Temporal development of total chlorine in the high-latitude stratosphere based on reference distributions of mean age derived from CO_2 and SF_6

Andreas Engel, Martin Strunk,[1] Melanie Müller, and Hans-Peter Haase
Institut für Meteorologie und Geophysik, Johann Wolfgang Goethe-Universität Frankfurt, Frankfurt, Germany

Christian Poss and Ingeborg Levin
Institut für Umweltphysik, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany

Ulrich Schmidt
Institut für Meteorologie und Geophysik, Johann Wolfgang Goethe-Universität Frankfurt, Frankfurt, Germany

Received 2 March 2001; revised 12 July 2001; accepted 17 July 2001; published 19 June 2002.

[1] We present balloon-borne observations of CO_2 and SF_6 and derived vertical profiles of mean age for polar winter (inside vortex) and for midlatitude (nonwinter) conditions. For SF_6-derived mean ages above 5 years a mesospheric SF_6 sink may lead to an overestimation of mean age, while for younger mean ages (below 2 years) the seasonal cycle of CO_2 may influence the mean age determination based on CO_2. We suggest that SF_6 be used as an age tracer in the lower part of the stratosphere (i.e., for low mean age), whereas CO_2 will be the better age tracer for older air. The mean age distributions together with an estimate of the width of the age spectrum are used to estimate the stratospheric chlorine loading. On the basis of an emission scenario and the lifetimes of chlorine-containing compounds we estimate the future stratospheric chlorine loading. Inside the polar vortex, at an altitude of 20 km, we expect total chlorine to return to the values present in this region in 1980, when the ozone hole first appeared, around the year 2060. This estimate is based on the assumption that the general transport characteristics will not change over the period of the analysis and can thus be regarded as a best estimate based on stationary transport, the assumed set of lifetimes and emissions, and the mean age distribution derived from our measurements. As other factors influencing ozone may undergo temporal changes, this does not mean that ozone will necessarily recover at this time. While total chlorine is probably a good proxy for inorganic chlorine at altitudes above 20 km inside the polar vortex, the changing halocarbon mix may actually lead to an earlier return of inorganic chlorine to pre-ozone-hole values at lower altitudes. *INDEX TERMS:* 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 3334 Meteorology and Atmospheric Dynamics: Middle atmosphere dynamics (0341, 0342); *KEYWORDS:* stratosphere, age, CO_2, SF_6, chlorine, trends

1. Introduction

[2] The emissions of chlorofluorocarbons (CFCs) and other chlorine compounds have been reduced because of the regulations enforced by the Montreal Protocol and its subsequent amendments. This is clearly visible in tropospheric [*Elkins et al.*, 1993; *Cunnold et al.*, 1994; *Montzka et al.*, 1996, 1999; *Prinn et al.*, 2000] and stratospheric [*Engel et al.*, 1998] time series of their mixing ratios. The question as to when this reduction in emissions will result in stratospheric chlorine levels which are comparable with the values observed before the onset of the Antarctic ozone hole in the late 1970s is subject to considerable debate. While *Solomon* [1999, p. 304] states that "by about 2040, the chlorine will return to levels close to those of the late 1970s" and that "all other things being equal, the Antarctic ozone hole and midlatitude ozone depletion will likely disappear around this time," other studies still assume levels of chlorine high enough for severe ozone depletion as late as 2070 [*Waibel et al.*, 1999; *Shindell et al.*, 1998]. As the stratosphere is also expected to cool in the future because of increased radiative cooling by greenhouse gases, it is important to understand when chlorine levels will drop in order to predict whether severe ozone depletion comparable to that observed in the austral spring could occur in the

[1] Now at TLC-GmbH, Frankfurt, Germany.

0148-0227/02/2001JD000584$09.00

Northern Hemisphere polar winter [e.g., *Shindell et al.*, 1998; *Waibel et al.*, 1999; *Dameris et al.*, 1998]. In any case, as it is uncertain how the dynamics of the stratosphere may change, it is important to reduce emissions as strongly as possible and to monitor the temporal trend of chlorine in the stratosphere.

[3] The source gases for stratospheric chlorine are emitted at the surface of the Earth and are then transported into the stratosphere. Thus a given tropospheric evolution can only be observed in the stratosphere with a temporal delay. During transport into and within the stratosphere, the air masses are further mixed. The mean effect of transport and mixing can be characterized by the concept of age of air [see, e.g., *Kida*, 1983; *Schmidt and Khedim*, 1991; *Hall and Plumb*, 1994]. A stratospheric air mass is not characterized by a single sharp age value, because it is composed of an irreversible mixture of parcels that have travelled along different pathways with different associated transport times. This distribution of transport times is called the age spectrum. Its first moment is the mean age, and the second moment is the width of the age spectrum (see *Hall and Plumb* [1994] for a thorough discussion and the definitions of the mean age and the width). Even for conserved species, the stratospheric mixing ratios of trace gases do not simply lag the tropospheric mixing ratios. Only in the case of linear growth rates, the width of the age spectrum would not influence the propagation of tropospheric mixing ratios into the stratosphere. As air masses containing different initial levels of total chlorine are mixed in the stratosphere, the nonlinearity observed in the tropospheric trends during the 1990s will affect stratospheric total chlorine levels. The use of a simple lag time to describe the evolution of total stratospheric chlorine during this time period, as applied in several previous studies [e.g., *Woodbridge et al.*, 1995; *Engel et al.*, 1997], does not take this effect into account and will introduce errors in the determination of total chlorine and also of inorganic available chlorine. As the age spectrum cannot be measured directly, it needs to be parameterized in some way for calculations of the propagation of trace gas trends from the troposphere into the stratosphere. Such parameterizations have been suggested by *Hall and Plumb* [1994] and *Volk et al.* [1997]. It should also be noted that most of the current models underestimate the mean age of stratospheric air [*Hall et al.*, 1999]. Consequently, they will not reproduce the temporal evolution of stratospheric chlorine correctly.

