Estimates of total organic and inorganic chlorine in the lower stratosphere from in situ and flask measurements during AASE II

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Abstract. Aircraft sampling has provided extensive in situ and flask measurements of organic chlorine species in the lower stratosphere. The recent Airborne Arctic Stratospheric Expedition II (AASE II) included two independent measurements of organic chlorine species using whole air sample and real-time techniques. From the whole air sample measurements we derive directly the burden of total organic chlorine (CCl_y) in the lower stratosphere. From the more limited real-time measurements we estimate the CCl_y burden using mixing ratios and growth rates of the principal CCl_y species in the troposphere in conjunction with results from a two-dimensional photochemical model. Since stratospheric chlorine is tropospheric in origin and tropospheric mixing ratios are increasing, it is necessary to establish the average age of a stratospheric air parcel to assess its total chlorine (Cl_{Total}) abundance. Total inorganic chlorine (Cl_y) in the parcel is then estimated by the simple difference, $Cl_y = Cl_{Total} - CCl_y$. The consistency of the results from these two quite different techniques suggests that we can determine the CCl_y and Cl_y in the lower stratosphere with confidence. Such estimates of organic and inorganic chlorine are crucial in evaluating the photochemistry controlling chlorine partitioning and hence ozone loss processes in the lower stratosphere.

Introduction

Anthropogenic chlorine is largely responsible for decreases in stratospheric ozone at the poles in springtime [*Anderson et al.*, 1989, 1991; *Solomon*, 1990; *Salawitch et al.*, 1993], and it may also play a role in the observed downward trend in ozone at mid-latitudes [*Rodriguez et al.*, 1991; *World Meteorological Organization (WMO)*, 1992]. Given this critical link between chlorine and ozone depletion, it is important that we quantitatively account for the total amount of chlorine (Cl_{Total}) in the stratosphere as well as describe the partitioning of that chlorine into organic (CCl_y) and inorganic (Cl_y) forms. In this work we extend a previous

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assessment of the photochemical partitioning of CCl_y and Cl_y in the lower stratosphere [*Kawa et al.*, 1992] with additional whole air sample measurements covering a wider range of latitude and season, and with new measurements from a real-time in situ gas chromatograph aboard the NASA ER-2 aircraft.

Key to this assessment of chlorine partitioning is the fact that chlorine in the stratosphere is almost exclusively tropospheric in origin and is transported from the troposphere to the stratosphere as CCl_y. Cl_{Total} in the sampled air is therefore estimated by summing the tropospheric mixing ratios of the CCl_y source gases at the time of stratospheric entry. CCl_y in the sampled stratospheric air is derived directly from the aircraft measurements, and Cl_y is estimated by the simple difference

$$Cl_y = Cl_{Total} - CCl_y \qquad (1)$$

Chlorine is also conserved in the stratosphere as CCl_y species are photochemically converted to Cl_y.

This straightforward analysis is complicated somewhat by the need to determine when the sampled air entered the stratosphere. Most of the principal CCl_y species in the troposphere exhibit a clear upward trend in their mixing ratios, with Cl_{Total} increasing at the rate of a few percent per year [*WMO*, 1992]. An accurate estimate of the age of the sampled air is therefore necessary to determine Cl_{Total} at the time of stratospheric entry.

A number of studies have estimated the average age of stratospheric air [*Schmidt and Khedim*, 1991; *Pollock et al.*, 1992; *Heidt et al.*, 1994; *Hall and Plumb*, 1994]. Age estimates have become more complex in recent years since observations have shown that long-lived species such as

carbon dioxide [*Conway et al.*, 1994], methane [*Dlugokencky et al.*, 1994] and nitrous oxide (*J. W. Elkins et al.*, manuscript in preparation, 1994, hereinafter referred to as E94) have all shown unforeseen decreases in their growth rates between 1990 and 1992. In addition, the tropospheric growth rates of some of the major CCl_y species have declined since 1989 [*Elkins et al.*, 1993]. These CCl_y changes result from mandatory (Montreal Protocol) and voluntary reductions in the emissions of substances that deplete the ozone layer.

Tropospheric Sources and Growth Rates

In Table 1 we present the tropospheric concentrations of the principal chlorine source gases for 1992 as measured by the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) surface flask network. Also included are mixing ratios extrapolated from the 1989 values reported in the World Meteorological Organization Assessment [*WMO*, 1992] and results from whole air sample measurements made at the tropical tropopause during AASE II [*Schauffler et al.*, 1993]. Estimated lifetimes and growth rates are also listed, where available.

NOAA/CMDL has maintained a long-term halocarbon monitoring program that includes most of the important chlorine-containing species in the troposphere. We use these values in the present work to determine the tropospheric chlorine abundance.

Although the timescale for full vertical mixing of the troposphere is short compared to that for troposphere-stratosphere exchange, it is still long compared to the photochemical lifetimes of some CCl_y species in the troposphere [*Brasseur and Solomon*, 1986]. Those with tropospheric lifetimes less than approximately 1 year are not uniformly mixed up to the tropical tropopause, where the majority of troposphere-stratosphere exchange occurs. These CCl_y species are therefore not transported into the stratosphere in quantities that accurately reflect their source strengths or lower-altitude mixing ratios [*Solomon and Garcia*, 1984; *Holton*, 1990; *Schauffler et al.*, 1993]. In this work, to assess the amount of chlorine transported to the stratosphere we include only those CCl_y species with lifetimes longer than approximately 1 year. This filtering allows us to estimate the CCl_y burden of an air parcel upon entry into the stratosphere using measurements of relatively few CCl_y species. Since all chlorine enters the stratosphere as CCl_y, this number also represents Cl_{Total} in that stratospheric air parcel. As shown in Table 1, completely neglecting those CCl_y species with lifetimes shorter than 1 year results in an

Table 1. Global Tropospheric Concentrations and Lifetimes for Cl Source Gases, 1992

