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S. M. Schauffler
National Center for Atmospheric Research

E. L. Atlas
National Center for Atmospheric Research

Stephen G. Donnelly Ph.D.
National Center for Atmospheric Research, sgdonnelly@fhsu.edu

A. Andrews
NASA Goddard Space Flight Center

S. A. Montzka
National Oceanic and Atmospheric Administration

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Authors

S. M. Schauffler, E. L. Atlas, Stephen G. Donnelly Ph.D., A. Andrews, S. A. Montzka, J. W. Elkins, D. F. Hurst, P. A. Romashkin, G. S. Dutton, and V. Stroud

Chlorine budget and partitioning during the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE)

S. M. Schauffler,[1] E. L. Atlas,[1] S. G. Donnelly,[1] A. Andrews,[2] S. A. Montzka,[3] J. W. Elkins,[3] D. F. Hurst,[3] P. A. Romashkin,[3] G. S. Dutton,[3] and V. Stroud[1]

[1] The amount of chlorine in the stratosphere has a direct influence on the magnitude of chlorine-catalyzed ozone loss. A comprehensive suite of organic source gases of chlorine in the stratosphere was measured during the NASA Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE) campaign in the arctic winter of 2000. Measurements included chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halon 1211, solvents, methyl chloride, N_2O, and CH_4. Inorganic chlorine contributions from each compound were calculated using the organic chlorine measurements, mean age of air, tropospheric trends, and a method to account for mixing in the stratosphere. Total organic chlorine measured at tropospheric levels of N_2O was on the order of 3500 ppt. Total calculated inorganic chlorine at a N_2O mixing ratio of 50 ppb (corresponding to a mean age of 5.5 years) was on the order of 3400 ppt. CFCs were the largest contributors to total organic chlorine (55–70%) over the measured N_2O range (50–315 ppb), followed by CH_3Cl (15%), solvents (5–20%), and HCFCs (5–25%). CH_3Cl contribution was consistently about 15% across the organic chlorine range. Contributions to total calculated inorganic chlorine at 50 ppb N_2O were 58% from CFCs, 24% from solvents, 16% from CH_3Cl, and 2% from HCFCs. Updates to fractional chlorine release values for each compound relative to CFC 11 were calculated from the SOLVE measurements. An average value of 0.58 was calculated for the fractional chlorine release of CFC 11 over the 3–4 year mean age range, which was lower than the previous value of 0.80. The fractional chlorine release values for HCFCs 141b and 142b relative to CFC 11 were significantly lower than previous calculations. *INDEX TERMS:* 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* chlorine, stratosphere, halogens, CFCs, HCFCs, solvents

1. Introduction

[2] The role of chlorine in stratospheric ozone depletion has been well documented. For recent in-depth discussions and review see *World Meteorological Organization* (*WMO*) [1995, 1999, and references therein]. Ongoing monitoring of chlorocarbon mixing ratios in the atmosphere over the last several decades has shown that the maximum atmospheric burden of chlorine in the troposphere occurred between mid-1992 and mid-1994 [*Montzka et al.*, 1996; *WMO*, 1999; *Prinn et al.*, 2000]. The maximum value observed was ∼3700 ppt which included ∼3150 ppt from anthropogenic sources and ∼550 ppt from CH_3Cl, the only known significant natural source of organic chlorine in the stratosphere (approximately 94% of known CH_3Cl emissions are from natural sources [*Lee-Taylor et al.*, 2001]). Anthropogenic sources include the chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), which are CFC replacements, and several chlorinated solvents, including methyl chloroform (Table 1).

[3] Production of CFCs, HCFCs, halons, methyl chloroform, and carbon tetrachloride is currently regulated in developed countries by the Montreal Protocol and subsequent amendments [*United Nations Environmental Programme* (*UNEP*), 1987, 1992, 1997]. The effect of these regulations on tropospheric trends of anthropogenic chlorocarbons has been evaluated through monitoring of atmospheric mixing ratios. The results show decreases in growth rates for the CFCs, and for CFCs 11 and 113 decrease in

[1]National Center for Atmospheric Research, Boulder, Colorado, USA.
[2]NASA Goddard Space Flight Facility, Greenbelt, Maryland, USA.
[3]NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado, USA.

Table 1. Chlorine-Containing Organic Compounds in the Atmosphere

Compound	Chemical Formula
CFC 11	CCl_3F
CFC 12	CCl_2F_2
CFC 13	$CClF_3$
CFC 112	CCl_3CClF_2
CFC 113	CCl_2FCClF_2
CFC 114	$CClF_2CClF_2$
CFC 114a	CF_3CFCl_2
CFC 115	$CClF_2CF_3$
HCFC 22	$CHClF_2$
HCFC 141b	CH_3CCl_2F
HCFC 142b	CH_3CClF_2
HCFC 123	CF_3CHCl_2
HCFC 124	CF_3CHClF
HCFC 21	$CHCl_2F$
Halon 1211	$CBrClF_2$
Halothane	$CF_3CHBrCl$
Methyl chloroform	CH_3CCl_3
Carbon tetrachloride	CCl_4
Methylene chloride	CH_2Cl_2
Chloroform	$CHCl_3$
Trichloroethylene	C_2HCl_3
Perchloroethylene	C_2Cl_4
Dichloroethane	$C_2H_4Cl_2$
Methyl chloride	CH_3Cl

mixing ratios, significant decrease in mixing ratios of methyl chloroform, a decrease in mixing ratios of carbon tetrachloride, and increases in mixing ratios of the HCFCs [*Elkins et al.*, 1993; *Kaye et al.*, 1994; *Irion et al.*, 1994; *Gunson et al.*, 1994; *Zander et al.*, 1994, 1996; *Prinn et al.*, 1995; *Oram et al.*, 1995; *Cunnold et al.*, 1997; *Hurst et al.*, 1998; *Fraser et al.*, 1999; *Montzka et al.*, 1996, 1999; *WMO*, 1999; *Hall et al.*, 2001]. The decrease in methyl chloroform mixing ratios is the primary reason for the current decrease in organic chlorine loading in the troposphere [*Montzka et al.*, 1996, 1999; *WMO*, 1999].

[4] The first measurements of CFCs in the troposphere were by *Lovelock* [1971], *Lovelock et al.* [1973], and *Su and Goldberg* [1973] who were investigating their potential usefulness as inert tracers for the study of mass transfer processes in the atmosphere and oceans. These measurements were cited as evidence for the presence of CFCs 11 and 12 in the atmosphere in the *Molina and Rowland* [1974] landmark publication, which suggested that chlorine atoms from the photodissociation of CFCs in the stratosphere could lead to destruction of ozone. As a result of the *Molina and Rowland* [1974] paper, measurements and monitoring of halogenated organics in the troposphere began as discussed above. The first measurements of CFCs in the stratosphere were by *Lovelock* [1974] from aircraft samples at a single altitude located just above the tropopause, which showed lower mixing ratios than those below the tropopause. The first vertical profiles of organic halocarbons in the stratosphere were measured by *Heidt et al.* [1975] and *Schmeltekopf et al.* [1975] from whole air samples collected from balloon flights over Texas and Wyoming, respectively. These studies confirmed the stratospheric loss of CFCs. Since that time numerous studies have measured various halocarbons in the stratosphere [*Krey et al.*, 1977; *Seiler et al.*, 1978; *Goldan et al.*, 1980; *Vedder et al.*, 1981; *Fabian et al.*, 1981, 1996; *Schmidt et al.*, 1984, 1994; *Zander et al.*,

1987, 1996; *Borchers et al.*, 1987; *Heidt et al.*, 1989; *Pollock et al.*, 1992; *Lal et al.*, 1994; *Woodbridge et al.*, 1995; *Lee et al.*, 1995; *Kourtidis et al.*, 1998; *Daniel et al.*, 1996; *Volk et al.*, 1997; *Wamsley et al.*, 1998; *Toon et al.*, 1999; *Ray et al.*, 1999; *Romashkin et al.*, 1999; *Sen et al.*, 1999; *Schauffler et al.*, 1999; *Pfeilsticker et al.*, 2000]. These measurements have been used to calculate halocarbon budgets and ozone loss and to evaluate lower stratospheric chemistry and dynamics in situ as well as in various models [see *WMO*, 1985, 1989, 1991, 1995, 1999, and references therein; *Kaye et al.*, 1994].

[5] The process of studying stratospheric ozone loss, chemistry, and dynamics is ongoing and requires continuously updated information on chlorocarbon mixing ratios, distributions, and budgets. In this work we use measurements from whole air samples collected during the NASA SAGE III Ozone Loss and Validation Experiment (SOLVE) [*Newman et al.*, 2002] in January–March 2000 to characterize the arctic lower stratospheric organic chlorine budget and, for each source gas, calculate inorganic chlorine contributions and fractional chlorine release relative to CFC 11. The organic chlorine budget is characterized using measurements of CFCs, HCFCs, solvents, and other chlorine containing organic compounds. Inorganic chlorine contributions from each compound refer to the amount of chlorine released during degradation since the compound entered the stratosphere. Fractional chlorine release relative to CFC 11 refers to the amount of chlorine released from a given compound in the stratosphere relative to the amount of chlorine released from CFC 11.

[6] Our inorganic chlorine calculations were based on measured organic chlorine mixing ratios, age of air calculations and age spectra based on carbon dioxide (CO_2) measurements, and measured tropospheric trends of chlorinated source gases. The basis of our calculations of inorganic chlorine is that air enters the stratosphere at time t_1 with a given amount of organic chlorine (as estimated from observations of organic chlorine species). At time t_2 we measure the organic chlorine remaining and subtract this amount from the amount of organic chlorine that entered at time t_1 as estimated from surface observations of chlorine species. This gives us the amount of inorganic chlorine released during time $t_2 - t_1$.

[7] The time difference $t_2 - t_1$ is estimated using the mean age of the air parcel derived from CO_2 observations. An air parcel in the stratosphere may be described as a composite of infinitesimal fluid elements with variable transport histories since crossing the tropical tropopause [*Hall and Plumb*, 1994]. The statistical distribution of transit times for the elements in a given air parcel is called the age spectrum and the mean age corresponds to the first moment of this distribution [*Hall and Plumb*, 1994; *Andrews et al.*, 2001b]. Therefore, mean age is the average transit time from the tropical tropopause as calculated over the ensemble of fluid elements of the air parcel. For a compound with linearly increasing tropospheric mixing ratios and no loss or production in the stratosphere, the mean age at a given location in the stratosphere would be equivalent to the elapsed time, or lag time, between the occurrence of a given mixing ratio at the tropical tropopause and the occurrence of that same mixing ratio at the given location in the stratosphere [*Hall and Plumb*, 1994;

Andrews et al., 2001b]. Mean age and lag time are not equivalent for compounds with nonlinear tropospheric trends, but in the case of CO_2, annual and interannual variations in the tropospheric time series can be taken into account and used to derive additional information about the age spectrum [*Andrews et al.*, 2001a, 2001b]. Mean age calculations for SOLVE were based on CO_2 measurements as described by *Andrews et al.* [2001b] with a correction to account for a large anomaly in the CO_2 growth rate between 1998 and 2000, as summarized below in section 2.2.

[8] Tropospheric trends were used to determine the mixing ratio in the troposphere for a given compound corresponding to a given mean age. We then calculated inorganic chlorine in two ways. The first used mean age as a lag time to determine the corresponding organic chlorine mixing ratio in the troposphere. For example, if a stratospheric sample collected in 2000 had a mean age of 3 years, we used the tropospheric mixing ratio of a given compound in 1997 as the mixing ratio that entered the stratosphere. We then subtracted our measured mixing ratio from the 1997 mixing ratio to determine the amount of inorganic chlorine released. We refer to these calculations as inorganic chlorine calculated using a lag time.

[9] The second technique used to calculate inorganic chlorine incorporated the effects of mixing on organic halogen mixing ratios at a given point in the stratosphere through the use of the age spectrum. We calculated the mixing ratio of a given compound that would be expected at a given stratospheric location if mixing were taken into account and there was no loss of the compound. We then subtracted our measured mixing ratio from this expected mixing ratio to determine inorganic chlorine released. We refer to these calculations as inorganic chlorine calculated using the age spectrum. These calculations are described in detail below in section 2.2. The difference in the projected stratospheric mixing ratio (not including chemical loss) of a given halocarbon between the two techniques is a function of the degree of nonlinearity of the tropospheric trend of a given halocarbon.