[4] In this paper we use simultaneous balloon-borne observations of SF_6 and CO_2 (extended from the study of *Strunk et al.* [2000]) to deduce the mean age of air. We discuss the effect of different parameterizations on the derived mean age values and present a best estimate of mean age which is based on a combination of the observations of SF_6 and CO_2. We deduce a correlation between N_2O and this best estimate and use this correlation to calculate reference profiles of mean age from N_2O reference profiles (average profiles calculated from many observations) in high latitudes (inside vortex) and midlatitudes (spring to fall, referred to as nonwinter in the following) of the Northern Hemisphere. A comparison of total chlorine levels in the Arctic and Antarctic polar vortices showed good agreement (see Figure 1.7.1–3 of *World Meteorological Organization* (*WMO*) [1989]), and the comparison of our Arctic polar vortex profile of N_2O also shows close agreement with typical distribution in the Antarctic [*Podolske et al.*, 1989]. The high-latitude observations in the Northern Hemisphere can thus be used as a proxy for high-latitude Southern Hemisphere values. The derived mean age distribution is used to determine the propagation of tropospheric trends into the stratosphere, again taking into account the width of the age spectrum. The tropospheric trends are taken from the observations of the monitoring networks [e.g., *Elkins et al.*, 1993; *Montzka et al.*, 1996; *Cunnold et al.*, 1994; *Prinn et al.*, 2000]. For future trend calculations we considered three scenarios: (1) the base scenario (A1) given by *WMO* [1999] based on the current status of the Montreal Protocol and including assumptions about future emissions in developing countries, (2) zero emissions, and (3) constant emissions at the level assumed for the year 2000 in the base scenario. From the increase in stratospheric total chlorine calculated for the past we determine the amounts of total chlorine that were present in the stratosphere at the onset of Antarctic ozone depletion at different altitudes. Finally, we estimate when these values should be present in the stratosphere again.

[5] Total stratospheric chlorine (ΣCl) is the sum of inorganic chlorine (Cl_y) and organic chlorine (ΣCl_{org}). The most relevant parameter for stratospheric ozone depletion is, however, the inorganic fraction of chlorine, Cl_y, rather than total chlorine. The mix in chlorine source gases will shift toward longer-lived gases in the future, because the shorter-lived species will disappear faster from the atmosphere than the longer-lived compounds. Therefore it is actually expected that at a given altitude the ratio of Cl_y to ΣCl will decrease in the future. While this should lead to a faster recovery of Cl_y values than of ΣCl levels, it is not expected to be crucial for altitudes above 20 km in the polar winter vortices, where the conversion of chlorine to the inorganic fraction is nearly complete [see, e.g., *Schmidt et al.*, 1991].

2. Experimental Procedure

[6] The SF_6, CO_2, and N_2O measurements presented in this study are based on gas chromatographic analysis of whole air samples collected by balloon-borne cryogenic whole air samplers [*Schmidt et al.*, 1987; *Engel et al.*, 1997] at high latitudes and midlatitudes of the Northern Hemisphere. While N_2O has been measured since 1978 at midlatitudes and since 1987 at high latitudes, SF_6 has only been measured regularly since 1997. CO_2 has been measured by *Schmidt and Khedim* [1991] in older samples, but since 1997 the measurements have been performed at the Institut für Umweltphysik, University of Heidelberg (IUP Heidelberg), and the precision of the analysis has been improved, allowing for a more precise mean age determination than that given by *Schmidt and Khedim* [1991].

[7] The analytical techniques have been described in detail elsewhere [*Strunk et al.*, 2000; *Engel et al.*, 1997; *Greschner*, 1995]. The precision of the SF_6 measurement is better than 2% of the current tropospheric value, which corresponds to an uncertainty of 4–5 months in the derived mean age. The measurements are reported relative to the calibration scale of M. Maiss and I. Levin (IUP Heidelberg). The N_2O data measured by our group since 1997 have a

precision of about 1% of the current tropospheric values, while those obtained prior to 1995 have a precision of better than 5% only. The data are reported relative to a standard from the National Oceanic and Atmospheric Administration Climate Modeling and Diagnostics Laboratory (NOAA CMDL), which has an absolute accuracy of 1% (J. Elkins, NOAA CMDL, private communication, 1994). CO_2 and CH_4 are measured by IUP using a gas chromatograph-flame ionization detector (GC-FID) system with a precision of better than 0.2 ppm and 2 ppb, respectively. High-quality simultaneous data for SF_6, CO_2, and N_2O are available for four flights performed in the years 1997 and 2000 (Table 1).