Source Gas	Trade Number	Common Name	WAS[a], Jan-March pptv	WMO[b] pptv	NOAA/CMDL pptv	NOAA/CMDL pptv Cl	Approx. Lifetime years	1986-1992 Growth-Rate %/yr
*CCl_2F_2	12		494	504	506±11[c]	1012	116[d]	3.5[c]
*CCl_3F	11		264	284-297	271±6.4[c]	813	55[d]	3.3[c]
*CCl_2FCClF_2	113		74.6	81	82±8[e]	246	110[d]	9.1[d]
$CClF_2CClF_2$	114		16.4	18-23			220[d]	6[d]
CCl_2FCF_3	114a			~6				6[d]
$CClF_2CF_3$	115		4.1[g]				550[d]	10[g]
$CClF_3$	13			~5			400[f]	
*CCl_4	10	carbon tetrachloride	109[h]	111	105±2.3[e]	420	47[d]	1.2[d]
*CH_3CCl_3	140a	methyl chloroform	117	150	139±3.3[e]	417	6.1[d]	3.7[d]
$CClF_2CH_3$	142b				3.2±0.2[j]	3.2	22.4[d]	25.6[j]
*$CHClF_2$	22		96	126	102±5[k]	102	15.8[d]	6[k]
$CBrClF_2$	1211		2.6	2.5-3.4	2.7±0.1[l]	2.7	14.3[d]	4.9[l]
*CH_3Cl	40	methyl chloride	531	600	570±29[i]	570	1.5[d]	
*$CHCl_3$	20	chloroform	3.13	~10	8.4±1.7[n]	25.2	0.7[m]	
CH_2Cl_2	30	methylene chloride	14.9	~35	21.5±4.3[n]	43	0.6[f]	
CCl_2CCl_2	1110			~30			0.6[f]	
CH_2ClCH_2Cl	150			~35			0.6[f]	
$CHBrCl_2$				1			0.6[f]	
$CHClCCl_2$	1120			~10			0.1[f]	
CH_2BrCl				1-2				
$CHBr_2Cl$				1				

Asterisk, Reported as part of the whole air sampler (WAS) data set for Airborne Arctic Stratospheric Expedition II (AASE II).
[a]One-sigma uncertainty is ±3-8% for those species with lifetimes longer than 1 year. See *Schauffler et al.* [1993].
[b]Concentrations extrapolated from 1989 concentrations and growth rates [*WMO*, 1992].
[c]*Elkins et al.* [1993].
[d]*WMO* [1992].
[e]*Swanson et al.* [1993].
[f]*WMO* [1989].
[g]Extrapolated from 1989 values. See *Pollock et al.* [1992].
[h]Set to 109 pptv to account for losses in sample cans. See *Schauffler et al.* [1993].
[i]*Thompson et al.* [1994]. This value is for the latter half of 1993. No growth is assumed [*WMO*, 1992].
[j]*Montzka et al.* [1994].
[k]*Montzka et al.* [1993a].
[l]*Butler et al.* [1992] and J. H. Butler et al., manuscript in preparation, 1994.
[m]*Makide and Rowland* [1981].
[n]*Thompson et al.* [1994]. Values from 1993.

underestimate of the total CCl_y abundance by about 8%, which should be considered an upper bound on the CCl_y or Cl_{Total} uncertainty.

Summing the CMDL measurements of average tropospheric mixing ratio for those species with lifetimes longer than 1 year and using the WMO extrapolations for those species not reported by CMDL results in a CCl_y mixing ratio in the troposphere for 1992 of 3670 parts per trillion by volume (pptv). This sum also includes $CHCl_3$, to provide consistency with the whole air sampler (WAS) data set from the Airborne Arctic Stratospheric Expedition II (AASE II) (see below).
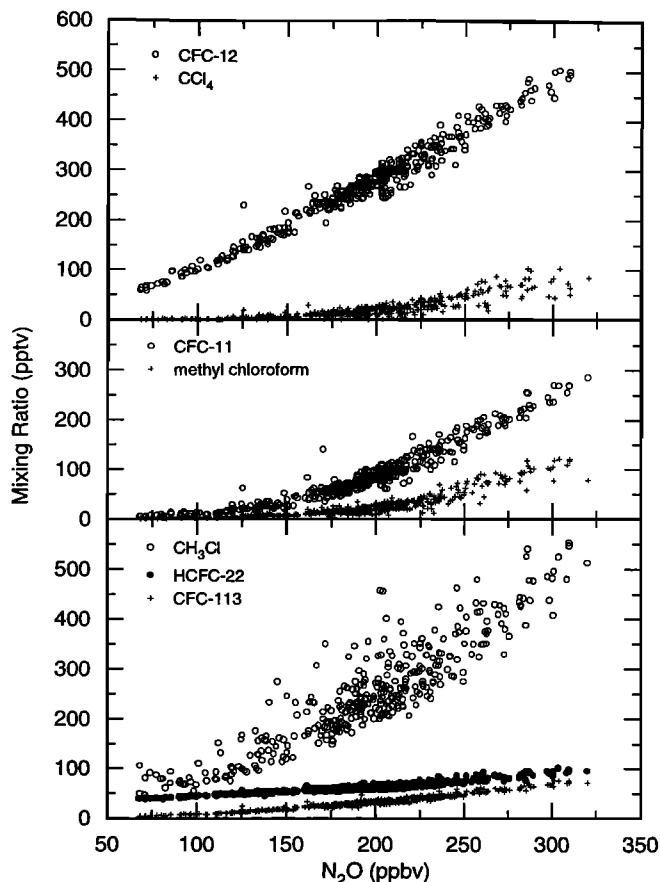
Measurements Of Individual CCl_y Species

AASE II began with test flights from Moffett Field, California (37°N, 122°W), in August 1991. The first mission segment took place in Fairbanks, Alaska (65°N, 147°W), in October 1991, with the mission moving to Bangor, Maine (45°N, 69°W) in November 1991 through March 1992. The goal of AASE II was to sample the Arctic stratosphere over the lifetime of the polar vortex, beginning in the fall before vortex genesis and concluding in the spring following vortex breakup. The large scale of the mission, coupled with the ability of the ER-2 to cruise between 17 and 20 km altitude with a mission radius >2500 km (23° latitude), allowed for sampling of the stratosphere over a wide range of latitude and season, from the subtropics to the pole and from late summer to early spring.

