plumb and Ko* :

$$\frac{1}{\tau_1} \approx m \frac{\sigma_2^{trop}}{\sigma_1^{trop}} \frac{f_1}{f_2} \frac{1}{\tau_2} \quad (20)$$

The AASE-II and SPADE campaigns were combined and linear least-squares correlations were calculated from the tropopause through the lower stratosphere (Figure 5). The two missions can be usefully combined since the growth rates of the species into the stratosphere have not changed drastically (prior to 1993) [*Elkins et al.*, 1993] and the missions were conducted at comparable latitudes. The tropospheric data, data below 410 K potential temperature (Θ), was filtered out of the correlation plots, thus, the lifetime calculations. The filtering is not essential when calculating atmospheric lifetimes of species that have negligible tropospheric sinks. However, the filtering removes any local pollution signals that could influence the slopes of the tracer correlations. Table 2 summarizes the input parameters, the WMO reported lifetimes, and the calculated lifetime using CFC-11's lifetime from *Elkins et. al.*, 1993.

Equation 20 can be used for CH_4 and N_2O lifetimes; but inequality 18a is marginal for CFC-113, so the growth rate dependent equation 19 is used. To help estimate the uncertainties, a Monte Carlo simulation was used. The simulation assumed that all input parameters had normal-distributions (Gaussian) with widths dependent on the parameters one standard deviation uncertainty. The CFC-113 lifetime probability distribution was skewed (similar to the distribution in Figure 6b), so the mode of the distribution was used as our lifetime estimate. The uncertainty range (see table 2) for the CFC-113 lifetime encloses about 66% of the distribution.

To check the validity of the CFC-11 input parameters equation 19 is solved for the growth rate of the dependent specie (r_1), assuming the lifetime of the dependent species is very long ($1/\tau_1 \approx 0$). The resultant growth rate can be measured growth rates.

$$r_1 \approx m \frac{\sigma_2^{trop}}{\sigma_1^{trop}} \frac{f_1 M}{(1 - f_1 M)} \left[r_2 \left(\frac{1}{f_2 M} - 1 \right) + \frac{1}{f_2 M \tau_2} \right] \tag{21}$$

As with the lifetime calculation, the r_2 term can be ignored if inequality 18a is met. Assuming the lifetime of CO_2 in the lower stratosphere is extremely long [*Tans* , 1996; *Tans and Bakwin*, 1995], we use the CO_2:CFC-11 correlation (Figure 6a) to estimate CO_2 growth rate. A Monte Carlo simulation was used to generate the probability distribution of the CO_2 growth rate (Figure 6b), where the mode or our best estimate is 0.5% (-0.2%, +0.8%). As with the CFC-113 lifetime uncertainty estimate the CO_2 growth rate uncertainty is skewed where 66% of the uncertainty is between 0.3% and 1.3% growth (dark area in Figure 6b). Though the uncertainty covers a large range of growth rates, it does not including the abnormally low growth period of 1992-93 measured by CMDL flask network (0.17% $\pm$ 0.04%). However, it is within the 95% limits (arrows in Figure 6b). Obviously, there are better methods for estimating and measuring growth rates, but equation 21 can be used to support the independent molecule (in our case CFC-11) parameters in the lifetime calculation.

Our estimate for N_2O lifetime of 105 $\pm$ 15 is lower but within one standard deviation when compared to the most recent WMO [1994] assessment of 120 years. When compared to inverse method calculations, we are considerably lower than *Prinn et al.*, [1990] which estimates 170 years. Based on new absorption cross sections for O_2 in the Schumann-Runge band, *Ko et al.*, [1991] calculate an atmospheric lifetime of 110 years. Using vertical profiles of N_2O from satellites and

Minschwaner et al., [1992] calculate a lifetime of 123 ± 20 years. Our results are in support of the more recent, shorter lifetime estimates.