Table 1. Simultaneous Balloon-Borne Observations of SF_6, CO_2, and N_2O

Flight Date	Latitude	Comments
11 Feb. 1997	68°N	inside vortex
23 June 1997	44°N	"blob" of polar air at 27 km [*Strunk et al.*, 2000]
27 Jan. 1997	68°N	deep inside vortex
1 March 2000	68°N	deep inside vortex

3. Comparison of SF_6- and CO_2-Derived Mean Age

[8] As explained in section 1, the transit time of air from the troposphere to a given location in the stratosphere is described by the age of the air [e.g., *Schmidt and Khedim*, 1991; *Hall and Plumb*, 1994; *Volk et al.*, 1997; *Kida*, 1983]. An ideal tracer for the determination of the mean age should have neither sinks nor sources in the stratosphere and should have shown a linear tropospheric trend over the past 10 to 15 years. The mean age derived from SF_6 and CO_2 (two tracers which fulfil these conditions rather well) shows very good agreement (±0.5 years) for observations performed in 1997 for values up to about 6 years [*Strunk et al.*, 2000]. Using observation of SF_6 and CO_2 in the Arctic stratosphere in early 2000 in the frame of the Third European Stratospheric Experiment on Ozone 2000/SAGE III Ozone Loss and Validation Experiment (THESEO 2000/SOLVE) campaign, we extend the study of *Strunk et al.* [2000]. The small amount of CO_2 produced in the stratosphere from the oxidation of CH_4 is taken into acocunt by correcting the CO_2 measurements based on the simultaneous CH_4 observations.

[9] The mean age derived from a conserved tracer is affected by nonlinearities in the tropospheric growth rates [*Hall and Plumb*, 1994; *Daniel et al.*, 1996; *Volk et al.*, 1997] due to the width of the age spectrum. For a second-order growth rate the nonlinearity can be accounted for by including a correction term if the width of the age spectrum is parameterized as a function of the mean age. This spectrum cannot be measured directly, but *Andrews et al.* [1999, 2001] have tried to derive the distribution from highly resolved CO_2 measurements in the lower tropical stratosphere and in the midlatitude lower stratosphere, where the age spectrum may actually be bimodal [*Andrews et al.*, 2001]. We have chosen to assume a monomodal age spectrum and a parameterization of the age spectrum as suggested by *Hall and Plumb* [1994] and as used by *Volk et al.* [1997]. According to *Hall and Plumb* [1994] the width of the age spectrum Δ is related to the value of the mean age Γ in such a way that the ratio Δ^2/Γ is rather constant throughout the stratosphere. The mean age derived in this way is sensitive to the parameterization used. Using an age tracer which shows an increasing tropospheric growth rate (i.e., the second-order term in the fit equation is positive), the assumption of a wider spectrum will result in larger mean age values. *Hall and Plumb* [1994] found values between 0.4 and 0.8 for the ratio Δ^2/Γ throughout the stratosphere, while *Volk et al.* [1997] assume a higher value (1.25) mainly based on the results of the model of *Waugh et al.* [1997].

[10] The calculated mean age values are also quite sensitive to the tropospheric input functions used in the calculation. As we are investigating mean ages with values as high as 7–8 years, it was necessary to use fit functions which cover a long time period. We have chosen to fit second-order functions and use a time period of 15 years prior to the year of observation. For CO_2 we have used the deseasonalized mean (12 month running mean) of Mauna Loa and American Samoa data of NOAA CMDL [*Conway et al.*, 1994]) back to 1980 and Mauna Loa annual means from *Keeling et al.* [1996] prior to that. As a reference function for the tropospheric increase of SF_6 we have used the temporal trend reported by *Geller et al.* [1997]. Note that the calibration scales of M. Maiss and I. Levin and those of NOAA CMDL (on which the fit function given by *Geller et al.* [1997] relies) differ slightly, the NOAA CMDL scale being 1% lower than the scale of M. Maiss and I. Levin [*WMO*, 1999]. In order to derive the mean age from our observations we have thus scaled the *Geller et al.* [1997] fit downward accordingly. As done by *Strunk et al.* [2000], we do not take into account a temporal delay in the trends between the global mean and the tropical tropopause.