CCl_y species were measured by two instruments on the ER-2. The first, the whole air sampler (WAS) from the National Center for Atmospheric Research (NCAR)/NASA Ames Research Center, has been described in detail elsewhere [*Schauffler et al.*, 1993; *Heidt et al.*, 1989]. The sampler collected 16 to 29 1.5 liter canisters of ambient air per flight on 23 of the AASE II flights. These canisters were returned to Boulder for gas chromatographic analysis utilizing either electron capture detection (GC-ECD), mass spectrometric analysis (GC-MS), or flame ionization detection (GC-FID). The WAS instrument provides values for the most important chlorine source gases, as shown in Table 1.

The atom-weighted sum of the species reported by WAS as part of the AASE II data set (CFC-12, CFC-11, CFC-113, CCl_4, CH_3CCl_3, HCFC-22, CH_3Cl, and $CHCl_3$) is 3605 pptv, or 98.2% of estimated tropospheric CCl_y in 1992. Within this uncertainty, the atom-weighted sum of the reported WAS values is used here as one measure of CCl_y in the air sampled.

Figure 1 shows the individual WAS measurements plotted versus nitrous oxide measured by the ATLAS instrument [*Loewenstein et al.*, 1990, 1993; *Podolske et al.*, 1993] for the entire AASE II mission. N_2O is used here as an independent variable for several reasons. Its similar photochemistry, lifetime, and source/sink relationship with the CFCs results in mixing ratio isopleths for N_2O and the CFCs that are in slope (compact) and in some cases gradient (compact and linear) equilibrium [*Plumb and Ko*, 1992]. N_2O is also a high-frequency measurement on the ER-2, available for most of the flight track with 1-s time resolution [*Loewenstein et al.*, 1990].

Because the WAS instrument stores stratospheric samples in flasks for later analysis the measurements may be subject to loss of the species of interest in the flasks, resulting in low values [*Schauffler et al.*, 1993]. The greatest concern is for CCl_4 and methyl chloroform (CH_3CCl_3), for which loss in

Figure 1. Measurements of the principal CCl_y species in the lower stratosphere from the National Center for Atmospheric Research/National Aeronautics and Space Administration (NCAR/NASA) whole air sampler plotted versus ATLAS N_2O.

sample cans has been noted previously [*Makide and Rowland*, 1981; *Montzka et al.*, 1993b]. We have excluded those samples where such loss is suspected, rejecting approximately 6% of the available cans. In addition, samples with no corresponding N_2O measurement have also been excluded, a criterion that removes approximately 34% of the cans from the analysis, leaving 360 valid samples out of a possible 615. Even with such strict filtering, AASE II provides a much larger data set than the previous Arctic mission (211 total samples) [see *Kawa et al.*, 1992].

The second instrument measuring CCl_y species from the ER-2 is the Airborne Chromatograph for Atmospheric Trace Species (ACATS), from CMDL and the NOAA Aeronomy Laboratory (E94). The ACATS instrument is an in situ gas chromatograph using electron capture detection to measure CFC-11 and CFC-113 with 2-min resolution along the aircraft flight track. These two molecules account for approximately 29% of the organic chlorine with lifetimes longer than 1 year (CFC-11 = 22.2%, CFC-113 = 6.7%; see Table 1). Figure 2 shows all of the CFC-11 and CFC-113 measurements from ACATS plotted versus N_2O. ACATS provides a much larger data set than WAS, with 2198 and 1917 measurements of CFC-11 and CFC-113, respectively. The agreement between the WAS and ACATS determinations of these two species, using two different experimental techniques, is extremely good. In fact, the best simple quadratic fit to the two CFC-11 data sets
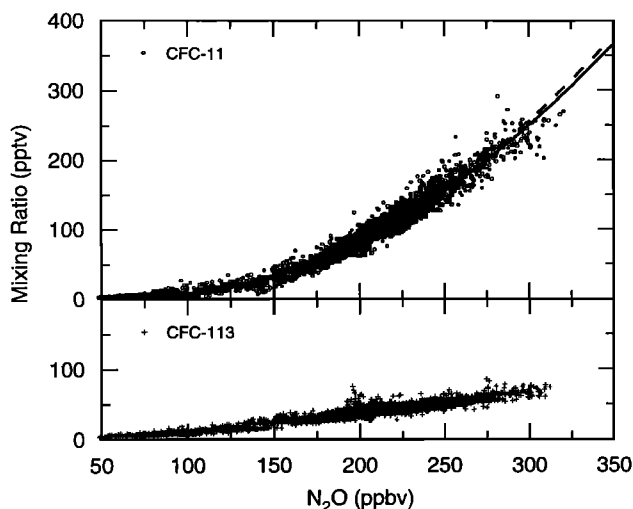
Figure 2. NOAA Airborne Chromatograph for Atmospheric Trace Species (ACATS) measurements of CFC-11 and CFC-113 plotted versus NASA ATLAS N_2O for the entire Airborne Arctic Stratospheric Expedition II (AASE II) mission. Uncertainty (1 σ) of the individual CFC-11 measurements is $\pm2.8\%$, CFC-113 $\pm4.5\%$. For CFC-11 we have plotted the best fit curves from ACATS (solid line; CFC-11 (pptv) = 20.8685 - .5915(N_2O (ppbv)) + .00452(N_2O)^2) and WAS (CFC-11 (pptv) = 26.6241 - .6544(N_2O (ppbv)) + .00474(N_2O)^2). The curves illustrate the excellent agreement between the two instruments' determinations of CFC-11.

indicates that no distinction of consequence can be made between the measurements.