[10] To facilitate the use of our measurements, we provide equations of correlations between each compound and nitrous oxide (N_2O) for both the measured organic and calculated inorganic mixing ratios. We also provide equations of correlations between expected mixing ratios and mean age. We use N_2O because it is a useful tracer of the dynamical motions of stratospheric air masses since it lacks significant tropospheric sinks, it has well-characterized photochemical sinks in the middle stratosphere, and it has an approximate 100-year atmospheric lifetime that is much longer than stratospheric transport timescales. Nitrous oxide can be thought of as a convenient surrogate for altitude, since it decreases with increasing altitude on average, but is insensitive to transient distortions of the tracer isopleths associated with planetary-scale waves [*Plumb and Ko*, 1992]. Nitrous oxide mixing ratios have been used to identify and quantify the roles of dynamics and chemistry in observed changes in stratospheric air mass composition, such as ozone loss, denitrification, and dehydration [*Proffitt et al.*, 1990; *Fahey et al.*, 1990; *Hintsa et al.*, 1998; *Popp et al.*, 2001; *Gao et al.*, 2001].

[11] As mentioned above, we also calculated fractional chlorine release (FC) for each compound. FC is the amount of chlorine released from a given compound at a given location in the stratosphere relative to the amount entering the stratosphere [*Solomon et al.*, 1992]. Fractional chlorine release of a given chlorine containing compound relative to the fractional chlorine release of CFC 11 is required in calculations of equivalent effective stratospheric chlorine (EESC) [*Daniel et al.*, 1995] and effective equivalent chlorine (EECl) [*Montzka et al.*, 1996, 1999]. EESC and EECl relate the active chlorine and bromine in the stratosphere to the tropospheric release of the halocarbons. EESC and EECl have been used to evaluate ozone loss and halocarbon radiative forcing [*Daniel et al.*, 1995; *WMO*, 1995, 1999]. In this work we update the widely used fractional chlorine release values from *Daniel et al.* [1995], which were partially based on measurements from the National Center for Atmospheric Research (NCAR) Whole Air Sampler (WAS) collected during the NASA Airborne Arctic Stratospheric Expeditions (AASE and AASE II) campaigns [*Turco et al.*, 1990; *Anderson and Toon*, 1993], and we also provide fractional chlorine release values for compounds not previously measured or reported during these campaigns.

2. Methods

2.1. Sampling, Analysis, and Calibration

[12] Whole air samples were collected by the NCAR Whole Air Sampler on board the NASA ER-2 aircraft during the SOLVE campaign. Measurements presented in this work were from samples collected during flights out of Kiruna, Sweden (67.8°N 20.3°E) in January–March 2000. Samples were collected between 52°N and 88°N latitude and over an altitude range of 10 to 21 km. The Whole Air Sampler [*Heidt et al.*, 1989; *Schauffler et al.*, 1993, 1998] included a four-stage metal bellows pump, a stainless steel manifold connecting 32 electropolished stainless steel canisters and an electronics control package to open and close canister valves in a preprogrammed sequence. The canisters were filled to ∼40 psi (corresponding to 4.4 standard liters), returned to the laboratory at NCAR for analysis, and analyzed within 3–21 days after sample collection. The filling time for each canister was about 10 s at 8 km and 3.5–5 min at 20 km.

[13] N_2O was analyzed using gas chromatography with electron capture detection (GC/ECD). The GC columns were 3-m and 2-m 3/16 inch 80/100 Porapak Q columns for the main and precolumn, respectively. The columns were maintained isothermal at 50°C. A sample loop with approximately 10 cc volume was flushed with sample or standard and injected onto the precolumn. Peaks rapidly eluting from the precolumn, such as oxygen, were vented to the laboratory. Later eluting peaks of CO_2 and N_2O were carried into the main column where they were further separated before eluting into the ECD. Each sample was analyzed twice between two analyses of the standard.

[14] Mixing ratios of N_2O were calculated based on a secondary standard of remote continental tropospheric air collected at Niwot Ridge, Colorado, in September 1997. The secondary standard was calibrated using a National Institute of Standards and Technology (NIST) certified Standard Reference Material (SRM) (SRM #2608 certified at 300 ppb). Linearity of the GC/ECD system was evaluated

Table 2. Chlorine-Containing Organic Compounds Measured During SOLVE: Instrument Precision, Sampling Precision for Samples With CFC 11 < 35 ppt, Sampling Precision for Samples With CFC 11 > 35 ppt, Total Uncertainty, and Detection Limits

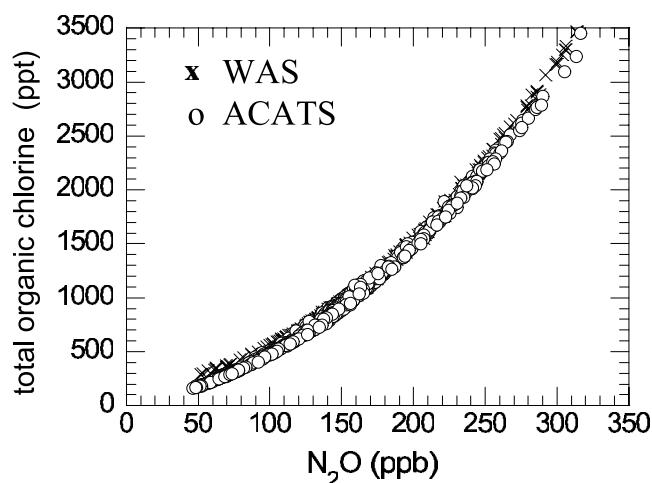| Compound	Instrument Precision, %	Sampling Precision, % (CFC 11 < 35 ppt)	Sampling Precision, % (CFC 11 > 35 ppt)	Total Uncertainty, %	Detection Limits, ppt
CFC 11	0.4	2.4	0.9	3.2	0.03
CFC 12	0.3	0.2	0.4	3.1	0.08
CFC 113	0.8	2.3	0.9	3.3	0.07
CFC 114	0.4	1.2	0.7	3.1	0.05
CFC 114a	2.6	6.5	3.4	5.8	0.05
CFC 115	2.4	1.4	2.3	5.1	0.02
HCFC 22	0.4	0.4	0.6	3.1	0.07
HCFC 141b	0.6	5.6	1.5	3.5	0.02
HCFC 142b	1.1	4.0	2.5	4.2	0.07
Halon 1211	0.4	33.6	4.4	5.4	0.05
CH_3CCl_3	0.8	6.4	4.6	5.6	0.07
CCl_4	0.8	9.8	3.0	4.4	0.09
CH_2Cl_2	0.5	9.7	3.2	4.4	0.02
$CHCl_3$	0.7	20.0	3.9	5.0	0.02
C_2Cl_4	0.6	na	11.1	11.5	0.03
CH_3Cl	0.4	3.1	1.3	3.3	0.10

using dilutions of the NIST SRM. Mixing ratios of N_2O were calculated taking into account the observed nonlinear response of the ECD.

[15] The halocarbons were analyzed using gas chromatography with mass selective detection (GC/MS). Approximately 0.5 liter of sample was concentrated at $-185°C$ in a glass-bead-packed nickel sample loop. The GC column was a 30-m fused silica column with a 0.25-mm ID and a 1.0 μm thick bonded nonpolar silicone phase (J&W Scientific DB-1). The column oven temperature profile was $-65°C$ for 1 min, 8°C/min to 120°C, and 70°C/min to 175°C for 2.1 min. Total analysis time was 27 min. The GC was a Hewlett Packard 5890, and the detector was a Hewlett Packard 5971A mass selective detector operated in the single-ion mode with electron impact ionization. Table 2 lists the compounds measured. We do not report CFC 13, HCFCs 21, 123, and 124, dichloroethane, trichloroethylene, and halothane because of a lack of reliable calibration and/or chromatography requirements (e.g., columns and temperature programming) that differ from the compounds listed in Table 2. Our preliminary estimate of the contribution of these unreported compounds to organic chlorine in the upper troposphere is less than 15 ppt.

[16] Mixing ratios of halocarbons were calculated based on secondary standards of remote continental tropospheric air collected at Coal Creek Canyon, Colorado, in August 1997. The secondary standards were calibrated against dilutions of commercially prepared multicomponent standards from Scott-Marrin, Inc. The secondary standards were run against each other during the SOLVE sampling period to check for drift of individual components over time. Changes over time were not observed in the secondary standards for the compounds reported here. The commercial multicomponent standards were not certified and were nominally listed as 100 ppb. These standards were calibrated in this laboratory against NIST certified standards using gas chromatography with atomic emission detection (GC/AED). The response of the AED is proportional to the number of atoms in the molecule (for our purposes we used carbon and chlorine). For this reason, a certified hydro-

carbon standard may be used to calibrate halocarbon mixtures. We evaluated the calibration on a certified NIST SRM 1813 cylinder containing four halocarbons ($\sim$250 ppb each) using a NIST prepared and certified butane/benzene mixture (10 ppb each). The calibration was within the stated values, so we subsequently used both standards to calibrate the commercially prepared multicomponent halocarbon mixtures. The analytical procedure for the GC/AED involved introduction of $\sim$1 liter of the standard onto a Supelco Carbotrap 200 adsorbent cartridge (80 mg glass beads, 170 mg Carbotrap B, 350 mg Carbosieve S III) followed by thermal desorption to a cryofocusing trap prior to introduction onto the GC column. The precision of the technique as described was $\sim$3% and was primarily attributable to the precision of a pressure transducer used to measure aliquot size. The accuracy of the NIST hydrocarbon standard was <1%, and that of the NIST halocarbon standard was ±1%. The ppb level primary halocarbon standards were diluted to ppt levels by both dynamic and static dilution systems for calibrating the secondary standards. Linearity of the instruments was evaluated using flow dilutions of background tropospheric air samples down to 10–20% of ambient values. Corrections for nonlinear effects were required for CFC 12, CFC 11, CFC 113, HCFC 22, CH_3CCl_3, CCl_4, and CH_3Cl. The corrections were on the order of 1.4–7.7% at mixing ratios that were half of the tropospheric values and 6.3–13.1% at mixing ratios that were approximately 10% of tropospheric values.

[17] The uncertainties in our measurements result from the following: instrument precision, sampling precision, standards calibration precision, and accuracy of the standards. To evaluate instrument precision, we determine the precision on repeated analysis of the working standard. We were unable to analyze a given canister enough times to evaluate instrument precision on ambient samples; therefore, for uncertainty calculations we assumed the precision from the working standard was equivalent to the precision from the samples. To evaluate the sampling precision, we compare samples collected in the same region consecutively, or nearly consecutively. Precisions of the GC systems

Figure 1. Total organic chlorine measured by WAS (x's) and calculated by ACATS (open circles) relative to N_2O.

for repeat runs of the secondary standard (instrument precision) for each compound and the sampling precision from analysis of multiple canisters are listed in Table 2. The sampling precision is listed separately for samples with CFC 11 mixing ratios less than 35 ppt, which represents polar vortex air with low mixing ratios, and for samples greater than 35 ppt of CFC 11. The sampling precision for the lower mixing ratio samples in Table 2 is an average and one standard deviation from 6 sets of multiple canisters with 2–4 samples per set. The precision for the higher mixing ratio samples represent an average and one standard deviation of 14 sets of multiple canisters with 2–9 samples per set. As expected, sampling precision was somewhat lower at the lower mixing ratios for most compounds. Also listed in Table 2 are the total uncertainties for each compound. These values were calculated by taking the square root of the sum of the squares of the percent uncertainties in standard preparation or dilution, the standard deviation in percent for repeated runs of the standards and samples, the standard deviation in percent for analysis of multiple canisters, and the standard deviation in percent of the standard mixing ratios.

[18] Our primary mechanism for evaluation of the NCAR calibration scales relative to those of other laboratories has been by comparison of measurements from whole air samples and standard mixtures. The comparison of most interest for SOLVE is with results from the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL), which operated the 4-channel Airborne Chromatograph for Atmospheric Trace Species (ACATS IV) in situ instrument on the ER-2. ACATS IV measured in situ N_2O, CFCs 11, 12, and 113, CH_3CCl_3, CCl_4, $CHCl_3$, halon 1211, SF_6, CH_4, and H_2 at measurement intervals of 70 or 140 s [*Elkins et al.*, 1996; *Romashkin et al.*, 2001]. *Woodbridge et al.* [1995] calculated total organic chlorine during the AASE II campaign from a combination of the ACATS measurements and correlations with either N_2O, CFC 11, or CH_4 for compounds not measured by ACATS. The correlations were based on measurements from samples collected by the NCAR Whole Air Sampler during AASE II. During

SOLVE, total organic chlorine was reported by ACATS and was calculated in a similar manner to that of *Woodbridge et al.* [1995]. In order to evaluate the comparison of measurements between WAS and ACATS we compared the WAS measured total organic chlorine with the ACATS calculated value (Figure 1). In general the agreement was good, however there were some discrepancies. WAS values were slightly higher than ACATS although there was not a constant offset. At N_2O levels of 50 ppb WAS measured and ACATS calculated organic chlorine values were 292 and 180 ppt, respectively, for a difference of 112 ppt. At N_2O levels of 315 ppb WAS measured and ACATS calculated organic chlorine values were 3503 and 3323 ppt, respectively, for a difference of 180 ppt. Total organic chlorine from compounds common to both instruments were within the uncertainties. About 25% of the difference at 50 ppb N_2O was due to compounds measured by WAS but not taken into account in the ACATS calculations, e.g. CFCs 114, 114a, and 115, HCFCs 141b and 142b, C_2Cl_4, and CH_2Cl_2. The remaining difference was due to discrepancies between the WAS measurements and the ACATS calculations for compounds not measured by ACATS, e.g. HCFC 22 and CH_3Cl. At N_2O levels of 315 ppb, the compounds measured by WAS, but not taken into account by ACATS calculations, represented about 60% of the difference between the two techniques. The remaining discrepancy between WAS and ACATS at tropospheric levels of N_2O was due to differences between the WAS measurements and the ACATS calculations for the compounds not measured by ACATS. We are currently evaluating discrepancies between measured and calculated compounds.