Polar to Mid-latitude Mixing Event

Perhaps the most interesting individual flight during the SPADE campaign was that of 930507 in which distinctly different air parcels were encountered. The ER-2 ascended to a cruising altitude of about 20 km (50 mbar) and flew repetitively over the coast of California such that the plane sampled the same locations several times (see Figure 3 and 7). Three distinct levels of mixing ratios are seen in the ACATS data. Background tropospheric levels of CH_4 and CFC-11 were measured during the ascent and descent with some pollution events during the ascent (CH_4 > 1.8 ppm). Mid-latitude and polar stratospheric vortex mixing ratios were measured during the main portion of the flight. The higher mixing ratios (CH_4 ~1.4 ppm and CFC-11 ~140 ppt), immediately following the ascent and throughout the constant altitude portion of the flight, are typical of mid-latitude lower stratospheric air. Similar mixing ratios were measured during the AASE-II and throughout SPADE campaigns (Figure 6 and 8). The lower mixing ratios (CH_4 < 1.0 ppm and CFC-11 < 50 ppt) are levels consistent with Arctic vortex air measured during AASE-II. The polar originating air parcel was located near the Pacific coast (South of 37 ˚N and West of 123.75 ˚W) and was encountered eight separate times.

A comparison of the ACATS tracers measured during AASE-II and SPADE shows that the 930507 flight's tracer correlations are not the same, and in some cases extremely different (Figure 6). The N_2O:CFC-11 correlation dramatically shows the deviation from the "standard" canonical relationship as defined by AASE-II and SPADE flights (Figure 6a) where the 930507 correlation virtually straddles the curvature in the canonical fit. We argue that slope equilibrium has not yet been achieve and that polar processed air is rapidly mixing into, the much more massive, mid-latitude air parcel. Further evidence that horizontal mixing has not yet reached equilibrium is seen in 930507 vertical profiles, where there is a huge range in mixing ratios between Θ 460-470 K (Figure 8). The AASE-II campaign sampled extremely low levels of CFC-11 within the polar vortex (CFC-11 < 20 ppt).

A linear fit through the 930507 N_2O:CFC-11 data intersects the canonical relationship at the original concentrations of the Arctic and mid-latitude air. To identify large scale mixing events, some curvature in the standard correlation is required and the two air parcels need to straddle the curvature. If tropospheric CFC-11 were to rapidly mix with CFC-11 air with 100 ppt mixing ratio, the event would not be seen in the CFC-11:N_2O canonical relationship due to lack of curvature. This is why correlations with species that have similar local lifetimes such as CH_4:N_2O do not show the 930507 mixing. The initial mixing ratios of the Arctic air parcel, prior to mixing, can be inferred by estimating where the linear fit through the 930507 flight intercepts the canonical fit. Thus, the Arctic parcel had 11 ± 5 ppt of CFC-11, 8 ± 8 ppt of CFC-113, 870 ± 50 ppb of CH_4, and 90 ± 10 ppb of N_2O. Extensive discussion on the mechanism and similar mixing events during the ASHOE/MAESA campaign can be found in *Waugh, et al.* [1995] and *Newman, et al.* [1995].

Conclusions:

Enhancements to ACATS between the AASE-II and SPADE campaigns helped improve the precision of the CFC measurements and facilitated the measurement of CH_4. ACATS and the tunable diode laser instrument, ALIAS, made simultaneous in situ measurements of CH_4 during the SPADE mission. Unfortunately, there is on average a 12% systematic difference between the CH_4 measurements. Laboratory intercomparisons have not succeeded in explaining the systematic in-flight offset; but have also not tested the in-flight conditions adequately. Though by limited arguments, we maintain the ACATS data is better calibrated than ALIAS measurement.

Similarly, there were three (NOAA/AL, NOAA/CMDL and Harvard University) in situ water vapor measurements conducted with two different techniques (Lyman-α and frost-point). A more extensive intercomparison has been carried out [*Vömel,* priv. comm.], with little further insight into the systematics. During the intercomparison the NOAA/AL Lyman-α instrument and the NOAA/CMDL frost-point hygrometer agreed well but the Harvard Lyman-α hygrometer was still high (*Number?*). Without better understanding of the systematics in the CH_4 and H_2O data it is, at best, difficult to estimate H_2O production via CH_4 oxidation. *Dessler et al.* [1994], incorporated old hydrogen measurements via a CH_4:H_2 correlation to help constrain the H_2O:CH_4 slope. This technique can bypass some of the measurement uncertainties but it also assumes CH_4 and H_2 chemistry is well characterized and more rapid than dynamic processes. Further measurements of H_2 and more accurate measurements of CH_4 and H_2O will help constrain such an argument.