[11] Figure 1 shows the mean age values based on our SF_6 and CO_2 observations using the parameterization value of 0.7 as suggested by *Hall and Plumb* [1994]. There is an indication that using SF_6 and CO_2 as age tracers does not yield the same results for SF_6-derived mean age values above 5 years. It has been suggested [*Hall and Waugh*, 1998; *Strunk et al.*, 2000] that SF_6 has a mesospheric sink and that this may interfere with the mean age determination for air masses which have experienced mesospheric influence. Figure 1 suggests that this may happen for SF_6 mean ages above 5 years under the conditions met during our flights in 2000; however, the effect is less pronounced for the observation in 1997 (where the observed mean age values were somewhat lower). For air masses with mean age values above 5 years the use of SF_6 as an age tracer may thus lead to an overestimation of the mean age, though this does not seem to be a general phenomenon, considering the good agreement for the observations from 1997. On the other hand, CO_2 has a pronounced seasonal cycle in the troposphere, which may influence the determination of mean age in the lower part of the stratosphere, where this seasonal cycle is not yet completely damped out. We have thus chosen to use the SF_6-derived mean age when its value is less than 2 years, the mean of the SF_6-derived and the CO_2-derived mean ages when SF_6-derived mean age is between 2 and 5 years, and the CO_2-derived mean age when the SF_6-derived mean age is above 5 years.

[12] Figure 2 shows the difference between SF_6- and CO_2-derived mean ages as a function of CO_2-derived

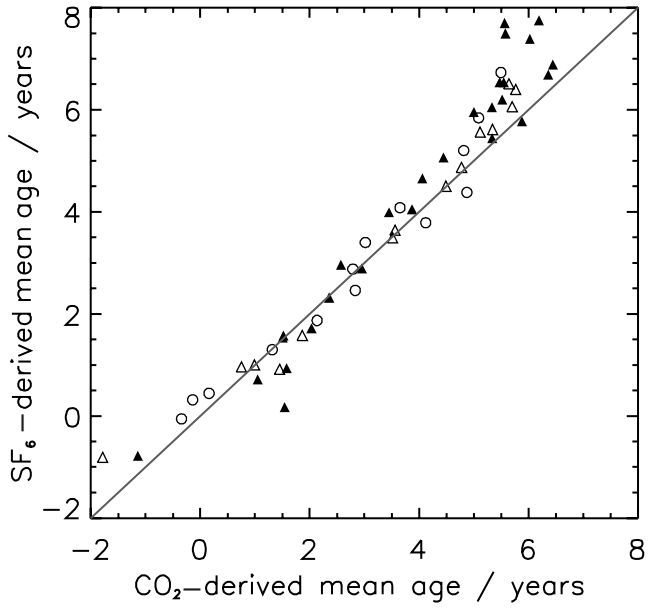

Figure 1. Correlation between CO_2- and SF_6-derived mean age from both high-latitude and midlatitude flights performed in the years 1997 and 2000. As a tropospheric reference the global trend published by *Geller et al.* [1997] is used. The midlatitude observations are shown by circles, and high-latitude observations are shown by triangles. The solid symbols mark 1997 observations, while the open symbols are for 2000 (only high latitude).

mean age for observations with a CO_2-derived mean age between 2 and 5 years, again using the parameterizations of the age spectrum as suggested by *Hall and Plumb* [1994], i.e., $\Delta^2/\Gamma = 0.7$. We have tested the effect of different parameterizations of the age spectrum, using different values for the ratio Δ^2/Γ, i.e. 0 (a sharp age spectrum), 0.7, and 1.25 (as suggested by *Volk et al.* [1997]) for the lower stratosphere. While the assumption of a sharp age leads to somewhat lower CO_2-derived mean age than SF_6-derived mean age, the use of the value of 1.25 gives systematically higher SF_6-derived mean ages. The differences are, however, quite small (below 0.5 years between the sharp age and the Δ^2/Γ = 1.25 parameterization). The value of 0.7 gave the best overall agreement between SF_6-derived and CO_2-derived mean ages. Although an effect of mesospheric loss of SF_6, which could produce a rather similar effect, cannot be excluded for air masses having mean ages below 5 years, this parameterization, which assumes a sharper age spectrum, is favored in order to avoid an overestimation of effects caused by the width of the spectrum. For all but two data points (see Figure 2) with SF_6-derived mean age between 2 and 5 years the observed difference between CO_2- and SF_6-derived mean ages is below 0.6 years, which is within the combined 1σ errors of the mean age determination. In the following, whenever there is no mention of how the age spectrum was parameterised, we have thus used the relation $\Delta^2 = 0.7\Gamma$ given by *Hall and Plumb* [1994].

[13] As shown by *Hall and Plumb* [1994], mean age and long-lived tracers like, e.g., N_2O are expected to be well correlated. Figure 3 shows the observed correlation between N_2O and mean age derived in the way described above. The third-order least squares fit to these data gives

$$\Gamma = 6.03 - 0.0136\,N_2O + 8.5892 \times 10^{-5}\,N_2O^2 - 3.376968 \times 10^{-7}\,N_2O^3$$

where the mean age is given in years and N_2O in ppb. It is interesting to note that the correlation between N_2O and mean age seems to be more compact at lower mean age (higher N_2O) values. This cannot be explained by measurement errors but is probably real atmospheric variability caused by the shorter lifetime of N_2O at higher altitudes, which leads to decorrelation, as shown by *Plumb and Ko* [1992].