Derivation of CCl$_y$

As noted above, the atom-weighted sum of the WAS measurements is one measure of CCl$_y$ in the sample. This sum is shown in Figure 3 versus N_2O. We can exploit this compact
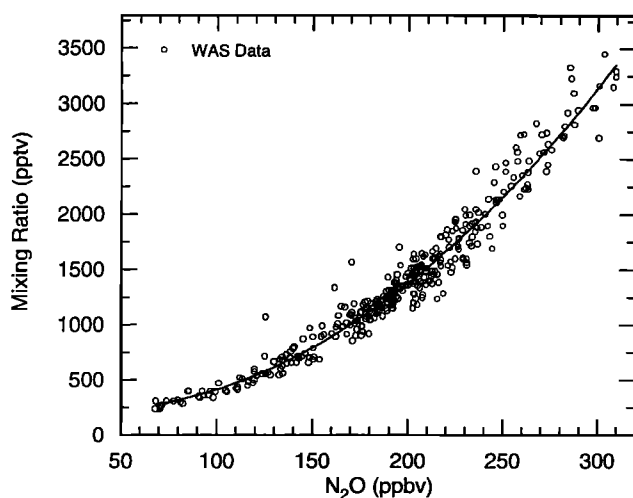
Figure 3. CCl$_y$ from the atom-weighted sum of the whole air sampler measurements shown in Figure 1 versus ATLAS N_2O. The measurements account for 98.2% of the CCl$_y$ available to the lower stratosphere. Also shown is the best second order polynomial fit, CCl$_y$ = 254.9948 - 2.4378(N_2O) + 0.04024(N_2O)^2.

correlation to map the relatively low-frequency WAS determinations of CCl$_y$ onto every point along the aircraft flight track using the higher-frequency N_2O data [*Kelly et al.*, 1989]. Thus at every point along the aircraft flight track we are provided with an estimated value for CCl$_y$.

For aircraft campaigns flying without the whole air sampler, it is crucial to be able to reconstruct the CCl$_y$ reservoir from the limited-species ACATS measurements. While ACATS measured only CFC-11 and CFC-113 during AASE II, the remaining components of CCl$_y$ can be estimated using modeled correlations with other long-lived tracers measured on the ER-2. These correlations are obtained from a full two-dimensional photochemical transport model initialized with measured concentrations of tropospheric CCl$_y$ species and using recommended [*Jet Propulsion Laboratory* (*JPL*), 1990] rate constants and photolysis rates [*Garcia and Solomon*, 1983; *Solomon and Garcia*, 1984; S. Solomon, private communication, 1994]. Compact, nearly linear correlations are found for CCl$_y$ species and tracers that have similar photochemical lifetimes and source/sink relationships (see Figure 4). The best-fit relations for the key CCl$_y$ species not measured by the ACATS instrument are

$$X_{CH_3Cl} = \left(\begin{array}{c} 0.3062F_{N_2O}^3 + 0.1299F_{N_2O}^2 + 0.4915F_{N_2O} \\ - 0.004918 \end{array} \right) X_{t,CH_3Cl} \qquad (2)$$

$$X_{CH_3CCl_3} = \left(\begin{array}{c} 0.3355F_{CFC-11}^2 + 0.6646F_{CFC-11} \\ - 0.001021 \end{array} \right) X_{t,CH_3CCl_3} \qquad (3)$$

$$X_{CCl_4} = \left(\begin{array}{c} 0.3814F_{CFC-11}^2 + 0.6275F_{CFC-11} \\ - 0.001350 \end{array} \right) X_{t,CCl_4} \qquad (4)$$

$$X_{CFC-12} = \left(\begin{array}{c} 0.2998F_{N_2O}^2 + 0.7315F_{N_2O} \\ - 0.02848 \end{array} \right) X_{t,CFC-12} \qquad (5)$$

$$X_{HCFC-22} = \left(\begin{array}{c} -0.4715F_{CH_4}^2 + 1.3225F_{CH_4} \\ + 0.1314 \end{array} \right) X_{t,HCFC-22} \qquad (6)$$

Here F_i is the fraction of the species remaining relative to its concentration upon entry into the stratosphere. F_i is expressed as $X_i/X_{t,i}$, where X_i is the measured mixing ratio and $X_{t,i}$ is the species concentration in the troposphere at the time of stratospheric entry. The latter can be derived from the expression

$$X_{t,i} = X_{0,i}(1.0 - G \cdot age/100) \qquad (7)$$

where $X_{0,i}$ is the present tropospheric mixing ratio, G is the present growth rate in percent per year, and age is the average age of the sampled air in years (see below).

The comparison between these model relations and the WAS data is also shown in Figure 4. For several species the model correlations lie slightly above the data, suggesting a combination of loss in the sample cans (e.g., CCl$_4$ and CH$_3$CCl$_3$, as discussed above) or discrepancies in the model chemistry or transport. In general, the good agreement indicates consistency between the modeled photochemical conversion of CCl$_y$ and that observed in the aircraft data.
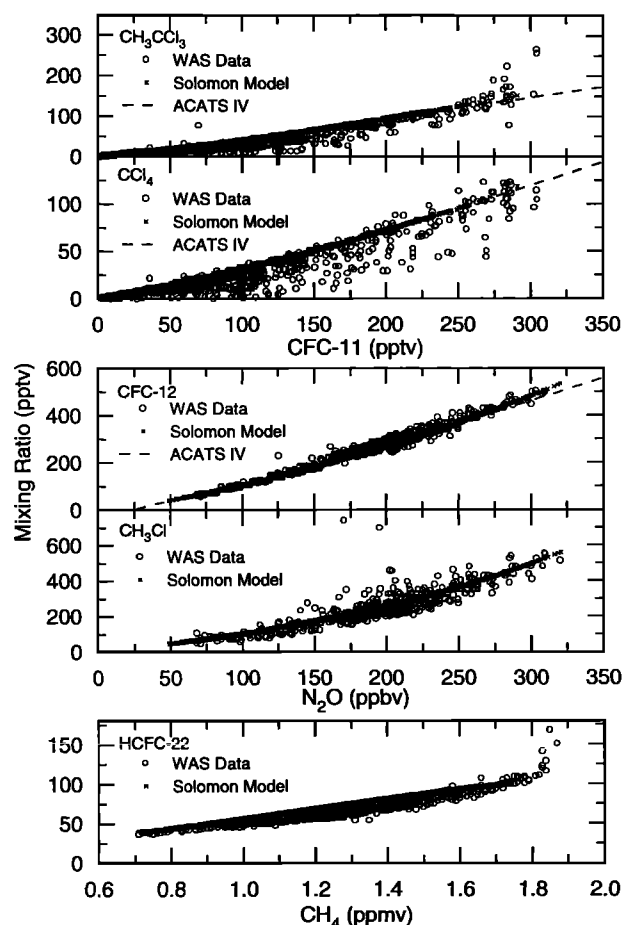
Figure 4. Two-dimensional model correlations (crosses) for five CCl_y species plotted along with corresponding measurements from the whole air sampler (WAS) (open circles). The model results for methyl chloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4) are correlated with CFC-11 measured by the Airborne Chromatograph for Atmospheric Trace Species (ACATS); the WAS data are correlated with WAS CFC-11; CFC-12 and methyl chloride (CH_3Cl) are correlated with N_2O measured by ATLAS, and HCFC-22 is correlated with CH_4 measurements from the ALIAS instrument [Webster et al., 1994]. The dashed lines are preliminary results from a new chromatograph aboard the ER-2 (ACATS IV). See text for details.