The mechanism for estimating stratospheric lifetimes of long-lived relatively slow growth molecules was put forth by Plumb and Ko [1992]. We extend their formalism to incorporate species with faster growth rates such as CFC-113 and CFC replacement compounds. Using the combined AASE-II and SPADE CFC-113:CFC-11 correlation and the NOAA/CMDL tropospheric network measurements for growth rates we estimate CFC-113 lifetime to be 84 (-14,+18) years. The Plumb and Ko non-growth rate dependent lifetime equation is adequate for estimating atmospheric N_2O lifetime and stratospheric CH_4 lifetime, in which we calculate 105 ± 16 and 125 ± 19 years respectively. The N_2O lifetime is less than the reported WMO lifetime but within the uncertainty and is in good agreement with *Ko et al.* [1991] and *Minschwaner et al.* [1992]. About 90% of the uncertainty in all of the lifetime calculations is the estimated error in the CFC-11 lifetime (55 ± 8 years). A better handle on CFC-11 emissions and a refinement in its lifetime will certainly improve the lifetime estimates of stratospheric trace gases.

Acknowledgments: We appreciate the assistance of Rich Lueb and Binu Lohani in the collection and analysis of the WAS samples, the assistance of Mike O'Neill and Frank Polacek III in the NOAA/CMDL balloon soundings, and the useful discussions with Michael C. Volk, Jonathan Gilligan, Ross Salawitch, and Michael McElroy. This work was supported in part by the Atmospheric Chemistry Project of NOAA's Climate and Global Change Program and by NASA's High Speed Research Program under grants HSRP#-528 (SJO) and 535(JWE).

Figure Captions:

Figure 1. Schematic of ACATS. The instrument contained two separate GC channels that measured CFC-11, CFC-113, and CH_4 every 180 seconds. ACATS and the adjacent instrument, AL reactive nitrogen experiment (NOy), shared a data acquisition system, pump motor, and cylinder rack. Both instruments were mounted in the ER-2 equipment-bay (Q-Bay). The GC's nitrogen (N_2) carrier gas was scrubbed in series through a hot zirconium column (Z), Hopcalite trap (H), and finally a molecular sieve 13X trap (M). Both the N_2 carrier and calibration gases were controlled with a Tylan mass flow controller. The CH_4 electron capture detector (ECD) was doped with N_2O through a crimped (C) stainless steel tube. A proportional-integral-differential (P) controller maintained the halocarbon ECD to about 975 ± 1 mbar while a pressure relief valve (T) was used on the CH_4 ECD to control it at 975 ± 6 mbar. The stream selection valve (SSV) was used to select either the air sample or the calibration gas sample. Each channel had a separate gas sample valve (GSV) that controlled the sample injection and backflush. Figures a and b show both positions of the GSV. Notice that the direction of flow through the main column (longer column in column oven) remains the same but the flow is reversed through the shorter pre-column, thus backflushing heavier, slower, species off of the pre-column.

Figure 2. There were two simultaneous measurements of CH_4 during the SPADE campaign. A comparison between the ALIAS (tunable diode laser) and ACATS (gas chromatograph) instruments shows a large systematic offset of ~12%. The solid dot on the 1:1 line (dotted line) is the mean Spring CH_4 tropospheric mixing ratio at Niwot Ridge. Niwot Ridge is at a comparable latitude to the ER-2 launch site at Moffett Field, California. The solid line is a linear-orthogonal-difference fit using both the average ALIAS and ACATS accuracy's (displayed as the error bar cross-hatch).

Figure 3. The SPADE campaign was based out of Moffett Field, California. The ER-2 flight track for May 7, 1993 is shown. The aircraft made seven separate isentropic passes over the Californian coast. A balloon borne frost-point hygrometer was launched from Crow's Landing, California, at approximate the same time as the ER-2. See Figure 4 for the comparison of the ER-2 and balloon H_2O measurements.