4. Reference Profiles of N_2O and Mean Age at Midlatitudes and Under Polar Winter Conditions

[14] In order to determine reference profiles or typical vertical distributions of trace gases it is desirable to have as many observations as possible performed in different years, so that year-to-year variations are minimized. Because we only have good simultaneous SF_6 and CO_2 data for observations in 1997 and 2000, we have chosen to use N_2O reference profiles and the correlation observed between N_2O and mean age.

[15] Reference profiles of N_2O are average profiles calculated from observations in different years but under similar meteorological conditions [*Schmidt et al.*, 1991]. As there is strong latitudinal and seasonal variation in the vertical distribution of long-lived trace gases in the strato-

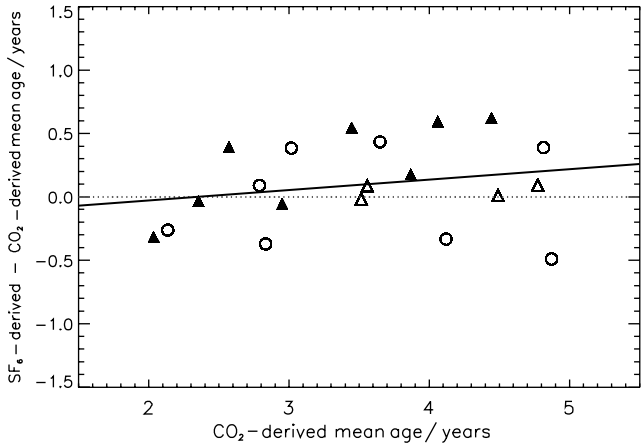

Figure 2. Difference between SF_6-derived age and CO_2-derived age for age values between 2 and 5 years using an age width parameterization of $\Delta^2/\Gamma = 0.7$ suggested by *Hall and Plumb* [1994] for the calculation of the mean age. The influence of the nonlinearity correction at these mean age ranges is rather small (less than 0.5 years between the assumption of a sharp age distribution and the value of $\Delta^2/\Gamma = 1.25$ suggested by *Volk et al.* [1997]). The solid line is the fit to the data, and the dashed line is the expected 1:1 correlation. Symbols are the same as in Figure 1.

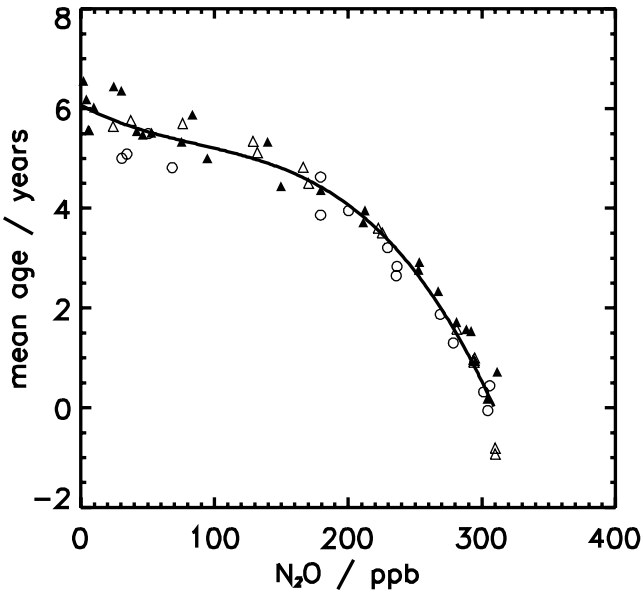

Figure 3. Correlation between N_2O and mean age as observed during the four flights listed in Table 1, using the best estimate of mean age based on a combination of CO_2 and SF_6 observations. The symbols are the same as used in Figure 1.

sphere, reference profiles must be calculated for specific conditions. Here we present two reference profiles, one for high-latitude winter conditions deep inside of the polar vortex and one for midlatitude nonwinter conditions. N_2O shows an increase with time in the troposphere which is rather small and rather constant with an average of about 0.25% per year [*WMO*, 1999]. Although this trend is small, we have chosen to correct for it in the calculation of the reference profiles in a very simple way, by taking the mean age of the air (calculated from the correlation given above) and scaling the measurements with the ratio of the tropospheric N_2O at entry for the reference date and the measurement date. Such a procedure ignores the effect of tracer transience described, e.g., by *Volk et al.* [1997] and may only be applied for chronological tracers, i.e., tracers with infinite lifetime and linear growth rates. The error introduced here is, however, very small (below 0.5%) because of the small and constant trend of N_2O in the troposphere. For other tracers like, e.g., CFCs such a procedure may give erroneous results. After this trend correction the measurements are binned according to pressure, altitude, or potential temperature, whichever reference profile is desired, and averaged. The flights used for the N_2O reference profiles presented here are listed in Table 2. The N_2O reference profiles for polar winter deep inside vortex and midlatitude nonwinter conditions and the mean age profiles deduced from these are shown in Figure 4. Because of the well-known effect of subsidence inside of the polar vortex, the N_2O values at a given altitude are lower inside the vortex, whereas the corresponding mean age values are higher.