[19] Three in situ N_2O instruments were included in the NASA ER-2 payload during SOLVE [*Elkins et al.*, 1996; *Romashkin et al.*, 2001; *Jost and Loewenstein*, 1999; *Webster et al.*, 2001]. A collaborative effort to combine data from the three in situ instruments, using an objective method, produced a self-consistent, high-resolution, unified N_2O data set for each SOLVE flight [*Hurst et al.*, 2002]. The quality of unified N_2O data was compared with N_2O data from the NCAR Whole Air Sampler. Typical agreement between these two data sets was 2.9 ppb (1.5% at 200 ppb N_2O), better than the typical agreement between any pair of N_2O instruments [*Hurst et al.*, 2002].

2.2. Inorganic Chlorine Calculations

[20] Inorganic chlorine calculations for each compound require information on tropospheric trends, mean age of air for each sample, and the age spectrum for each mean age. Tropospheric trends of the halogenated compounds were obtained from CMDL measurements at Samoa, 14.2S, 170.6W, and Mauna Loa, 19.5N, 155.6W, [*Hall et al.*, 2001], from global values reported by *Montzka et al.* [1999], and from archived samples at NCAR [*Atlas et al.*, 2000]. Polynomial equations representing trends for the CFCs, HCFCs, solvents, and N_2O that were used in this work are presented in Table 3. The equations are based on mixing ratio versus year before 2000. Representative examples of tropospheric trends for CFC 12, HCFC 142b, and CH_3CCl_3 are shown in Figure 2. The tropospheric CFCs and CCl_4 mixing ratios over the last 6 years showed rather small changes whereas the HCFCs and CH_3CCl_3 mixing ratios changed significantly.

**Table 3.** Polynomial Equations of Tropospheric Trends[a] For CFCs, HCFCs, HFCs, Solvents, and N_2O[b]

Compound	Years	Intercept	b	c	d	e
CFC 11	0–9	265.29	2.3528	−0.46161	0.088173	−0.0073591
CFC 11	9–22	−75.766	109.48	−11.9	0.50936	−0.0079142
CFC 12	0–6	535.00	−3.5118	0.33833	−0.055056	
CFC 12	6–22	462.23	26.644	−3.6775	0.12383	−0.0013855
CFC 113	0–10	82.243	0.70957	−0.043476	0.0070423	−0.0024064
CFC 113	10–18	126.2	−5.80			
CFC 114	0–22	13.531	0.30844	−0.046638	9.8575e−04	
CFC 114a	0–22	1.6461	0.019065	−0.0051377	1.0267e−04	
CFC 115	0–22	6.3682	−0.078666	−0.020527	5.866e−04	
HCFC 22	0–20	139.61	−5.3725	0.049866	−0.0012236	
HCFC 141b	0–6.77	11.185	−1.3455	−0.21869	0.025616	
HCFC 142b	0–10.35	11.81	−0.97239	0.00472	−0.0020176	
Halon 1211	0–2.25	3.9014	−0.092683			
Halon 1211	2.25–13.0	4.088	−0.17552			
CCl$_4$	0–9.5	100.21	1.2672	−0.21749	0.036186	−0.0021273
CCl$_4$	9.5–21.5	118.71	−1.30			
CH$_3$CCl$_3$	0–9	52.919	9.4568	1.0794	−0.0088144	−0.013238
CH$_3$CCl$_3$	9–22	182.89	−5.4992			
N$_2$O	6.2	315.94	−0.9992	−0.0020332	0.0047104	

[a]Tropospheric trends are expressed in ppt for the organic halogens and ppb for N_2O.
[b]The years column refers to the number of years before 2000 that the equations are valid. Several compounds with changing growth rates required two equations for two different time intervals. Equations are for mixing ratio (y) versus age (x) before 2000, that is, 1995 = 5 years, 1990 = 10 years, and so on. Equations are in the form: $y = intercept + bx + cx^2 + dx^3 \ldots$

[21] Mean age of air values were determined by A. Andrews based on measurements of CO_2, N_2O, and CH_4 [*Boering et al.*, 1996; *Andrews et al.*, 2001a, 2001b]. CO_2 mixing ratios in the lower stratosphere are characterized by strong seasonal and interannual variations that originate in the troposphere. As air moves into the interior of the stratosphere, mixing among air parcels dampens these periodic variations, and CO_2 exhibits a nearly linear trend. *Andrews et al.* [2001a] showed that seasonal and interannual variations in CO_2 mixing ratios observed from 1992 to 1998 at northern midlatitudes provide information about the shape of the age spectrum for air with $N_2O > 275$ ppb. Mean ages were obtained from the derived age spectra by calculating the first moment. For air with $N_2O < 275$ ppb, seasonal and interannual variations in CO_2 are negligible, and mean age can be estimated by assuming a linear increase with a constant growth rate of 1.47 ppm yr^{-1} [*Andrews et al.*, 2001b]. Simultaneous observations of CH_4 were used to correct the derived mean ages for CO_2 production by CH_4 oxidation.

[22] As mentioned earlier, mean age calculated using a linearly increasing compound is equivalent to the lag time. The anticorrelation between mean age and N_2O averaged over all seasons and years was determined to be compact and invariant over a wide range of latitudes [*Andrews et al.*, 2001b]. *Andrews et al.* [2001b] developed a formulation for calculating mean age for a given flight using a combination of CO_2 measurements (corrected for CH_4 oxidation) to calculate mean age assuming a linear trend (equivalent to lag time) for air with $N_2O < 235$ ppb and N_2O measurements to calculate mean age based on the mean age calculated from the age spectrum versus N_2O relationship for air with $N_2O > 275$ ppb, with a smooth transition between the two regimes. This formulation, with an additional correction to account for an unusually strong anomaly in the tropospheric CO_2 growth rate between 1998 and 2000, was used to calculate mean ages for the SOLVE flights.
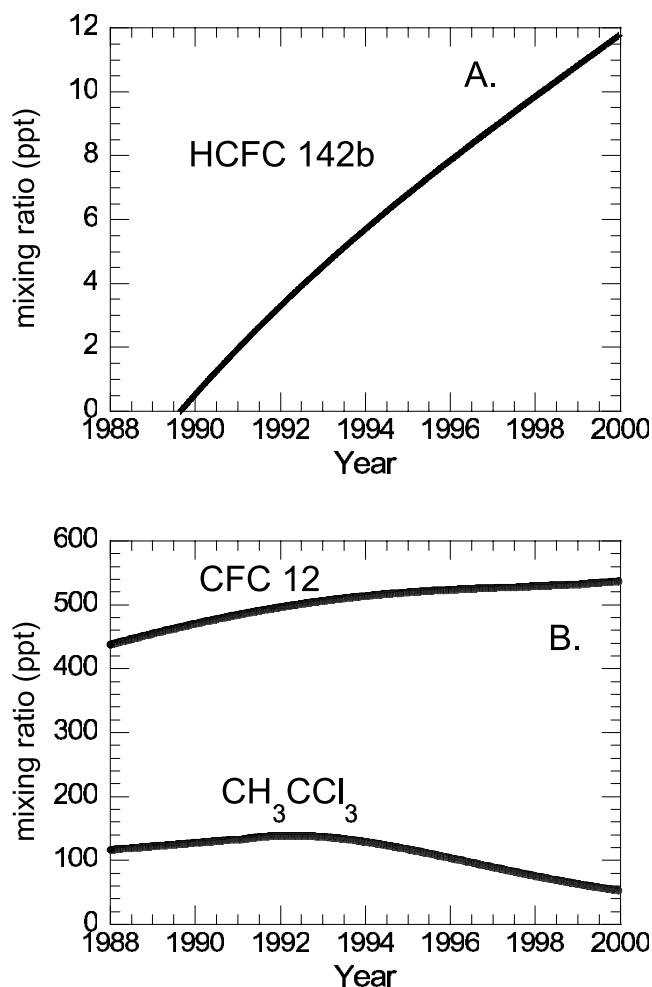
Figure 2. Tropospheric trends of (a) HCFC 142b and (b) CFC 12, CH_3CCl_3, used in calculations of inorganic chlorine.

Table 4. Mean Age and Spectral Width From *Andrews et al.* [2001a]

Mean Age	Spectral Width
0.89	1.31
1.44	1.50
1.91	1.57
2.28	1.73
2.62	1.72
2.91	1.73
3.25	1.70

[23] In order to provide a more accurate evaluation of inorganic chlorine released from the organic source gases, we used estimates of the age spectrum to take into account the effects of mixing in the stratosphere in our calculations. As mentioned earlier, the age spectrum is the probability distribution function of transit times between when a parcel entered the stratosphere and when it was sampled [*Hall and Plumb*, 1994; *Andrews et al.*, 2001a]. The age spectrum describes how trace gas levels in air parcels change as they mix with older and newer air parcels. An age spectrum for each mean age was estimated using the methods of D. W. Waugh and T. M. Hall (Age of stratospheric air: Theory, observations, and models, submitted to *Reviews of Geophysics*, 2001, hereinafter referred to as Waugh and Hall, submitted manuscript, 2001). In this work, we used the estimated age spectra, together with measured tropospheric trends, to calculate the "expected" mixing ratio of a trace gas for a given mean age. The calculated expected mixing ratio includes the effects of mixing but does not include any photochemical loss of organic chlorine. It represents the amount of organic chlorine that would be expected at a given location in the stratosphere if there were no photochemical loss. The difference between the measured and expected organic chlorine mixing ratio of a trace gas provides a measure of the amount of inorganic chlorine released, i.e., the amount lost through degradation processes.

[24] The expected mixing ratio of a given trace gas i at location r and time t ($X_i(r, t)$) was determined by:

$$X_i(r,t) = \int_0^t X_i(r_o, t') G(r, t; r_o, t') dt \qquad (1)$$

where $X_i(r_o, t')$ is the mixing ratio of trace gas i as a function of time t at the point of stratospheric entry and $G(r, t; r_o, t')$ is the age spectrum represented by the Green's function (Waugh and Hall, submitted manuscript, 2001, and references therein). This is the same formulation used by *Andrews et al.* [2001a] to calculate age spectra from tropospheric and lower stratospheric measurements of CO_2. Equations for $X_i(r_o, t')$ are the polynomials representing the tropospheric trends of organic chlorine compounds in Table 3. Because most of our trends were determined from low latitude and global measurements, we did not include a lag time between the tropospheric trends and entry into the stratosphere. $G(r, t; r_o, t')$ effectively propagates mixing ratios from the point of stratospheric entry at location r_o and t' time to location r at time t. In our calculations we use $G(r, t; r_o, t')$ in the form of:

$$G(\Gamma, \Delta, t) = \frac{1}{2\Delta\sqrt{\pi \hat{t}^3}} \exp\left(\frac{\Gamma^2(\hat{t}-1)^2}{4\Delta^2\hat{t}}\right) \qquad (2)$$