Figure 4. There were three in situ water vapor measurements during the SPADE campaign. Two aboard the ER-2 launched at Moffett Field and one aboard a balloon launched at Crow's Landing (see Figure 3). Unfortunately, there were systematic differences between both ER-2 Lyman-α hygrometers (a and b) and between the balloon frost-point hygrometer (c) on all flights (May 7, 1993 flight shown). Though there is a great deal of structure in the H_2O profile the difference between the ER-2 instruments is fairly constant (0.8 ± 0.1 ppm) above the tropopause. Below the tropopause, the difference can be as large as 200 ppb.

Figure 5. Combined AASE-II and SPADE data provide compact correlations with CFC-11 and (a) N_2O, (c) CFC-113, and (e) CH_4. Linear correlations in the lower stratosphere can be used to estimate stratospheric lifetimes [*Plumb and Ko*, 1992]. We extend the Plumb and Ko steady state lifetime calculation (Equation 20) to molecules that have non-negligible growth rates (in particular CFC-113, Equation 19). To help estimate lifetime uncertainties, a Monte Carlo simulation was run with 100,000 iterations. The probability distribution from the simulations are shown in Figures b, d, and f. The N_2O and CH_4 lifetime probability distributions are normal (Gaussian) so the mean and the standard deviation (dark gray area) are used. For the non-normal distribution of CFC-113, our best estimate for lifetimes is the mode of the distributions with the 2/3 of the area enclosed as our uncertainty estimate. See Table 2 for the input parameters.

Figure 6. The CO_2 growth rate from the CO_2:CFC-11 correlation (a) and the growth rate dependent lifetime equation solved for growth rate (equation 21 in the text) can be used to validate the CFC-11 input parameters (lifetime, f-factor, and tropospheric mixing ratio) to the lifetime calculation (equation 19). A Monte Carlo simulation using the CFC-11 input parameters and uncertainties generates a probability distribution of CO_2 growth rates (b). The mode of the distribution is 0.6% with a skewed uncertainty of -0.2% to +0.8%. The CMDL measured tropospheric growth rate is 0.5% and agrees within 66% uncertainty. Though, a crude method for estimating growth rates, this does help validate the independent specie input parameters in the lifetime calculation.

Figure 7. ACATS CH_4 and CFC-11 mixing ratios measured during the flight of May 7, 1993 with accompanying pressure profile. Tropospheric measurements were obtained on the ascent and descent. Two distinct air parcels (Arctic and mid-latitude origin) were encountered several times as the aircraft repeatedly circled through the same location (see Figure 3 for flight track).

Figure 8. The N_2O:CFC-11 correlation (a) and vertical profile (b) for the combined campaigns, AASE-II and SPADE. In both figures the SPADE May 7, 1993 flight is shown separately. The AASE-II campaign was predominately an Arctic campaign and had several flights that enter the Arctic vortex (values with CFC-11 < 20 ppt). The SPADE campaign designed to assess mid-latitude chemistry encountered polar originating air on May 7, 1993 as far South as 40 °N. The May 7 flight encountered a huge range of mixing ratios at virtually the same potential temperature (Θ) surface. The May 7 flight clearly demonstrates that mixing along a constant isentropic surface ($\Theta \approx 460$ K) has not yet reached equilibrium. The intersection "standard" correlation (solid black curve) with the linear fit through the May 7 N_2O:CFC-11 correlation can be used to estimate the mixing ratios of trace gas constituents in the polar air parcel.

References

Brasseur, G. and S. Solomon, *Aeronomy of the middle atmosphere : chemistry and physics in the stratosphere and mesosphere*, D. Reidel Pub. Co., Boston, 1984.

Butler, J.H., J.W. Elkins, B.D. Hall, S.O. Cummings, and S.A. Montzka, A decrease in the growth rates of atmospheric halon concentrations, *Nature, 359*, 403-405, 1992.

Dessler, A.E., E.M. Weinstock, E.J. Hintsa, J.G. Anderson, C.R. Webster, R.D. May, J.W. Elkins, and G.S. Dutton, An examination of the total hydrogen budget of the lower stratosphere, *Geophys. Res. Lett.*, *21(23)* 2563-2566, 1994.