[16] These profiles are used to calculate the propagation of the tropospheric trends into the stratosphere. We will discuss in section 6 the chlorine loading of the Antarctic winter stratosphere, which we will base on our Arctic observations. In order to do this, we need to ensure that mean N_2O profiles in the two polar vortices are comparable. A comparison with the average N_2O profiles given by *Podolske et al.* [1989] shows that their N_2O values observed up to 20 km in the austral vortex are in very good agreement with our observations in the Arctic. The increase in N_2O over the time period between these observations (about 3%) has been taken into account but does not affect this comparison very strongly. A comparison of organic chlorine measured in the Arctic vortex (68°N) in February 1988 [*Schmidt et al.*, 1989] with observations at 70°S in August and September 1987 [*Heidt et al.*, 1989] also gave excellent agreement (see Figure 1.7.1-3 of *WMO* [1989]). Vertical distributions of trace gases deep inside the vortices of the two hemispheres are thus quite similar. A comparison of mean age derived at 20 km altitude (5.3 years) with the values given by *Daniel et al.* [1996], based on observations of CO_2 and CFC-115 for the Arctic stratosphere (5 to 6 years), also shows good consistency.

[17] The vertical profiles of mean age based on the combination of CO_2 and SF_6 measurements from the years 1997 and 2000 and N_2O reference profiles are also in good agreement with earlier observations by *Schmidt and Khedim* [1991], who noted a region of rather constant mean age both in high-latitude and midlatitude observations above a given pressure level. This can also be obsMerved in our reference profiles and is also in agreement with CO_2 observation over Japan by *Nakazawa et al.* [1995]. The mean age value reported by *Schmidt and Khedim* [1991] was 5.6 ± 1.1 years. This is in excellent agreement with the values obtained in the upper part of our reference profiles, which range between 5 and 6 years, indicating that there has been little change in mean age over the past 20 years.

5. Past and Future Time Series of Tropospheric Mixing Ratios of Chlorine Source Gases

[18] As explained in section 4, we will use the average mean age profiles to calculate the propagation of tropospheric trends of total chlorine into the stratosphere. The chlorine compounds considered in this study are the most abundant source gases for stratospheric chlorine, i.e., CFC-12 (CCl_2F_2), CFC-11($CClF_3$) and CFC-113 ($C_2Cl_3F_3$), HCFC-22 ($CHClF_2$), CH_3CCl_3, CCl_4, and CH_3Cl. Together

Table 2. Balloon Observations Used in the Calculation of the Reference Profiles of N_2O

High Latitude/Deep Inside Vortex 68°N	Midlatitude 44°N
5 Feb. 1987	10 Sept. 1983
27 Jan. 1995	31 March 1985
3 Feb. 1995	21 Oct. 1985
27 Jan. 2000	16 Sept. 1987
1 March 2000	5 Nov. 1990
	10 Nov. 1990
	20 June 1991
	15 March 1993
	20 Sept. 1993
	7 Oct. 1994
	23 June 1997