Indeed, correlations obtained from preliminary in situ measurements using the new airborne chromatograph on the ER-2 (ACATS IV) indicate that the model correlations for methyl chloroform, CCl_4, and CFC-12 are remarkably good (see Figure 4). Thus we can use ACATS measurements of CFC-11 and CFC-113 along with simultaneous measurements of CH_4 and N_2O to determine CCl_y anywhere along the aircraft flight track.

Figure 5 shows the ACATS determination of CCl_y versus N_2O using this semi-empirical approach. Because model correlations are used for 5 of the 7 species that go into the CCl_y sum, there is much less scatter in this determination than in that from the WAS measurements. The agreement between this semi-empirical CCl_y and that derived from the WAS data is again remarkably good. Only a slight offset separates the two best fit curves, amounting to at most 75 pptv at the highest N_2O values.

Age of Air and Photochemical Partitioning of Cl_{Total}

As noted in the introduction and shown in Table 1, the tropospheric concentrations of most of the critical CCl_y species are increasing at a rate of 1-10%/yr. The resulting increase in Cl_{Total} is approximately 2.8%/yr [WMO, 1992]. Since our assessment of photochemical partitioning of stratospheric chlorine depends on accurately estimating Cl_{Total}, it is necessary to know the average age of the sampled air. If we know when the sampled air entered the stratosphere, then we can derive Cl_{Total} by relating that age to the present tropospheric value of Cl_{Total} and the overall growth rate, as in (7).

The average age of an air parcel can be estimated from the difference between the stratospheric and tropospheric mixing ratios of a tracer that has a known growth rate in the troposphere but does not have a stratospheric sink. Hall and Plumb [1994] calculate that the difference between the stratospheric and tropospheric concentrations of a tracer may well represent the average age of a stratospheric air parcel when that tracer exhibits linear growth in the troposphere or has a time constant for exponential growth greater than about 7 years. CO_2 is one such tracer, with a small stratospheric source, no sink, and approximately linear growth in the troposphere. Figure 6a illustrates this upward trend as well as the seasonal cycle of CO_2 in the troposphere [Conway et al., 1994]. This seasonal cycle varies in magnitude in the troposphere and is well damped in the stratosphere within six months at mid-latitudes [Boering et al., 1994]. In this work we will use the CO_2:N_2O relationship in the stratosphere to relate an N_2O measurement to the average age of a sample; the influence of the seasonal cycle on the newest stratospheric air is minimized by fitting the relationship for $N_2O < 300$ ppbv. As shown in Figure 6b, the change in CO_2 mixing ratio in the stratosphere is correlated with N_2O by the following
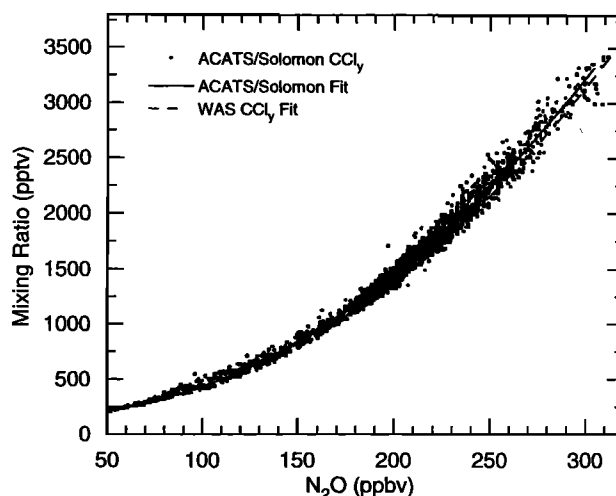
Figure 5. Semi-empirical determination of CCl_y in the lower stratosphere from the atom-weighted sum of the Airborne Chromatograph for Atmospheric Trace Species (ACATS) measurements and the model correlations shown in Figure 4, plotted versus ATLAS N_2O. Also shown is the best second-order polynomial fit, $CCl_y = 215.4721 - 1.7262(N_2O) + 0.03922(N_2O)^2$. The dashed line is the WAS instrument CCl_y fit shown in Figure 3. See text for details.