where Γ is the mean age, Δ is the spectral width and $\hat{t}$ is t/Γ (Waugh and Hall, submitted manuscript, 2001). The spectral width for each mean age was determined from values presented by *Andrews et al.* [2001a] (Table 4). A linear fit of spectral width versus mean age was used for mean ages between 0.89 and 2.28 years. The spectral width between 0 and 0.89 years was extrapolated from the 0.89 value. A width of 1.72 was used for mean ages between 2.28 and 3.25 years and a width of 1.70 was used for mean ages greater than 3.25 years. *Andrews et al.* [2001a] reported that a bimodal functional form of the age spectrum provided the best fit to CO_2 measurements. For simplicity, we use a single peak 1-D advection–diffusion form with the *Andrews et al.* [2001a] spectral widths (Figure 3). Use of the single peak form is adequate for our purposes because changing the shape of the age spectrum has little effect for compounds whose tropospheric mixing ratio time series are nonlinear for a period longer than a few years (D. Waugh, personal communication, 2001).
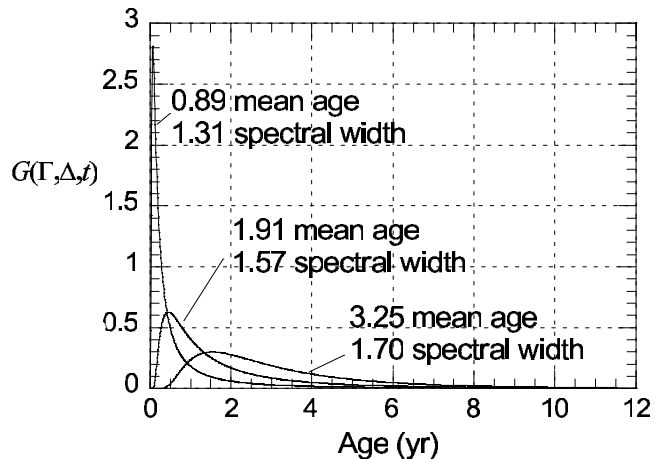
[25] $X_i(r, t)$ the expected stratospheric mixing ratio, was calculated for mean ages of 0–5.5 years for each compound that has a tropospheric trend (5.5 years was the oldest age of WAS samples). The correlation between $X_i(r, t)$ and mean age was then used to calculate $X_i(r, t)$ for each WAS sample using the mean age for that sample. Table 5 lists the equations for these relationships for each trace gas. Inorganic chlorine released from each compound, Cl_{yi}, was then calculated by:

$$Cl_{yi} = (X_i(r, t) - x_i(r, t)) n_x \qquad (3)$$

where $x_i(r, t)$ was the measured mixing ratio of compound i at time t and n_x is the number of chlorine atoms in halocarbon i. For compounds without a tropospheric trend, inorganic chlorine was calculated by:

$$Cl_{yi} = (X_i(r_o) - x_i(r, t)) n_x \qquad (4)$$

where $X_i(r_o)$ was the average measured mixing ratio at the tropical tropopause from measurements obtained by WAS onboard the ER-2 during the 1996 NASA Stratospheric

Figure 3. Age spectra, $G(\Gamma, \Delta, t)$, calculated using three of the mean age/spectral width values from *Andrews et al.* [2001a].

Table 5. Polynomial Equations for the Expected Stratospheric Mixing Ratio[a] for Each Compound (i.e., Organic Plus Inorganic Mixing Ratios) Versus Mean Age[b]

Compound	Intercept	b	c	d	e
CFC 11	264.98	1.3956	−0.2211	0.063604	−0.008214
CFC 12	536.32	−5.1465	0.65378	−0.096664	
CFC 113	82.278	0.078086	−0.015383	0.020141	−0.0046725
CFC 114	13.587	0.0611	0.039207	−0.011258	6.3809e−04
CFC 114a	1.662	−0.0079474	0.0041332	−0.0012041	6.7259e−05
CFC 115	6.3799	−0.15206	−2.4029e−04	−0.0010723	
HCFC 22	139.44	−5.1017			
HCFC 141b	11.072	−1.2433	−0.16889	0.020532	
HCFC 142b	11.81	−0.95111	−0.010691		
Halon 1211	3.9051	−0.12009	−5.8477e−04	−6.6977e−04	
CCl$_4$	100.34	0.63198	0.067523	−0.0097257	
CH$_3$CCl$_3$	53.966	7.9987	1.4145	−0.15628	

[a]The expected stratospheric mixing ratio is expressed in ppt.
[b]The expected mixing ratios were calculated using tropospheric trends, mean age, and the age spectrum. Equations are only valid for N$_2$O 50–315 ppb. See text for details. Equations are in the form: $y = \text{intercept} + bx + cx^2 + dx^3 \ldots$

Tracers of Atmospheric Transport (STRAT) campaign from flights on 13 February 1996, 1 and 8 August 1996, and 11 December 1996. The stratospheric entry mixing ratios for CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$, and C$_2$Cl$_4$ were 589.0 ± 15, 13.6 ± 1.2, 4.2 ± 1.0, and 0.67 ± 0.31 ppt, respectively. These values represent averages of 23–32 samples.

[26] The CH$_3$Cl value of 589 ppt is somewhat higher than the global average of 550 ± 30 ppt reported by the *WMO* [1999]. However, CH$_3$Cl tropospheric mixing ratios show significant temporal and spatial variability. For example, monthly mixing ratios (1996–2000) at Samoa (14°S) vary seasonally from 525–600 ppt. Also, CH$_3$Cl tropospheric measurements from GTE PEM Tropics A campaign in July 1996 between 5°S and 5°N averaged 562 ± 25 ppt. Therefore, our upper tropical troposphere value of 589 ppt is within the range previously observed in the tropics (The NCAR calibration for CH$_3$Cl is within a few percent of the CMDL calibration scale based on secondary standard intercomparisons). Because of the natural variability in CH$_3$Cl mixing ratios in the troposphere, we evaluate fractional chlorine release (in the section below) from CH$_3$Cl using three entry mixing ratios representing the low seasonal mean at Samoa (525 ppt), the global average (550 ppt), and our measured value at the tropical tropopause (589 ppt).

[27] Measurements from PEM Tropics A showed significant latitudinal variation in mixing ratios of CH$_2$Cl$_2$, CHCl$_3$, and C$_2$Cl$_4$ with higher mixing ratios in the northern hemisphere. The average mixing ratio between 5°S and 5°N was 12.1 ± 1.2 ppt for CH$_2$Cl$_2$, 6.0 ± 0.7 ppt for CHCl$_3$, and 1.12 ± 0.24 ppt for C$_2$Cl$_4$. Based on our measurements, the tropical tropopause mixing ratios of CHCl$_3$, and C$_2$Cl$_4$ were about 60% of the troposphere values while those of CH$_2$Cl$_2$ were equivalent.

[28] In order to test the impact of including the age spectral width in our calculations of expected mixing ratios, we calculated stratospheric entry mixing ratios using mean age as a lag time and tropospheric trends only (equivalent to assuming that the age spectrum is a delta function). The difference in total organic chlorine (the sum of chlorine from all measured compounds) between entry mixing ratios calculated using lag time and tropospheric trends only and the expected mixing ratio, $X_i(r, t)$, calculated using the age spectrum to take into account stratospheric mixing, was

about 25 ppt at N$_2$O of 250 ppb and 53 ppt at N$_2$O of 50 ppb (Figure 4a). Over half of the difference was due to CH$_3$CCl$_3$, (due to rapidly decreasing tropospheric mixing ratios since 1993) with the remaining difference due to CFCs 11, 12, 113, and CCl$_4$ (Figure 4a). For compounds with significant nonlinear temporal changes that are decreasing (increasing) in the troposphere, the calculated entry mixing ratios using lag time are higher (lower) than the age spectrum calculated expected mixing ratios as seen in Figures 4a and 4b.

[29] For compounds with nonlinear temporal changes whose mixing ratios are increasing in the troposphere over
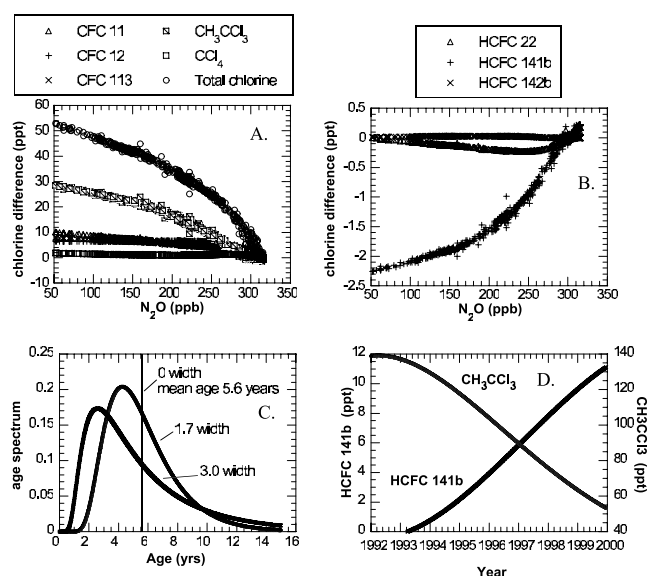
Figure 4. The difference between total mixing ratios calculated based on mean age only and those calculated based on age spectra for (a) CFCs 11 (open triangles), 12 (+'s), and 113 (x's) and CH$_3$CCl$_3$ (slash squares), CCl$_4$ (open squares), and total organic chlorine (open circles), and (b) HCFCs 22 (open triangles), 141b (+'s), and 142b (x's). (c) age spectra for mean age of 5.6 years and spectral widths of 1.7 and 3.0. (d) tropospheric mixing ratios of CH$_3$CCl$_3$ and HCFC 141b from 1992 to 2000.

time, larger (smaller) spectral widths for a given mean age result in higher (lower) expected mixing ratios. For compounds with nonlinear temporal changes whose mixing ratios are decreasing in the troposphere over time, larger (smaller) spectral widths for a given mean age result in lower (higher) expected mixing ratios. The reason for these differences is that larger spectral widths include a larger fraction of younger air. For example, Figure 4c shows the age spectrum for a mean age of 5.6 years using spectral widths of 1.7 and 3.0 and Figure 4d shows the tropospheric temporal trends of HCFC 141b and CH_3CCl_3. A spectral width of 3.0 was the largest width calculated by *Andrews et al.* [2001a] using a 1-D single peak age spectrum distribution. The entry mixing ratio of HCFC 141b derived for a lag time of 5.6 years was 2.6 ppt. The expected mixing ratios calculated using the age spectrum with widths of 1.7 and 3.0 were 4.8 and 7.1 ppt, respectively. The entry mixing ratio of CH_3CCl_3 derived for a lag time of 5.6 years was 125 ppt. The expected mixing ratios with widths of 1.7 and 3.0 were 116 and 79 ppt, respectively. Clearly the width of the age spectrum impacts calculations of $X_i(r, t)$ for compounds with nonlinear temporal changes in tropospheric mixing ratios. We chose to use the *Andrews et al.* [2001a] spectral widths that provided the best fit to their CO_2 measurements, corresponding to bimodal age spectra. As discussed above, the results presented in the paper are not sensitive to whether the age spectra are bimodal or single-mode, only to the mean age and the width. Their study was the first comprehensive use of measurements to calculate spectral widths and age spectrum distribution. Current studies are also underway evaluating the use of WAS measurements of HFC 134a and HCFCs from SOLVE, STRAT, and Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) to constrain the spectral width−mean age relationship (D. Waugh, personal communication, 2001).

3. Results

3.1. Organic Measurements and Inorganic Calculations

[30] Correlations with N_2O for the measured organic and calculated inorganic chlorine for individual compounds are presented in Figures 5 and 6. The figures represent total chlorine from each compound, i.e. the measured organic and calculated inorganic mixing ratios were multiplied by the number of chlorine atoms in the respective compounds. Polynomial equations for the organic and inorganic curves shown in the figures are presented in Tables 6 and 7, respectively. The figures also include the expected chlorine mixing ratios, i.e. the expected mixing ratios multiplied by the number of chlorine atoms in the respective compounds. As discussed above, the measured mixing ratios were subtracted from the expected mixing ratios to calculate inorganic chlorine. Mixing ratios at 50 ppb N_2O correspond to a mean age of approximately 5.5 years.