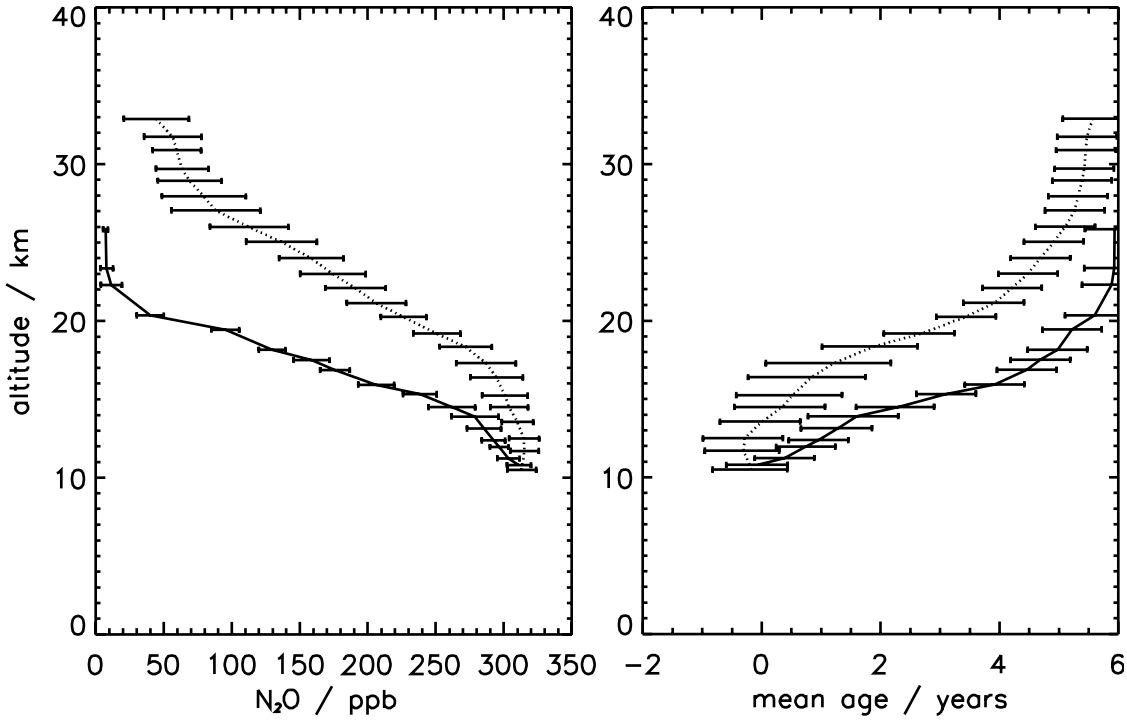

Figure 4. Reference profiles for N_2O (left plot) for midlatitudes (nonwinter conditions) and high latitudes (deep inside the polar vortex conditions) calculated from the measurements shown in Table 2. While many flights exist with observations of N_2O for both midlatitudes and high latitudes, there are not enough observation of SF_6 to calculate reference profiles. The mean age references (right plot) have thus been derived from the N_2O reference profiles, using the correlation function given above. Dashed lines represent the midlatitude reference, and solid lines represent the high-latitude reference. The error bars represent 1σ variability.

these species account for more than 98% of the organic chlorine source in the stratosphere, based on the compilation of source gas data given by *WMO* [1999]. The mixing ratio of CH_3Cl was included at a constant level of 600 ppt. The tropospheric data for the other compounds have been compiled from observations by NOAA CMDL and the Atmospheric Lifetime Experiment-Global Atmospheric Gases Experiment-Advanced Global Atmospheric Gases Experiment (ALE-GAGE-AGAGE) network until 1999 [e.g., *Elkins et al.*, 1993; *Montzka et al.*, 1996; *Cunnold et al.*, 1994; *Prinn et al.*, 2000]. For the early period prior to 1976 only sparse data exist, and best estimates are based on the data compiled by *WMO* [1981]. Future levels of chlorinated source gases were calculated on the basis of the predicted emissions of CFCs as given in the base scenario of *WMO* [1999] and on the basis of the best estimate of the respective lifetimes (CCl_3F, 45 years; CCl_2F_2, 87 years; $C_2Cl_3F_3$, 100 years; CCl_4, 32 years; CH_3CCl_3, 5 years; and $CHClF_2$, 16years; based on *WMO* [1999]) using

$$X_i(t) = X_i(t_0) + \frac{E_i(t-t_0)}{M_i}\frac{M_{\mathrm{atm}}}{m_{\mathrm{atm}}} - X_i(t_0)\exp\left(-\frac{(t-t_0)}{\tau_i}\right), \quad (1)$$

where $X_i(t)$ is the mixing ratio of compound i at time t, which is calculated from the mixing ratio at time t_0, $X_i(t_0)$, the emissions $E_i(t - t_0)$ in the time period, and the lifetime τ_i of the compound. M_i and M_{atm} are the molar masses of the compound and the atmosphere, and m_{atm} is the mass of the atmosphere. Total chlorine was calculated from the individual compounds, each weighted by the number of chlorine atoms. Quadratic fits were then applied for each year using the data for the last 15 years in order to be consistent with the fit period of the CO_2 data. As a sensitivity test, two other scenarios were calculated; one assuming an immediate stop of all emissions and one assuming that emissions are kept at the levels estimated for the year 2000 in the base scenario. These scenarios can be regarded as upper and lower limits of the possible future evolution, showing the large uncertainties in the future evolution of total chlorine. The calculated tropospheric organic chlorine loading (ΣCl_{org}, which is equal to ΣCl for the stratosphere) is shown in Figure 5. A further uncertainty is given by the atmospheric lifetimes of the chlorine gases. Our calculations are based on the best estimates for the lifetimes given by *WMO* [1999], which are partly based on model calculations which may not represent stratospheric transport correctly, as shown by *Hall et al.* [1999]. These lifetimes are lower than previous estimates [e.g., *WMO*, 1994] and imply a faster recovery of atmospheric chlorine levels. If the lifetimes of the chlorine source gases were indeed longer than assumed here, the decrease of atmospheric chlorine will take longer than estimated here.

[19] The uncertainties in the future evolution of the tropospheric chlorine are by far the largest error source in estimating future stratospheric chlorine loading, as it

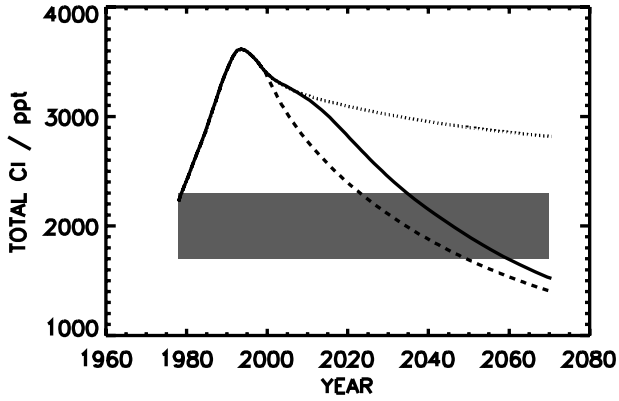

Figure 5. Comparison of predicted tropospheric chlorine loading based upon three different scenarios: (1) the base scenario (A1) given by *WMO* [1999] based on the current status of the Montreal Protocol and including assumptions about future emissions from developing countries (solid line), (2) zero emissions (dashed line), and (3) constant emissions at the level assumed for the year 2000 in the base scenario (dotted line). In the case that emissions stabilise at the values predicted for 2000, pre-ozone-hole values (1770 ppt at 20 km altitude) as derived in section 6 will never be reached. If all emissions were stopped immediately, the pre-ozone-hole values could be reached again about 10 years earlier. Because of the banking of CFC this is, however, not a realistic possibility.