$$\Delta CO_2 = 0.02801(310 - X_{N_2O}) \tag{8}$$

where X_{N_2O} is the measured mixing ratio of N_2O in parts per billion by volume (ppbv) in the stratosphere and 310 ppbv is the mean tropospheric N_2O mixing ratio in 1991-1992 [*Boering et al.*, 1994]. For our purposes the annual growth of N_2O can be neglected (0.32%/yr) [*Thompson et al.*, 1994]. For the lowest values of N_2O sampled during AASE II (50 ppbv) the corresponding change in the CO_2 mixing ratio is approximately 7.3 parts per million by volume (ppmv). This change in CO_2 may be related to the average age of the stratospheric air by accounting for the linear growth of CO_2 in the troposphere

$$age = \left[0.02801\left(310 - X_{N_2O}(ppbv)\right) + \left(1.7 - X_{CH_4}(ppmv)\right) \right] / 1.65 \tag{9}$$

where 1.65 ppmv/yr is the mean CO_2 growth rate in the troposphere from 1986 to 1992 [*Conway, et al.*, 1994; see Figure 6a]. Also included in this expression is a correction for CO_2 produced by CH_4 oxidation in the stratosphere [*Heidt et al.*, 1994]; 1.7 ppmv is the tropospheric mixing ratio of CH_4 in 1991-1992 [*Swanson et al.*, 1993]. For this work we have used a mean fit to both the WAS and the ALIAS CH_4 data [*Webster et al.*, 1994] from AASE II to relate CH_4 to N_2O:

$$CH_4(ppbv) = 571.3 + 3.634\left(N_2O(ppbv) \right). \tag{10}$$

At the lowest values of N_2O measured during AASE II (50 ppbv, the "oldest" air), this age expression returns a value of 5 years, in excellent agreement with previous assessments of the age of the air in the middle and lower stratosphere [*Schmidt and Khedim*, 1991; *Heidt et al.*, 1994].

Measurements of N_2O thus allow us to determine, by referencing the CCl_y concentration in the troposphere at the time of stratospheric entry, the value of Cl_{Total} in the sample. Combining equations (7) to (10):

$$Cl_{Total} =$$

$$X_{Cl_{Total}}\left(1 - \frac{G\left[.02801\,(310 - X_{N_2O}) + \left(1.7 - (.5713 + .003634\,(X_{N_2O}))\right) \right]}{165} \right) \tag{11}$$

where $X_{Cl_{Total}}$ is the 1992 tropospheric mixing ratio of total chlorine (3670 pptv), G is the growth rate in %/yr of total chlorine in the troposphere (2.8%) [*WMO*, 1992], and X_{N_2O} is the measured mixing ratio of N_2O in the sampled stratospheric air parcel.

The result for Cl_{Total} versus N_2O from (11) is shown in Figure 7. Using this curve and the ACATS semi-empirical determination of CCl_y shown in Figure 5, we can estimate the Cl_y concentration anywhere along the aircraft flight track using the simple difference in (1). Critical to this derivation of Cl_y is the assumption that chlorine in the stratosphere is a conserved quantity; that is, there is no selective removal of CCl_y versus Cl_y from the stratosphere. Also important is the fact that Cl_y in the troposphere is a negligible source of stratospheric Cl_y. The primary example is HCl, present in
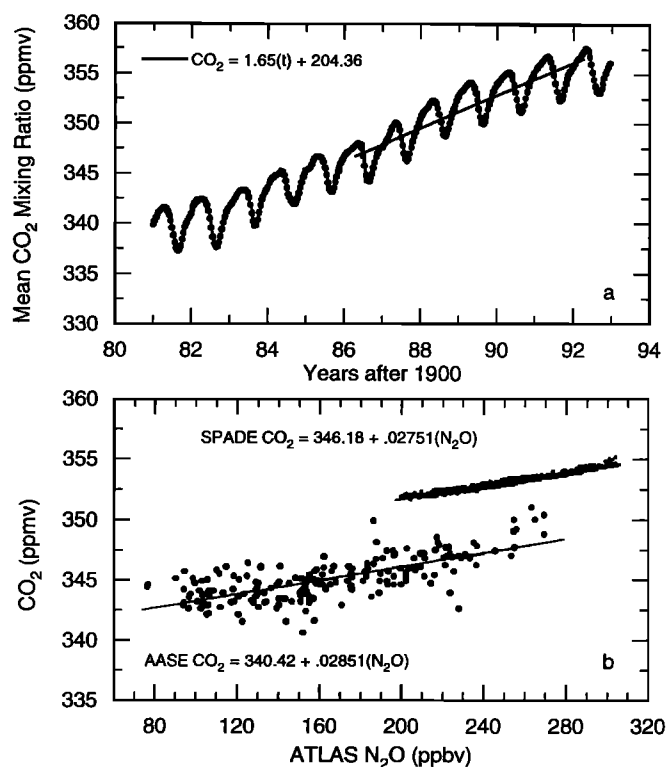
Figure 6. (a) Global mean CO_2 values from the National Oceanic and Atmospheric Administration/Climate Monitoring Diagnostic Laboratory (NOAA/CMDL) tropospheric flask network [*Conway et al.*, 1994]. The solid line is a fit for March 1986 to March 1992, encompassing the range of the age of the air encountered in AASE II. (b) The CO_2 versus ATLAS N_2O correlation from the 1993 Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE) data set [*Boering et al.*, 1994], and the 1989 Airborne Arctic Stratospheric Expedition (AASE) data set [*Heidt et al.*, 1994]. Measurements from SPADE and the 1994 Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) campaign show that this slope varies slightly with season due to the seasonality of vertical transport [*Wofsy et al.*, 1994] as well as the seasonal cycle of tropospheric CO_2 propagation into the stratosphere [*Boering et al.*, 1994]. Propagation of errors in the slope yields an uncertainty (2 σ) in the age of the air of ±1.8 years at N_2O = 50 ppbv and ±1 month at N_2O = 290 ppbv. SPADE data for N_2O < 200 ppbv is not shown because of atypical rapid mixing of polar and mid-latitude air. For this work we have used the mean value of the slope provided by these two data sets.

large quantities in volcanic plumes, which is removed quantitatively in the troposphere as a result of its water solubility [*Tabazadeh and Turco*, 1993].