Dlugokencky, E.J., K.A. Masarie, P.M. Lang, P.P. Tans, L.P. Steele, and E.G. Nisbet, A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992, *Geophys. Res. Lett.*, *21(1)*, 45-48, 1994.

Ehhalt, D.H. and L.E. Heidt, The concentration of molecular H_2 and CH_3 in the stratosphere, *pagophys.*, 106-108, 1352, 1973.

Ehhalt, D.H. and A. Tonnissen, Hydrogen and carbon compounds in the stratosphere, pp. 129-151: Nicolet M. and Aiken, A.C. (eds.), *Proceedings of the Nato Advanced Study Instute of Atmospheric Ozone: Its Variation and Human Influences*, US Dept. of Transportation, Washington, D.C., 1980.

Elkins, J.W., D.W. Fahey, J.M. Gilligan, G.S. Dutton, T.J. Baring, C.M. Volk, R.E. Dunn, R.C. Myers, S.A. Montzka, P.R. Wamsley, A.H. Hayden, J.H. Butler, T.M. Swanson, E.J. Dlugokencky, P.C. Novelli, D.F. Hurst, J.M. Lobert, S.J. Ciciora, R.J. McLaughlin, T.L. Thompson, R.H. Winkler, P.J. Fraser, L.P. Steele, and M.P. Lucarelli, Airborne gas chromatograph for in situ measurements of long-lived species in the upper troposphere and lower stratosphere, *Geophys. Res. Lett* ., in press, 1996.

Elkins, J.W., T.M. Thompson, T.H. Swanson, J.H. Butler, B.D. Hall, S.O. Cummings, D.A. Fisher, and A.G. Raffo, Decrease in the growth rates of atmospheric chlorofluorocarbons 11 and 12, *Nature*, *364*, 780-783, 1993.

EPA (Environmental Protection Agency), Protection of stratospheric ozone, *Federal Register*, *58*, 15,014-15,048, 1993.

Fisher, D.A., and P.M. Midgley, Uncertainties in the calculation of atmospheric releases of chlorofluorocarbons, *J. Geophys. Res.*, *99 (D8)*, 16643-16650, 1994.

Hansen, A.R. and G.D. Robinson, Water vapor and methane in the upper stratosphere: an examination of some of the nimbus 7 measurements, *J. Geophys. Res.*, 94(D6), 8474-8484, 1989.

Hintsa, E. J., E.M. Weinstock, A.E. Dessler, and J.G. Anderson, SPADE H_2O measurements and the seasonal cycle of stratospheric water vapor, *Geophys. Res. Lett.*, *21(23)*, 2559-2562, 1994.

Jones, R.L., J.A. Pyle, J.E. Harries, A.M. Zavody, J.M. Russell II, and J.C. Gille, The water vapour budget of the stratosphere studied using LIMS and SAMS satellite data, *Q.J.R. Meterorl. Soc.*, 112, 1127-1143, 1986.

Kawa, S.R., D.W. Fahey, L.E. Heidt, W.H. Pollock, S. Solomon, D.E. Anderson, M. Loewenstein, M.H. Proffitt, J.J. Margitan, and K.R. Chan, Photochemical partitioning of the reactive nitrogen and chlorine reservoirs in the high-latitude stratosphere, *J. Geophys. Res.*, *97(D8)*, 7905-7923, 1992.

Kelly, K.K., A.F. Tuck, D.M. Murphy, M.H. Proffitt, D.W. Fahey, R.L. Jones, D.S. McKenna, M. Loewenstein, J.R. Podolske, S.E. Strahan, G.V. Ferry, K.R. Chan, J.F. Vedder, G.L. Gregory, W.D. Hypes, M.P. McCormick, E.V. Browell, and L.E. Heidt, Dehydration in the lower antarctic stratosphere during late winter and early spring, 1987, *J. Geophys. Res.*, *94*, 11,317-11,357, 1989.

Ko, M.K.W., N.D. Sze, and D.K. Weisenstein, Use of satellite data to constrain the model-calculated atmospheric lifetime for N_2O: Implications for other trace gases, *J. Geophys. Res., 96*, 7547-7552, 1991.