[31] The expected chlorine mixing ratios of the individual compounds in Figures 5 and 6 reflect the trends in stratospheric entry mixing ratios over the last 5 years combined with the effect of mixing. CH_3CCl_3 shows a dramatic difference between the expected mixing ratios at 50 ppb N_2O and that at 315 ppb N_2O as a result of the recent decline in tropospheric mixing ratios (Figure 6f). The effects
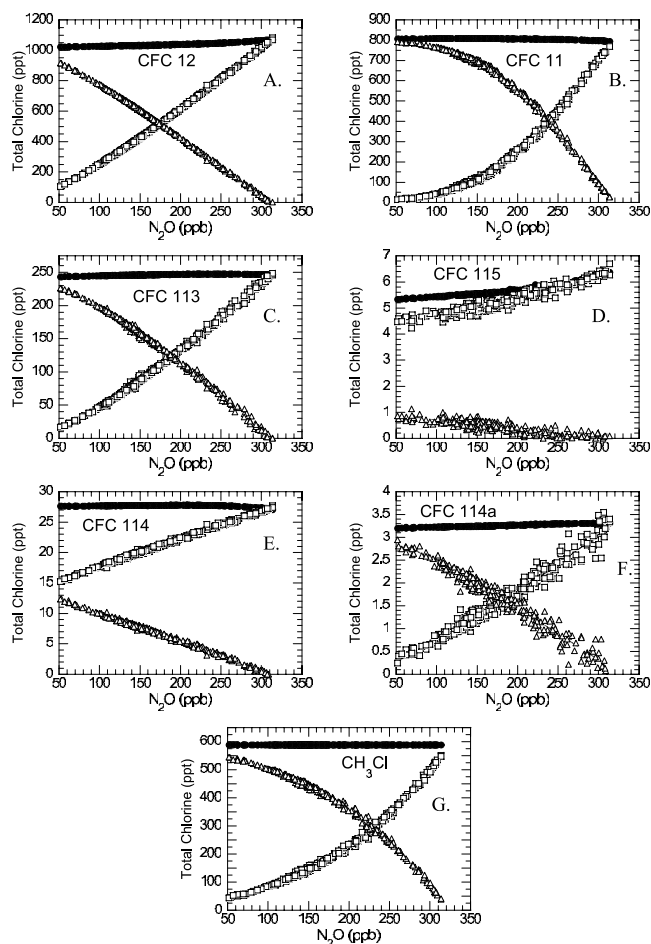
Figure 5. Measured organic chlorine (open squares), calculated inorganic chlorine (open triangles), and calculated expected total chlorine (solid circles) relative to N_2O mixing ratios from SOLVE samples for the CFCs (a) 12, (b) 11, (c) 113, (d) 115, (e) 114, and (f) 114a and (g) CH_3Cl. Total chlorine on the y axis for each compound represents the mixing ratios times the number of chlorine atoms.

of increases in tropospheric mixing ratios are seen in the HCFC results with significantly lower expected mixing ratios at 50 ppb N_2O relative to 315 ppb N_2O (Figures 6a–6c). Trends in the stratospheric entry mixing ratios for the CFCs were relatively small over the last 5 years as reflected in the expected mixing ratios (Figures 5a–5f) and result from production regulations defined in the Montreal Protocol and subsequent amendments [*UNEP*, 1992; *WMO*, 1999]. CH_3Cl was assumed to have no tropospheric trend (Figure 5g) [*WMO*, 1999]. Total organic chlorine (the sum of chlorine from all compounds) measured at tropospheric values of N_2O was about 3500 ppt. Calculated total inorganic chlorine was about 3400 ppt at N_2O values of 50 ppb (Figure 7).

[32] CFCs were the largest contributors to both total organic chlorine and calculated total inorganic chlorine (Figures 8a and 8d) and CFCs 11, 12, and 113 were the largest contributors to the CFC fraction of organic and inorganic chlorine (Figures 8b and 8e). Contributions to total organic and total inorganic chlorine from CFCs 114,
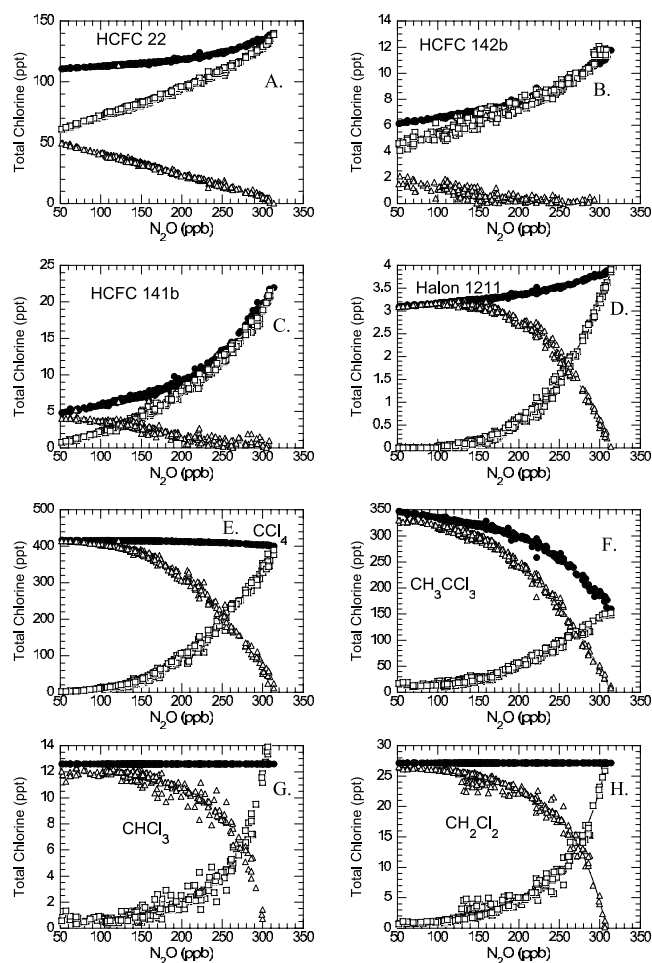
Figure 6. Measured organic chlorine (open squares), calculated inorganic chlorine (open triangles), and calculated expected total chlorine (solid circles) relative to N_2O mixing ratios from SOLVE samples for HCFCs (a) 22, (b) 142b, and (c) 141b, (d) halon 1211, and solvents (e) CCl_4, (f) CH_3CCl_3, (g) $CHCl_3$, and (h) CH_2Cl_2.

114a, and 115 were considerably smaller, with the CFC 114 organic contribution between 15 and 28 ppt and the 114a and 115 contributions less than 4 ppt and 7 ppt, respectively.

[33] HCFC 22 was the major contributor to the HCFC fraction of total organic chlorine and calculated total inorganic chlorine (Figures 8c and 8f). A significant amount of the decrease of HCFCs relative to decreasing N_2O was a result of trends in the stratospheric entry mixing ratios, i.e. lower entry mixing ratios in older air corresponding to lower N_2O (Figures 6a–6c). Therefore, the calculated inorganic chlorine values were low relative to the measured organic chlorine for each HCFC. In addition, the reported stratospheric lifetimes of HCFCs 22 and 142b are 306 and 372 years, respectively while that of HCFC 141b is 81 years [*WMO*, 1999]. Intuitively, longer-lived chlorinated source gases release their chlorine more slowly.

[34] CCl_4 and CH_3CCl_3 were the largest contributors to the solvent fraction of total organic chlorine and calculated total inorganic chlorine (Figures 9a and 9e). CH_2Cl_2 and $CHCl_3$ contributed significantly smaller amounts and C_2Cl_4 was only observed in samples with higher N_2O values (Figures 9b and 9e). The latter three chlorinated compounds were assumed to have no tropospheric trends.

[35] CFC contribution to total organic chlorine over the N_2O range 50 to 315 ppb measured during SOLVE was 55–70% followed by CH_3Cl (15%), solvents (5–20%), and HCFCs (5–25%) (Figure 10a). CH_3Cl contribution was consistently about 15% across the organic chlorine range (Figure 10a). This was also true for the NASA 1996 STRAT, and 1997 POLARIS campaigns (Figure 10b). Fractional contributions to total inorganic chlorine at 50 ppb N_2O were 58% from CFCs, 24% from solvents, 16% from CH_3Cl, and 2% from HCFCs (Figure 10c).

[36] The individual contributions to total organic chlorine from CFCs 115 and 114a, HCFCs 141b and 142b, and solvents CH_2Cl_2, $CHCl_3$, and C_2Cl_4, all with tropospheric mixing ratios less than 15 ppt, were small, however the sum of organic chlorine from these compounds was significant. At upper tropospheric levels, these compounds represented about 90 ppt of organic chlorine, which was 3% of total organic chlorine. At 50 ppb N_2O these compounds repre-

Table 6. Polynomial Equations for Total Organic Chlorine Mixing Ratios[a] for Each Compound Versus N_2O[b]

Compound	Intercept	b	c	d	e	f
CFC 11	−43.089	1.7871	−0.020271	1.289e−04	−1.7848e−07	
CFC 12	−24.875	2.1849	0.006559	−7.4659e−06		
CFC 113	−9.6771	0.3815	0.0021013	−2.2076e−06		
CFC 114	12.908	0.048469	−6.9316e−06			
CFC 114a	−0.11026	0.007794	9.3264e−06			
CFC 115	4.3711	0.0020755	1.41e−05			
HCFC 22	46.885	0.30755	−8.4497e−04	2.4589e−06		
HCFC 141b	−1.0833	0.036978	−1.1291e−04	7.0898e−07		
HCFC 142b	2.1339	0.050035	−2.2208e−04	5.2578e−07		
Halon 1211	−0.26521	0.0080184	−8.266e−05	3.1592e−07		
CCl_4	−36.751	1.3333	−0.015847	8.2801e−05	−1.0326e−07	
CH_3CCl_3	9.8249	0.31727	−0.0058041	3.7258e−05	−5.5261e−08	
CH_2Cl_2	−3.2665	0.17357	−0.0028784	2.3327e−05	−8.6246e−08	1.2425e−10
$CHCl_3$	−5.2522	0.26386	−0.0042629	3.1387e−05	−1.0648e−07	1.3841e−10
CH_3Cl	9.6511	0.59321	6.7228e−04	9.2893e−06		
Total Org. Chlorine	165.97	1.2972	0.023603	1.8765e−05		

[a]Total organic chlorine mixing ratios are expressed in ppt.
[b]The total organic chlorine mixing ratios for each compound were calculated by multiplying the measured mixing ratios by the number of chlorine atoms per molecule. Equations are only valid for N_2O 50–315 ppb. Equations are in the form: $y = intercept + bx + cx^2 + dx^3 \dots$

Table 7. Polynomial Equations for Total Inorganic Chlorine Mixing Ratios[a] For Each Compound Versus N_2O[b]

Compound	Intercept	b	c	d	e	f
CFC 11	839.12	−1.4715	0.017426	−1.1796e−04	1.6217e−07	
CFC 12	1030.1	−1.7354	−0.0091151	1.3222e−05		
CFC 113	247.99	−0.26551	−0.0025708	2.8124e−06		
CFC 114	14.599	−0.043364	−1.1112e−05			
CFC 114a	3.379	−0.0084708	−5.8841e−06			
CFC 115	1.1517	−0.0041629	1.2059e−06			
HCFC 22	57.067	−0.12626	−2.7029e−04	4.0441e−07		
HCFC 141b	3.0245	0.037904	−3.6742e−04	7.2145e−07		
HCFC 142b	2.1202	−0.0045065	−5.7242e−05	1.7922e−07		
Halon 1211	3.2338	−0.0048681	6.7278e−05	−2.688e−07		
CCl_4	453.67	−1.3184	0.015544	−8.1392e−05	9.9753e−08	
CH_3CCl_3	326.76	0.066775	−2.6458e−04	−1.0336e−05		
CH_2Cl_2	30.155	−0.16402	0.0027807	−2.2888e−05	8.537e−08	−1.2364e−10
$CHCl_3$	16.497	−0.21144	0.0035183	−2.6442e−05	9.0971e−08	−1.1992e−10
CH_3Cl	578.98	−0.58507	−7.219e−04	−9.2002e−06		
Total Inorganic Chlorine	3479.6	−1.698	−0.020181	−2.9742e−05		

[a]Total inorganic chlorine mixing ratios are expressed in ppt.

[b]The total inorganic chlorine mixing ratios for each compound were calculated by multiplying the calculated mixing ratios by the number of chlorine atoms per molecule. Equations are only valid for N_2O 50–315 ppb. Equations are in the form: $y = \text{intercept} + bx + cx^2 + dx^3 \dots$

sented about 26 ppt of organic chlorine, or about 9% of the total. The contribution of these compounds to total inorganic chlorine was about 2–3%. The contributions of all compounds to organic and inorganic chlorine will change with time as the CFC and HCFC tropospheric mixing ratios change.