Note that the Cl_y:N_2O relation shown in Figure 7 does not go to zero at the nominal tropospheric N_2O value of 310 ppbv. This discrepancy arises because both the WAS and the ACATS/Solomon CCl_y determinations yield a lower value for total chlorine at the tropopause (approximately 3400 pptv) than that derived from the CMDL surface flask sampling network (3670 pptv). This discrepancy of approximately 270 pptv may be attributed in part to the difference (7-15 ppbv) in
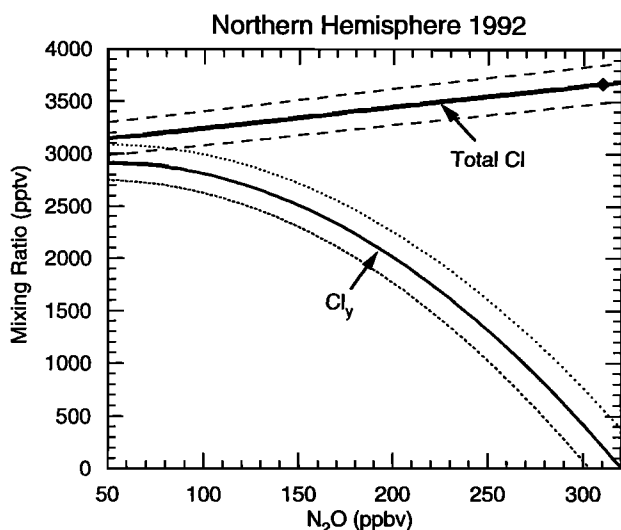
Figure 7. Cl_{Total} (Equation 11) and the partitioning of that chlorine into CCl_y and Cl_y plotted versus ATLAS N_2O for the winter of 1991-1992. Lower N_2O values indicate older air (longer residence time in the stratosphere) and hence more conversion of CCl_y to Cl_y. The diamond indicates the tropospheric (N_2O,CCl_y) reference point for 1991-1992 (310, 3670). The Cl_y abundance is expressed as the difference of this Cl_{Total} and the CCl_y abundance shown in Figure 5. The dashed lines are ±5% uncertainty on Cl_{Total} from the weighted uncertainties listed for the National Oceanic and Atmospheric Administration/Climate Monitoring Diagnostic Laboratory (NOAA/CMDL) data in Table 1. The dotted lines are the uncertainty in Cl_y from the combined uncertainties in Cl_{Total} and the CCl_y determination shown in Figure 5.

the absolute calibration of tropospheric N_2O between ATLAS (317-325 ppbv) and the CMDL network (309-310 ppbv). In addition, some long-lived CCl_y species may exhibit losses in the troposphere that contribute to a small gradient in CCl_y between the surface and the tropopause (CH_3CCl_3 and HCFC-22 via reaction with OH, for example; see Figure 4). This tropospheric gradient of CCl_y could explain a loss of almost 150 pptv. Given that the uncertainty in the ground-based measurement of CCl_y (Table 1, Figure 7) is of similar magnitude (approximately ±200 pptv), the discrepancy of 270 pptv cannot be quantitatively addressed within the precision of the current work.

Figure 7 graphically illustrates the photochemical conversion of CCl_y to Cl_y that takes place in the stratosphere through photolysis and subsequent reactions [*Brasseur and Solomon*, 1986]. At the lowest values of N_2O encountered during AASE II, nearly 3 ppbv of Cl, or >92% of Cl_{Total}, resides in inorganic chlorine reservoir molecules like HCl and $ClONO_2$ [*Kawa et. al.*, 1992]. These reservoirs are readily converted to more reactive forms through heterogeneous chemistry on polar stratospheric clouds (PSCs). If accompanied by decreases in NO_x, such PSC processing can lead to rapid ozone depletion when sunlight returns to the polar regions in spring.

Conclusions

1. The Airborne Arctic Stratospheric Expedition II provides a greatly expanded set of measurements of CCl_y species in the lower stratosphere spanning a large range of latitude and season. These measurements significantly enhance the database at high latitudes, away from the source and sink regions for CCl_y species.

2. Independent measurements of CFC-11 and CFC-113 from two different instruments cover a very wide range of values in the stratosphere, and the respective correlations with N_2O show excellent agreement.

3. CCl_y in an air parcel can be determined directly by the atom-weighted sum of the WAS measurements, or in a semi-empirical approach that combines the ACATS measurements of CFC-11 and CFC-113 with correlations for other CCl_y species derived from a full two-dimensional photochemical transport model. CCl_y mixing ratios determined by these methods are in excellent agreement, with differences of less than 100 pptv throughout the N_2O range sampled.

4. Since Cl_{Total} is increasing in the troposphere, age of air estimates are necessary for an accurate determination of Cl_{Total} in the sample. The relationship between CO_2 and N_2O in the stratosphere may be exploited to provide an index to the age of air.

5. Using derived Cl_{Total} and a semi-empirical determination of CCl_y, we can accurately estimate Cl_y in the sampled air parcel by the simple difference in (1).

6. We emphasize that although this type of semi-empirical approach can be used to estimate the chlorine burden and chlorine partitioning in the lower stratosphere, changing growth rates for key species in the troposphere make continued measurements absolutely critical to this type of assessment. In addition, although these results may be extrapolated to other parts of the stratosphere, they are strictly applicable only in the year and latitude region sampled by the ER-2.

References

Anderson, J. G., W. H. Brune, and M. H. Proffitt, Ozone destruction by chlorine radicals within the Antarctic vortex: The spatial and temporal evolution of the ClO-O_3 anticorrelation based on in situ ER-2 data, *J. Geophys. Res.*, *94*, 11,465-11,479, 1989.

Anderson, J. G., D. W. Toohey, and W. H. Brune, Free radicals within the Antarctic vortex: The role of CFCs in Antarctic ozone loss, *Science*, *251*, 39, 1991.

Boering, K.A., B.C. Daube, Jr., S.C. Wofsy, M. Loewenstein, J.R. Podolske, and E.R. Keim, Tracer-tracer relationships and lower stratospheric dynamics: CO_2 and N_2O correlations during SPADE, *Geophys. Res. Lett.*, *21*, 2567, 1994.

Brasseur, G. and S. Solomon, *Aeronomy of the Middle Atmosphere*, 2nd ed., 452 pp., D. Reidel, Norwell, Mass., 1986.

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.