Le Texier, H., S. Solomon, and R.R. Garcia, The role of molecular hydrogen and methane oxidation in the water vapor budget of the stratosphere, *Q.J.R. Meteorol. Soc.*, *114*, 281-295, 1988.

Loewenstein, M., J.R. Podolske, and S.E. Strahan, ATLAS Instrument Characterization: Accuracy of the AASE and AAOE nitrous oxide data sets, *Geophys. Res. Lett.*, *17*, 481-484, 1990.

Loewenstein, M., J.R. Podolske, D.W. Fahey, E.L. Woodbridge, P. Tin, A. Weaver, P.A. Newman, S.E. Strahan, S.R. Kawa, M.R. Schoeberl, and L.R. Lait, New observations of the NO_y/N_2O correlation in the lower stratosphere, *Geophys. Res. Lett.*, 20(22), 2531-2534, 1993.

Minschwaner, K., R.J. Salawitch, and M.B. McElroy, Absorption of solar radiation by O_2: implications for O_3 and lifetimes of N_2O, $CFCl_3$, and CF_2Cl_2, J. Geophys. Res., 98, 10543-10561, 1993.

Mote, P.W., K.H. Rosenlof, J.R. Holton, R.S. Harwood, and J.W. Waters, Seasonal variations of water vapor in the tropical lower stratosphere, *Geophys. Res. Lett.*, 22(9), 1093-1096, 1995.

Murphy, D.M., D.W. Fahey, and M.H. Proffitt, Reactive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res.*, *98*, 8751-75, 1992.

Novelli, P.C., J.W. Elkins, and L.P. Steele, The Development and Evaluation of a Gravimetric Reference Scale for Measurements of Atmospheric Carbon Monoxide, *J. Geophys. Res.*, *96(D7)*, 13,109-13,121, 1991.

Numerical Recipes

Oltmans, S.J., Measurements of water vapor in the stratosphere with a frostpoint hygrometer, *Proceedings of 1985 International Symposium on Moisture and Humidity*, 251-258, Instrument Society of America, Washington, DC, 1985.

Phillips, M.P., R.E. Sievers, P.D. Goldan, W.C. Kuster, and F.C. Fehsenfeld, Enhancement of electron capture detector sensitivity to nonelectron attaching compounds by addition of nitrous oxide to the carrier gas, *Analytical Chemistry*, 51 (11), 1819-1825, 1979.

Plumb, R.A., A "tropical pipe" model of stratospheric transport, *J. Geophys. Res.*, in press, 1996.

Plumb, R.A., and M.K.W. Ko, Interrelationships between mixing ratios of long-lived stratospheric constituents, *J. Geophys. Res.*, *97*, 10145-56, 1992.

Pollock, W.H., L.E. Heidt, R. Lueb, and D.H. Ehhalt, Measurement of stratospheric water vapor by cryogenic collection, *J. Geophys. Res.*, 85, 5555-5568, 1980.

Pollock, W.H., L.E. Heidt, R.A. Lueb, J.F. Vedder, M.J. Mills, and S. Solomon, On the age of stratospheric air and ozone depletion potentials in polar regions, *J. Geophys. Res.*, *97(D12)*, 12,993-12,999, 1992.

Prather M., and C.M. Spivakovsky, Tropospheric OH and the lifetimes of hydrochlorofluorocarbons, *J. Geophys. Res.*, *95(D11)*, 18,723-18,729, 1990.

Prinn, R., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, and R. Rosen, Atmospheric emissions and trends of nitrous oxide deduced from 10 years of ALE-GAGE data, *J. Geophys. Res.*, *95(D11)*, 18,369-18,385, 1990.

Schauffler, S.M., L.E. Heidt, W.H. Pollock, T.M. Gilpin, J.F. Vedder, S. Solomon, R.A. Lueb, and E.L. Atlas, Measurements of halogenated organic compounds near the tropical tropopause, *Geophys. Res. Lett.*, *20(22)*, 2567-2570, 1993.

Schauffler, S.M., W.H. Pollock, E. L. Atlas, L.E. Heidt, and J.S. Daniel, Atmospheric distributions of HCFC-141b, *Geophys. Res. Lett., 22(7)*, 819-825, 1995.