3.2. Fractional Chlorine Release Relative to CFC 11

[37] As mentioned earlier, fractional chlorine release of a given chlorine containing compound is required in calculations of EESC (effective equivalent stratospheric chlorine) [*Daniel et al.*, 1995; *WMO*, 1995, 1999] and EECl (effective equivalent chlorine) [*Montzka et al.*, 1996, 1999]. Both calculations use tropospheric mixing ratios weighted by relative decomposition rates in a given region of the stratosphere to calculate current and future stratospheric inorganic halogen (chlorine and bromine) mixing ratios. *Daniel et al.* [1995] used calculations of tropospheric mixing ratios based on emissions and lifetimes while *Montzka et al.* [1996, 1999] used measurements of tropospheric mixing ratios. *Daniel et al.* [1995] defined EESC in year t as:

$$EESC^t = \left(\begin{array}{c} \sum n_x Cl_{trop}^{t-3}\left(\dfrac{FC_x}{FC_{CFC-11}}\right) + \\ \sum n_x \alpha Br_{trop}^{t-3}\left(\dfrac{FC_x}{FC_{CFC-11}}\right) \end{array} \right) FC_{CFC-11}$$

where n_x is the number of chlorine or bromine atoms in halocarbon x, Cl_{trop}^{t-3} and Br_{trop}^{t-3} represents the stratospheric halocarbon mixing ratio at time t, which accounts for an approximate three year lag time from the emission source to the midlatitude lower stratosphere, and α accounts for the increased ability of a bromine atom to destroy ozone relative to a chlorine atom. Values used for α range from 40–100 [*Daniel et al.*, 1995; *WMO*, 1995, 1999; *Montzka et al.*, 1996, 1999]. Fractional chlorine release, FC_x, was calculated as defined by *Solomon et al.* [1992],

$$FC_x = \frac{\mu_{entry,x} - \mu_{\theta,z,x}}{\mu_{entry,x}} \tag{5}$$

where $\mu_{entry,x}$ is the mixing ratio of halocarbon x when it enters the stratosphere, and $\mu_{\theta,z,x}$ is the mixing ratio of halocarbon x at latitude θ and altitude z. FC_x represents the fractional dissociation, or fraction of halocarbon x destroyed, between the time of entry into the stratosphere and the time of measurement. The ratio $\frac{FC_x}{FC_{CFC-11}}$ is the fractional halogen release of halocarbon x normalized to FC_{CFC-11}. *Montzka et al.* [1996, 1999] used the same basic formulation as equation 4 but did not include the time lag for transport into the midlatitude lower stratosphere so they designated their formulation effective equivalent chlorine (EECl). They state that their EECl values are relevant for the stratosphere only after considering time lags on the order of 3–5 years [*Montzka et al.*, 1996, 1999].

[38] *Daniel et al.* [1995] used calculations of EESC to evaluate halocarbon radiative forcing and global warming potentials. *Montzka et al.* [1996] used their EECl calculations to evaluate the decline in tropospheric abundance of
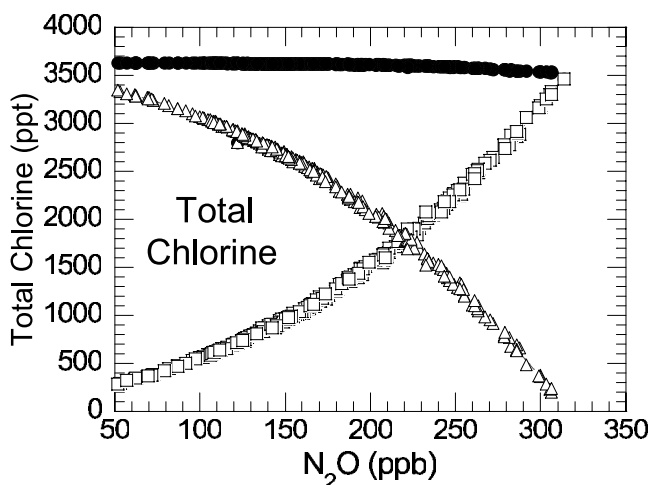
Figure 7. Measured total organic chlorine (open squares), calculated total inorganic chlorine (open triangles), and calculated expected total organic chlorine (solid circles) from SOLVE samples.
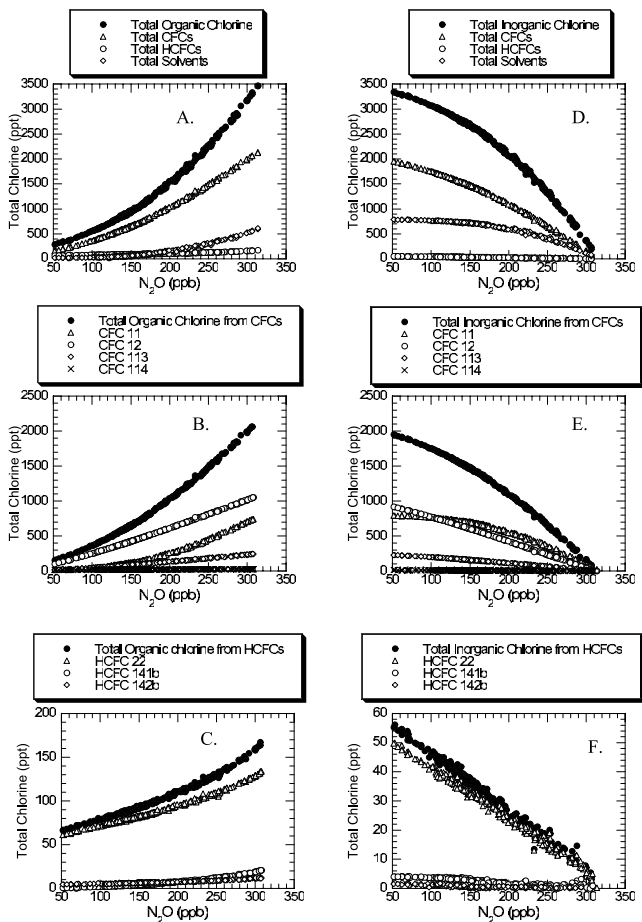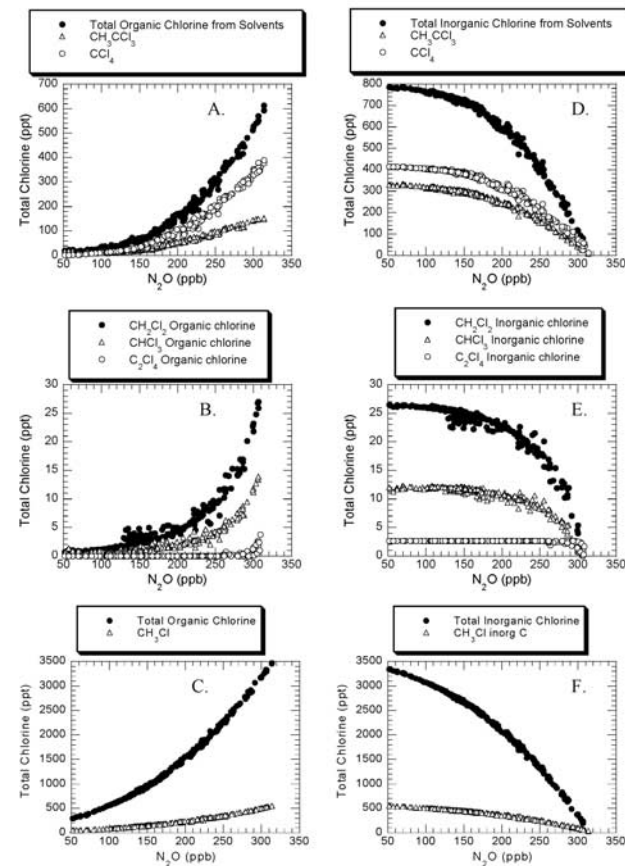
Figure 8. Measured organic chlorine contributions by (a) CFCs (open triangles), HCFCs (open circles), and solvents (open diamonds) relative to total organic chlorine (solid circles), (b) within the CFCs by CFCs 11, 12, 113, and 114, and (c) within the HCFCs by HCFCs 22, 141b, and 142b. Calculated inorganic chlorine contributions by (d) CFCs, HCFCs, and solvents, (e) within the CFCs by CFCs 11, 12, 113, and 114, (f) within the HCFCs by HCFCs 22, 141b, and 142b.

halocarbons and the implications of that decline for stratospheric ozone. *Montzka et al.* [1999] used EECl calculations to evaluate present and future trends of various halocarbons that contribute to ozone depletion. *Solomon and Wuebbles* [1995] and *Madronich and Velders* [1999] evaluated the effect on stratospheric halogen levels of various scenarios for future chlorine and bromine loading using EESC calculations. *Madronich and Velders* [1999] also examined the effect of changing EESC levels on the ozone column and the subsequent impact of those effects on the ultraviolet radiation reaching the Earth's surface.

[39] *Daniel et al.* [1995] evaluated $\frac{FC_x}{FC_{CFC-11}}$ ratios using a combination of model calculations and measurements from whole air samples collected during Airborne Arctic Stratospheric Expedition (AASE) I in 1989 [*Pollock et al.*, 1992; *Solomon et al.*, 1992] and globally averaged values of $\frac{FC_x}{FC_{CFC-11}}$ based on measurements from whole air samples from AASE II in 1991. For compounds with a temporal trend, $\mu_{entry,x}$ was determined by *Daniel et al.* [1995] using

mean age determined from CFC 115 measurements and tropospheric trends calculated from emission data and atmospheric lifetimes. Our purpose here is to update those values, using measurements from SOLVE and our expected mixing ratio calculations, and to include additional compounds not considered by *Daniel et al.* [1995].

[40] In the remaining discussion we refer to $\frac{FC_x}{FC_{CFC-11}}$ as FC_{ratio}. The FC_{ratio} value for a given compound is a function of the vertical distribution of loss relative to the vertical distribution of loss for CFC 11. For example, if the vertical distribution of loss for a given compound were identical to that of CFC 11, FC_{ratio} would be equal to one. If a given compound has greater loss at lower/higher altitudes (corresponding to younger/older ages) than CFC 11, FC_{ratio} would be greater/less than one. The relationship between FC_x and FC_{CFC-11} from SOLVE measurements was not constant, as seen for CFC 12, HCFC 22, CH_3CCl_3, and halon 1211 in Figure 11a. As a result, FC_{ratio} was not constant relative to FC_{CFC-11} as shown in Figure 11b for CFC 12. Also shown in Figure 11b is the relationship between mean age and FC_{CFC-11}. Since the FC_{ratio} ratios were not constant with respect to age we averaged over three age ranges to examine the magnitude of the variability over age ranges commonly used in calculations of equiv-

Figure 9. Measured organic chlorine contributions by (a) solvents CH_3CCl_3 and CCl_4, (b) solvents CH_2Cl_2, $CHCl_3$, and C_2Cl_4, and (c) CH_3Cl. Calculated inorganic chlorine contributions by (d) solvents CH_3CCl_3 and CCl_4, (e) solvents CH_2Cl_2, $CHCl_3$, and C_2Cl_4, and (f) CH_3Cl.
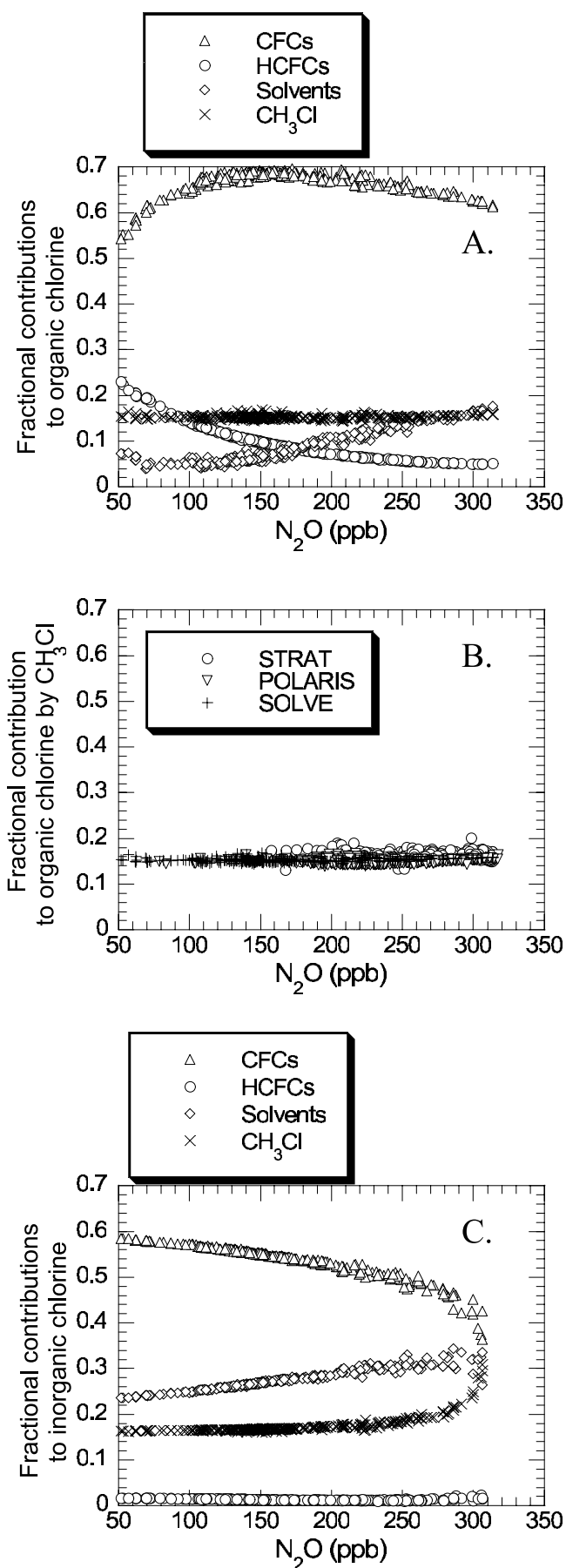
alent stratospheric chlorine (Table 8). *Solomon and Wuebbles* [1995] and *Madronich and Velders* [1999] assumed a mean age of about 3 years and *Montzka et al.* [1999] indicated their calculations would be relevant in the stratosphere after accounting for a 3−5 year time lag. The first age range of 2.0−4.5 years was chosen to represent the extratropical lower stratosphere between approximately 14−20 km. The second age range of 3−4 years was chosen to provide a more focused value for FC_{ratio}. The third age range of 4.75−5.2 years was chosen to represent high-latitude lower stratosphere between approximately 18−20 km.