Conway, T. J., P. P. Thans, L. S. Waterman, K. W. Thoning, D. R. Kitzis, K. A. Masarie, and N. Zhang, Evidence for interannual

variability of the carbon cycle from the NOAA/CMDL global air sampling network, *J. Geophys. Res., 99*, 22,831-22,855, 1994.

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

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.

Garcia, R. R., and S. Solomon, A numerical model of the zonally averaged dynamical and chemical structure of the middle atmosphere, *J. Geophys. Res., 88*, 1379-1400, 1983.

Hall, T. M., and R. A. Plumb, Age as a diagnostic of stratospheric transport, *J. Geophys. Res., 99*, 1059-1070, 1994.

Heidt, L. E., J. F. Vedder, W. H. Pollock, R. A. Lueb, and B. E. Henry, Trace gases in the Antarctic atmosphere, *J. Geophys. Res., 94*, 11,599-11,611, 1989.

Heidt, L. E., S. Hovde, A. Tuck, J. F. Vedder, and R. Weiss, The age of the air in the Arctic lower stratospheric vortex during late winter 1988/1989, *J. Geophys. Res.*, in press, 1994.

Holton, J. R., On the global exchange of mass between the stratosphere and troposphere, *J. Atmos. Sci., 47*, 392-395, 1990.

Jet Propulsion Laboratory (JPL), Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ. 90-1*, 1990.

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*, 7905-7923, 1992.

Kelly, K. K., et al., Dehydration in the lower Antarctic stratosphere during late winter and early spring, 1987, *J. Geophys. Res., 94*, 11,317-11,357, 1989.

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., et al., New observations of the NO_y/N_2O correlation in the lower stratosphere, *Geophys. Res. Lett., 20*, 2531, 1993.

Makide, Y., and F. S. Rowland, Tropospheric concentrations of methyl chloroform, CH_3CCl_3, in January 1978 and estimates of the atmospheric residence times for hydrohalocarbons, *Proc. Natl. Acad. Sci., 78*, 5933-5937, 1981.

Montzka, S. A., R. C. Myers, J. H. Butler, S. C. Cummings, and J. W. Elkins, Global topospheric distribution and calibration scale of HCFC-22, *Geophys. Res. Lett., 20*, 703-706, 1993a.

Montzka, S. A., R. C. Myers, J. H. Butler, J. W. Elkins, and S. C. Cummings, Atmospheric measurements of HCFC-22 at the South Pole, *Ant. J. U. S. 28*, 267-269, 1993b.

Montzka, S. A., R. C. Myers, J. H. Butler, and J. W. Elkins, Early trends in the global topospheric abundance of hydrochlorofluorocarbon-141b and -142b, *Geophys. Res. Lett., 21*, 2483-2486, 1994.

Plumb, R. A., and M. K. W. Ko, Interrelationships between mixing ratios of long-lived stratospheric constituents, *J. Geophys. Res., 97*, 10,145-10,156, 1992.

Podolske, J. R., M. Loewenstein, A. Weaver, S. E. Strahan, and K. R. Chan, Northern hemisphere nitrous oxide morphology during the 1989 AASE and the 1991-2 AASE II campaigns, *Geophys. Res. Lett., 20*, 2535-2538, 1993.

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*, 12,993-12,999, 1992.

Rodriguez, J. M., M. K. W. Ko, and N. D. Sze, Role of heterogeneous conversion of N_2O_5 on sulphate aerosols in global ozone losses, *Nature, 352*, 134-137, 1991.

Salawitch, R. J., et al., Chemical loss of ozone in the Arctic polar vortex in the winter of 1991-1992, *Science, 261*, 1146-1149, 1993.

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*, 2567-2570, 1993.

Schmidt, U., and A. Khedim, In situ measurements of carbon dioxide in the winter Arctic vortex and at midlatitudes: An indicator of the 'age' of the stratospheric air, *Geophys. Res. Lett., 18*, 763-766, 1991.

Solomon, S., Progress towards a quantitative understanding of Antarctic ozone depletion, *Nature, 347*, 347, 1990.

Solomon, S., and R. R. Garcia, On the distributions of long-lived tracers and chlorine species and the middle atmosphere, *J. Geophys. Res., 89*, 11,633-11,644, 1984.

Swanson, T. H., et al., Nitrous Oxide and Halocarbons Division, *Climate Monitoring and Diagnostics Laboratory, 21 Summary Report 1992*, edited by J. T. Peterson and R. M. Rosson, pp. 59-75, U.S. Department of Commerce, NOAA/ERL, Boulder, Colo., 1993.

Tabazadeh, A., and R. P. Turco, Stratospheric chlorine injection by volcanic eruptions: HCl scavenging and implications for ozone, *Science, 260*, 1082-1086, 1993.

Thompson, T. M., et al., Nitrous Oxide and Halocarbons Division, *Climate Monitoring and Diagnostics Laboratory 22 Summary Report 1993*, edited by, J. T. Peterson and R. M. Rosson, in press, U.S. Deptartment of Commerce, NOAA/ERL, Boulder, Colo., 1994.

Webster C. R., R. D. May, C. A. Trimble, R. G. Chave, and J. Kendall, Aircraft (ER-2) laser infrared absorption spectrometer (ALIAS) for in situ stratospheric measurements of HCl, N_2O, CH_4, NO_2 and HNO_3, *Appl. Opt., 33*, 454, 1994.

Wofsy, S. C., K. A. Boering, J. B. C. Daube, M. B. McElroy, M. Loewenstein, J. R. Podolske, J. W. Elkins, G. S. Dutton, and D. W. Fahey, Vertical transport rates in the stratosphere in 1993 from observations of CO_2, N_2O, and CH_4, *Geophys. Res. Lett., 21*, 2571-2574, 1994.

World Meteorological Organization (WMO), Scientific assessment of stratospheric ozone: 1989, *WMO Global Ozone Res. Monit. Proj. Rep. 20*, Geneva, 1989.

World Meteorological Organization (WMO), Scientific assessment of ozone depletion: 1991, *WMO Global Ozone Res. Monit. Proj. Rep. 25*, Geneva, 1992.

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