Tans, P.P., and P.S. Bakwin, Climate change and carbon dioxide forever, *Ambio*, 24 (6), 376-378, 1995.

Tans, P.P., Why carbon dioxide from fossil fuel burning won't go away, *Perspectives in Environmental Chemistry*, edited by D.M.e. al., Oxford University Press, Oxford, UK, 1996.

Volk, C.M., J.W. Elkins, D.W. Fahey, R.J. Salawitch, G.S. Dutton, J.M. Gilligan, K. Minschwaner, M.H. Proffitt, M. Loewenstein, and J.R. Podolske, In-situ measurements constraining exchange between the tropics and the middle latitudes in the lower stratosphere, *Science*, submitted for publication, 1996.

Warneck, P., *Chemistry of the natural atmosphere*, Academic Press Inc., London, UK, 1988.

Webster, C.R., R.D. May, C.A. Trimble, R.G. Chave, and J. Kendall, Aircraft laser infrared absorption spectrometer (ALIAS) for in situ stratospheric measurements of HCl, N_2O, CH_4, NO_2, and HNO_3, *Appl. Opt.*, 33(3), 454-472, 1994.

Weinstock, E.M., E.J. Hintsa, and J.G. Anderson, A new fast response photofragment fluorescence hygrometer for use on the NASA ER-2 and Perseus remotely piloted aircraft, *Rev. Sci. Instrum.*, 65, 3544, 1994.

Woodbridge, E.L., J.W. Elkins, D.W. Fahey, L.E. Heidt, S. Solomon, T.J. Baring, T.M. Gilpin, W.H. Pollock, S.M. Schauffler, E.L. Atlas, M. Loewenstein, J.R. Podolske, C.R. Webster, R.D. May, J.M. Gilligan, S.A. Montzka, K.A. Boering, and R.J. Salawitch, Estimates of total organic and inorganic chlorine in the lower stratosphere from in situ and flask measurements during AASE II, *J. Geophys. Res.*, 1995.

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 1991, WMO Global Ozone Res. and Monitoring Proj. Rep. 25, WMO Global Ozone Research And Monitoring Project, Geneva, Switzerland, 1991.

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 1991, WMO Global Ozone Res. and Monitoring Proj. Rep. 37, WMO Global Ozone Research And Monitoring Project, Geneva, Switzerland, 1995.

J.H. Butler, J.W. Elkins, E.J. Dlugokencky, S.A. Montzka, R.C. Myers, S.J. Oltmans, and T.M. Thompson, NOAA/CMDL, M.S. R/E/CG1, 325 Broadway, Boulder, CO 80303-3000 U.S.A.

G.S. Dutton, A.H. Hayden, J.M. Lobert, and P.C. Novelli, CIRES, CU, Campus Box 214, Boulder, CO 80309 U.S.A.

D.W. Fahey and K.K. Kelly, NOAA/AL, M.S. R/E/AL6, 325 Broadway, Boulder, CO 80303 U.S.A.

P.J. Fraser and L.P. Steele, CSIRO, DAR, Private Bag 1, Mordilloc, Victoria, Australia, 3195.

M. Loewenstein, J.R. Podolske, and K.R. Chan, NASA, ARC, Mail Stop 245-5, Moffett Field, CA 94035-1000 U.S.A.

C.R. Webster and R.D. May JPL, Cal Tech, 4800 Oak Grove Drive, Pasadena, CA 91109 U.S.A.

L.E. Heidt, S.M. Schauffler, and T.J. Gilpin, NCAR, P.O. Box 3000, Boulder, CO 80307-3000 U.S.A.

A.E. Dessler, E.M. Weinstock, and E.J. Hinsta, Harvard University, Atmospheric Research Project, The Link, 35 Oxford Street, Cambridge, MA.02138 U.S.A.

W.T. Sturges, University of East Anglia, UEA Norwich, Norwich, England, NR4JTJ, United Kingdom.

T.J. Baring, Arctic Region Supercomputing Center, University of Alaska, P.O. Box 756020, Fairbanks, AK.