[41]   The FC_{ratio} values averaged over the 2.0−4.5 year mean age range correspond to a FC_{CFC-11} range of about 0.25−0.80 and an N_2O range of about 175−275 ppb. The FC_{ratio} values averaged over the 3.0−4.0 year mean age range correspond to a FC_{CFC-11} range of about 0.45−0.65 and an N_2O range of about 205−245 ppb. The FC_{ratio} values averaged over the 4.75−5.25 year mean age range correspond to a FC_{CFC-11} range of about 0.87−0.95 and an N_2O range of about 95−150 ppb.

[42]   The CFCs and HCFCs all show the greatest loss relative to CFC 11 in the oldest age range. Halon 1211 and the solvents show the greatest loss relative to CFC 11 in the two lower age ranges (Figure 11a and Table 8). As seen in Figure 11a this is due to the shape of the curve representing the fractional loss of a given compound relative to FC_{CFC-11}.

[43]   Also included in Table 8 are the FC_{ratio} values reported by *Daniel et al.* [1995]. With the exception of CFC 12, HCFC 141b, and HCFC 142b, the *Daniel et al.* [1995] values were closest to the 4.75−5.25 values. The *Daniel et al.* [1995] value of 0.60 for CFC 12 was within the range of our value of 0.57 ± 0.05 from the 2.0−4.5 year mean. As mentioned previously, the *Daniel et al.* [1995] FC_{ratio} values were based on a combination of steady state model calculations, measurements from AASE I assuming a 3 year time period for transport into the lower stratosphere, and measurements from AASE II using mean age and tropospheric trends to calculate $\mu_{entry,x}$. Therefore, we were unable to precisely match our calculations to those of *Daniel et al.* [1995]. The agreement between our 4.75−5.25 values and those of *Daniel et al.* [1995] may be a result of the high latitude sample collection during both AASE I and II.

[44]   The HCFC 141b and 142b values for all three age ranges were significantly lower than the *Daniel et al.* [1995] values, which were adapted from *Solomon et al.* [1992]. HCFC 141b FC_{ratio} values ranged from 0.19−0.54 over the three age ranges. The *Daniel et al.* [1995] value was 0.72. HCFC 142b FC_{ratio} values were 0.06−0.14 over the three age ranges, while the *Daniel et al.* [1995] value was 0.36. Since very few stratospheric measurements were available for calculating the fractional loss of HCFCs 141b and 142b,

Figure 10. (opposite) Fractional contributions to measured organic chlorine from (a) CFCs, HCFCs, solvents, and CH_3Cl, and (b) from CH_3Cl during STRAT, POLARIS, and SOLVE. Fractional contributions to calculated inorganic chlorine from (c) CFCs, HCFCs, solvents, and CH_3Cl.
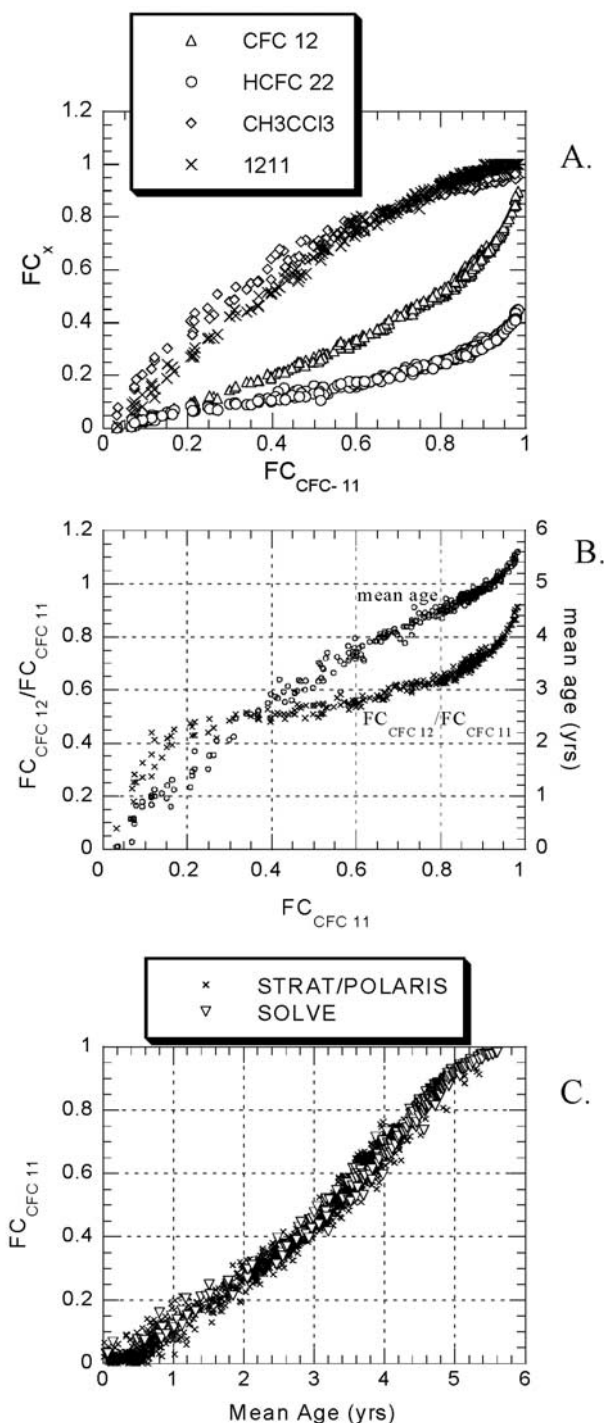
Figure 11. (a) Fractional chlorine release of CFC 12 (open triangles), HCFC 22 (open circles), CH_3CCl_3 (open diamonds), and halon 1211 (x's) relative to fractional chlorine release of CFC 11, (b) the ratio $\frac{FC_{CFC-12}}{FC_{CFC-11}}$ (x's) and mean age (open circles) relative to the fractional chlorine release of CFC 11, (c) fractional chlorine release of CFC 11 from STRAT and POLARIS (crosses) and SOLVE (triangles) relative to mean age.

the *Solomon et al.* [1992] values were calculated from steady state correlations of HCFC 142b with methane and HCFC 141b with N_2O using the Garcia/Solomon two dimensional chemistry/transport model. *Solomon et al.* [1992] used global measurements of methane and the HCFC 142b/methane correlation from their model to calculate a global FC_{ratio} for HCFC 142b. To calculate FC_{ratio} of HCFC 141b, they used high northern latitude measurements of N_2O from AASE and the HCFC 141b/N_2O correlation from their model. Both calculations assumed a 3 year time lag for transport between the troposphere and polar lower stratosphere.

[45] The differences between our calculations of FC_{ratio} for HCFCs 141b and 142b and those of *Daniel et al.* [1995] likely result from a combination of factors. *Daniel et al.* [1995] values may be influenced by the choice of lag time and the stratospheric loss of each compound, which was used to determine the correlations used by *Solomon et al.* [1992]. Our calculations included the effects of stratospheric mixing by incorporating the age spectrum. To test the sensitivity of incorporating the effects of mixing, we calculated FC_{ratio} from the SOLVE measurements using lag time and tropospheric trends only to calculate $\mu_{entry,x}$. For all compounds except HCFC 141b, the differences between FC_{ratio} calculated incorporating the age spectrum and those calculated using lag time only for the three age ranges were within the errors stated in Table 8. For HCFC 141b, the FC_{ratio} values calculated using mean age were lower by about 40% for the $4.75-5.25$ age range. This was because the expected mixing ratio for HCFC 141b calculated taking into account the age spectrum was higher than that calculated using the lag time as a result of mixing with younger air containing higher mixing ratios. For example, at 50 ppb N_2O the expected chlorine mixing ratio for HCFC 141b calculated taking into account the age spectrum was about 5 ppt (corresponding to the mixing ratio times the number of chlorine atoms) (Figure 6c), which was about 2.2 ppt higher than that calculated using the lag time only (Figure 4b). The higher expected mixing ratios from the age spectrum

Table 8. Fractional Chlorine Release Values Relative to CFC 11 Averaged Over Age Ranges $2.0-4.5$, $3.0-4.0$, and $4.75-5.25$ Years From SOLVE Measurements[a]

Compound	2.0–4.5-Year Mean	3–4-Year Mean	4.75–5.25-Year Mean	*Daniel et al.* [1995]
CFC 12	0.57 ± 0.05	0.55 ± 0.03	0.73 ± 0.04	0.60
CFC 113	0.65 ± 0.05	0.63 ± 0.03	0.79 ± 0.04	0.75
CFC 114	0.28 ± 0.02	0.27 ± 0.02	0.34 ± 0.02	na
CFC 114a	0.63 ± 0.10	0.63 ± 0.09	0.74 ± 0.05	na
Halon 1211	1.24 ± 0.07	1.27 ± 0.05	1.09 ± 0.02	1.10
HCFC 22	0.29 ± 0.02	0.28 ± 0.02	0.35 ± 0.02	0.35
HCFC 141b	0.23 ± 0.11	0.19 ± 0.07	0.54 ± 0.07	0.72
HCFC 142b	0.08 ± 0.04	0.06 ± 0.04	0.14 ± 0.06	0.36
CH_3CCl_3	1.29 ± 0.16	1.32 ± 0.09	1.05 ± 0.03	1.08
CCl_4	1.14 ± 0.06	1.16 ± 0.04	1.06 ± 0.02	1.06
CH_2Cl_2	1.31 ± 0.17	1.34 ± 0.10	1.04 ± 0.03	na
$CHCl_3$	1.34 ± 0.19	1.38 ± 0.12	1.05 ± 0.03	na
CH_3Cl 525 ppt	0.80 ± 0.04	0.80 ± 0.03	0.86 ± 0.03	na
CH_3Cl 550 ppt	0.85 ± 0.03	0.84 ± 0.03	0.87 ± 0.02	na
CH_3Cl 589 ppt	0.91 ± 0.05	0.90 ± 0.04	0.89 ± 0.01	na
FC_{CFC-11}	0.54 ± 0.15	0.58 ± 0.07	0.90 ± 0.03	na

[a]FC_{CFC-11} values are from SOLVE, STRAT, and POLARIS.

calculations resulted in a higher fractional loss after the measured mixing ratios were subtracted. The FC_{ratio} values calculated using lag time for the other two age ranges were also lower and were more variable because the difference between the calculated expected mixing ratio and the measured mixing ratios corresponding to N_2O values greater than 170 ppb was small. Clearly, the effect of how stratospheric mixing is taken into account in FC_{ratio} calculations is most important for compounds with significantly increasing nonlinear tropospheric mixing ratios over several years prior to sampling. For these compounds, the error of the mean age calculations is also important, however, the mean ages used here had an error of <0.5 years (<0.3 years for air with N_2O < 275 ppb) [*Andrews et al.*, 2001b], which does not account for the discrepancy between our FC_{ratio} values of HCFCs 141b and 142b and those of *Daniel et al.* [1995].

[46] In order to determine the effect of using our FC_{ratio} values on calculations of EESC, the following formula was adapted from *Daniel et al.* [1995] to calculate $EESC_p$ (partial EESC) based only on the compounds in Table 8 that contain fractional chlorine release values common to both this work and *Daniel et al.* [1995].

$$EESC_p = \left(\sum n_x X_i(r,t) \frac{FC_x}{FC_{CFC-11}} \right) FC_{CFC-11} \qquad (6)$$

where $X_i(r,t)$ is as defined in equation (1).

[47] $EESC_p$ was calculated using our revised values of FC_{ratio} for the three age ranges and the *Daniel et al.* [1995] values. $EESC_p1$ was calculated using the 2.0–4.5 year age range, $EESC_p2$ was calculated using the 3–4 year range, and $EESC_p3$ was calculated using the 4.75–5.25 year range. The difference between our $EESC_p$ values for each age range and those of *Daniel et al.* [1995] are shown in Figure 12a. The primary contributor to the difference in $EESC_p3$ was CFC 12. The FC_{ratio} for CFC 12 in the 4.75–5.25 age range was 0.73 while that of *Daniel et al.* [1995] for CFC 12 was 0.60. $EESC_p3$ was about 75 ppt at 315 ppb N_2O and 2550 ppt at 50 ppb N_2O. Therefore, the difference shown in Figure 12a at 50 ppb N_2O was about 5% of the total $EESC_p3$.

[48] The differences between the, $EESC_p1$, $EESC_p2$, and those of *Daniel et al.* [1995] were a combination of higher values of FC_{ratio} for the solvents and halon 1211 and lower values of FC_{ratio} for the CFCs and HCFCs. The differences using the $EESC_p1$ and $EESC_p2$ at 50 ppb N_2O (Figure 12) represent about 1.5% of the total $EESC_p1$.

[49] The differences between $EESC_p1$ and $EESC_p2$ were relatively small and ranged from 0.5 (out of 75 ppt $EESC_p1$) to about 8 ppt (out of about 2450 ppt $EESC_p1$) over the N_2O range sampled (Figure 12b).

[50] The FC_{ratio} values presented in Table 8 that were not calculated by *Daniel et al.* [1995] were for CFCs 114 and 114a, CH_3Cl, CH_2Cl_2, and $CHCl_3$. Of these compounds, only CH_3Cl was included in the *Daniel et al.* [1995] calculations of EESC and it was assumed to have a FC_{ratio} value of 1.0. Table 8 includes three values for CH_3Cl based on three different expected mixing ratios. The first was based on our measurement of 589 ppt at the tropical tropopause, the second was based on 550 ppt which was the global average reported by the *WMO* [1999], and the
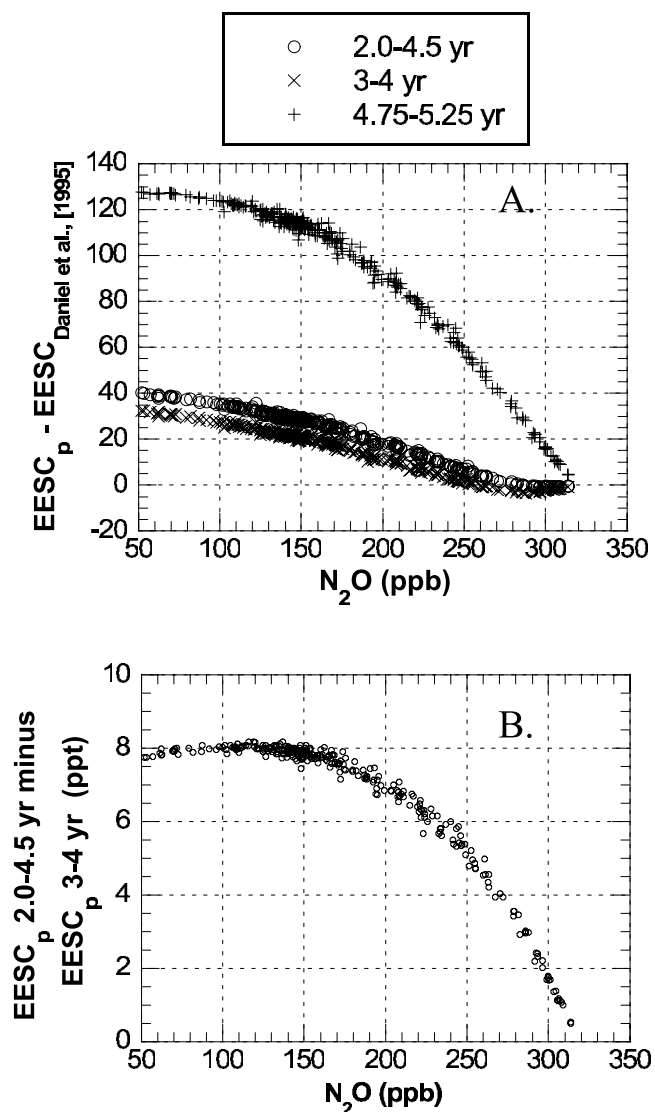
Figure 12. (a) The difference in ppt between $EESC_p$ and EESC *Daniel et al.* [1995] (see text for details) using average $\frac{FC_x}{FC_{CFC-11}}$ values over mean age ranges of 2.0–4.5 years (open circles), 3.0–4.0 years (x's), and 4.75–5.25 years (+'s), (b) The difference in ppt between $EESC_p$ calculated using the average values $\frac{FC_x}{FC_{CFC-11}}$ over the 2.0–4.5 year mean age range and $EESC_p$ calculated using the average $\frac{FC_x}{FC_{CFC-11}}$ values over the 3.0–4.0 year mean age range.

third was based on 525 ppt which was the lowest monthly average observed by CMDL at Samoa. The $\frac{FC_{CH_3Cl}}{FC_{CFC-11}}$ values were lowest for the lower mixing ratio and ranged from 0.80 to 0.91 for the two lower age ranges and 0.86–0.89 for the 4.75–5.25 year age range. The difference between our calculated value using 589 ppt CH_3Cl and the assumed value of *Daniel et al.* [1995] was about 10%, i.e., the chlorine contribution to EESC from CH_3Cl would be about 10% lower using our value. The difference would be about 20% lower using the value based on an expected mixing ratio of 525 ppt CH_3Cl. Inclusion of CFCs 114 and 114a, CH_2Cl_2, and $CHCl_3$ would add about 53 ppt of inorganic chlorine at 50 ppb N_2O (see Figures 5 and 6). This value

represents about 2–4% of the EESC values given by *Daniel et al.* [1995] and the EECl values given by *Montzka et al.* [1999].

[51] The most appropriate FC_{ratio} values to use for EESC or EECl calculations targeted at midlatitude lower stratospheric conditions would be the 3–4 year range. The most appropriate FC_{ratio} values for calculations targeted at maximal loss conditions as seen in polar vortex air would be the 4.75–5.25 year range. Inclusion of CFCs 114 and 114a, CH_2Cl_2, and $CHCl_3$ in EESC or EECl calculations would enhance the accuracy of the calculations and would have the greatest impact on calculations of future loadings as the influence of the shorter lived CFCs declines.

[52] *Montzka et al.* [1996, 1999] assumed a value of 0.8 for FC_{CFC-11} in their EECl calculations (the FC_{CFC-11} term outside the parenthesis in equation (6)). This value represented destruction of CFC 11 in a single pass through the stratosphere. However, Figure 11c, which includes SOLVE, STRAT, and POLARIS values, shows that an FC_{CFC-11} value of 0.8 corresponds to a mean age of about 4.5 years. The average FC_{CFC-11} values from all three campaigns for the 3–4 year and 4.75–5.25 mean age ranges are 0.58 and 0.90, respectively (Table 8). This suggests that for EECl calculations assuming a single pass through the stratosphere, a lower value of FC_{CFC-11} might be more appropriate.

4. Summary

[53] Measurements of organic chlorine containing compounds from whole air samples collected during the NASA SOLVE campaign in 2000 in the arctic region during northern hemisphere winter were used to provide a quantitative and comprehensive characterization of the organic chlorine budget. These measurements, together with calculations of mean age, measurements of tropospheric trends, and calculated effects of stratospheric mixing, were used to calculate the inorganic chlorine contributions from each compound to total inorganic chlorine. Tropospheric trends were determined from a combination of CMDL [*Montzka et al.*, 1999; *Hall et al.*, 2001] and NCAR surface measurements. Mean age and spectral width calculations were derived from CO_2 measurements [*Andrews et al.*, 2001a, 2001b]. Calculations of expected mixing ratios using age spectra to account for stratospheric mixing were based on the work of Waugh and Hall (submitted manuscript, 2001). Expected mixing ratio for a given compound represents the total amount of chlorine in both organic and inorganic forms from that compound present at a given sampling location and time and was determined using mean age of the sample, the age spectrum, and the tropospheric trend of the compound. Inorganic chlorine was calculated as the difference between the expected mixing ratios and the measured mixing ratios for each compound. Correlations between the measured organic and calculated inorganic mixing ratios of each compound versus N_2O provide useful information for correlative measurement studies and model validation studies.

[54] Inorganic chlorine calculations that accounted for mean age, tropospheric trends, and stratospheric mixing were compared to those calculated using mean age as a lag time and tropospheric trends only. For compounds with nonlinearly increasing (decreasing) tropospheric mixing ratios the calculated expected mixing ratios were higher (lower) when stratospheric mixing was included than calculations based only on lag time and tropospheric trends. CH_3CCl_3, and CFCs 11,12, and 113 showed the greatest differences in chlorine amounts between calculations that included stratospheric mixing relative to those that included lag time and tropospheric trends only. The total chlorine difference between calculations based on lag time and tropospheric trends only and those that included stratospheric mixing was about 53 ppt chlorine at 50 ppb N_2O.

[55] Total organic chlorine (the sum of chlorine from all compounds) measured at tropospheric values of N_2O was about 3500 ppt. Calculated total inorganic chlorine was about 3400 ppt at N_2O values of 50 ppb. CFCs contributed 55–70% of the measured total organic chlorine. CFCs 11, 12, and 113 were the major contributors to the CFC fraction of total organic chlorine. HCFCs and solvents each contributed 5–25% to total organic chlorine while CH_3Cl contributed about 15%. The fractional contribution from CH_3Cl was the same (15%) across the total organic chlorine range and was consistent with results from STRAT and POLARIS. Within the HCFC and solvent groups, HCFC 22, CCl_4, and CH_3CCl_3 were the major contributors to organic chlorine. CFCs, HCFCs, and solvents with upper tropospheric mixing ratios less than 15 ppt contributed a total of about 90 ppt to total organic chlorine. In general, contributions of individual compounds to total inorganic chlorine mirrored the contributions to total organic chlorine.

[56] We calculated fractional chlorine release relative to CFC 11 for each compound ($\frac{FC_x}{FC_{CFC-11}}$ or FC_{ratio}) for three age ranges, 2.0–4.5, 3–4, and 4.75–5.25 years. We then compared our values with those of *Daniel et al.* [1995]. The most significant differences between our FC_{ratio} calculations and those of *Daniel et al.* [1995] were for HCFCs 141b and 142b. Our HCFC 141b FC_{ratio} values were 0.19–0.54 over the three age ranges, while the *Daniel et al.* [1995] value was 0.72. Our HCFC 142b FC_{ratio} values were 0.06–0.14 over the three age ranges, while the *Daniel et al.* [1995] value was 0.36. We are uncertain of the reasons for these differences.

[57] We calculated FC_{ratio} over three age ranges to examine the magnitude of the variability over age ranges commonly used in calculations of equivalent stratospheric chlorine. We calculated EESC using only those compounds with fractional chlorine release relative to CFC 11 reported by *Daniel et al.* [1995]. The differences between EESC calculations using our relative fractional chlorine release values for the first two ranges and those of *Daniel et al.* [1995] were on the order of 32–40 ppt chlorine at 50 ppb N_2O. These differences were a result of a combination of our lower values of FC_{ratio} for CFCs 12 and 113 and higher values for the solvents and halon 1211 relative to the values reported by *Daniel et al.* [1995]. The greatest difference in EESC calculations based on chlorine release values of [*Daniel et al.*, 1995] relative to our values were in the 4.75–5.25-year range with a difference of almost 130 ppt chlorine at 50 ppb N_2O. Most of this difference was due to our higher fractional chlorine release value of 0.73 for CFC 12 relative to the 0.60 value of *Daniel et al.* [1995].

[58] Our evaluation of FC_{CFC-11} relative to mean age showed average values of about 0.58 for the 3–4 year age

range and about 0.90 for the 4.75–5.25 age range. *Montzka et al.* [1996, 1999] assumed a value of 0.8 for FC_{CFC-11} in their EECl calculations and also assumed it represented CFC 11 loss from a single pass through the stratosphere. Based on our measurements, an FC_{CFC-11} value of 0.8 corresponds to a mean age of about 4.5 years. This suggests that for EECl calculations assuming a single pass through the stratosphere, a lower value of FC_{CFC-11} might be more appropriate.

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E. L. Atlas, S. G. Donnelly, S. M. Schauffler, and V. Stroud, National Center for Atmospheric Research, Boulder, CO, USA. (sues@acd.ucar.edu)

A. Andrews, NASA Goddard Space Flight Facility, Greenbelt, MD, USA.

G. S. Dutton, J. W. Elkins, D. F. Hurst, S. A. Montzka, and P. A. Romashkin, NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, CO, USA.