depends on the adherence of the international regulations. In order to focus on the propagation of trends into the stratosphere we will not discuss these uncertainties further, but one should remember that the discussion in section 6 is based on an emission scenario with high uncertainties.

6. Trend of Total Stratospheric Chlorine

[20] The trend of total chlorine ΣCl at various altitudes in the stratosphere can be derived from the observed tropospheric trends of ΣCl_{org} by considering the temporal delay (the age of the air) with which these propagate into the stratosphere. The budget studies presented by, e.g., *Zander et al.* [1996], *Russell et al.* [1996], and *Anderson et al.* [2000] clearly indicate that the organic sources gases observed in the troposphere can account for total chlorine (ΣCl) observed in the stratosphere and that their tropospheric evolution can thus be used to derive the stratospheric chlorine loading. There are two main uncertainties associated with this. One is the knowledge of the typical vertical distribution of mean age, which is addressed in section 4, and the other is again the age spectrum, which is parameterized in the same way as explained in section 3. Note that this parameterization is only valid for conserved species, but not for species with chemical loss, like, e.g., CFCs [*Hall and Plumb*, 1994; *Volk et al.*, 1997; *Plumb et al.*, 1999], because the spectrum of relevant transport times for species with atmospheric loss will be dominated by younger air masses (the molecules which were present in the older air masses of the spectrum have been subject to photolysis). However, though the individual CFCs are not conserved species, total chlorine is conserved in the stratosphere, where there are no known sinks for total chlorine (photochemistry leads to a change in the partitioning between the organic and inorganic fractions but does not change the amount of total stratospheric chlorine). By using the average mean age profile $\Gamma(z)$ shown in Figure 4 together with the fit functions for tropospheric chlorine derived in section 5, we can thus derive the level of total stratospheric chlorine at a time t and an altitude z in analogy to equation (17) of *Volk et al.* [1997]

$$\Sigma Cl(t,z) = a + b[t - \Gamma(z)] + c[t - \Gamma(z)]^2 + 2c\Delta[\Gamma(z)]$$

using the fit parameters a, b, and c for the quadratic fit to the tropospheric data for the respective time period. As for CO_2, we have chosen to apply fits to 15 years of tropospheric data prior to each year. The results of this procedure for high latitudes under polar winter conditions are shown in Figure 6a for the time period from 1978 to 1999 and in Figure 6b for the time period 1978 to 2070. There are several aspects to note in these figures. First of all, as can be seen in Figure 6a, the maximum chlorine levels have already been reached in the lowest part of the stratosphere in 2000, where ΣCl has started to decline. At an altitude of about 20 km the maximum chlorine level was reached in 1999, whereas in the altitude region around 25 km, chlorine levels were still increasing in 2000, albeit very slowly. Another interesting feature is the maximum amount of ΣCl which is reached at different altitudes. Because of the width of the age spectrum the rather sharp maximum in tropospheric chlorine is ''smeared out'' in the stratosphere, leading to a lower peak level of ΣCl at higher altitudes, where the mean age is older and the spectrum is broader. This is in agreement with the findings of *Waugh et al.* [2001], who noted that the surprising observation of a very sharp peak in stratospheric HCl levels at 55 km altitude in Halogen Occultation Experiment (HALOE) data [*Anderson et al.*, 2000] is inconsistent with the expected smearing out. The effect is depicted in Figure 7, where the propagation of trends at 20 km altitude for the high-latitude winter reference is calculated using different parameterizations. The curves calculated without including the width of the spectrum show a peak in stratospheric chlorine which is just as sharp as in the troposphere. How strongly this smearing out occurs in the stratosphere will depend on the age spectrum and on its width. This effect is only of minor importance (about 50 ppt difference between sharp spectrum and parameterization with a very wide age spectrum, $\Delta^2 = 2\Gamma$) around 15 km, where the age spectrum is still rather sharp, but leads to a larger difference in the maximum values derived in the stratosphere above 20 km (difference of about 150 ppt). Even for the period around the turn of the century the error induced by ignoring the width of the age spectrum will thus be below 5%, showing that this will not change the qualitative results of chlorine budget studies which ignored this effect, like, e.g., those of *Woodbridge et al.* [1995] and *Engel et al.* [1997]. As the shape of the age spectrum only influences the propagation of compounds with nonlinear trends, no influence of the parameterization of the age spectrum is expected for the period prior to 1990 or after 2010, when the tropospheric trends in total chlorine are very close to linear.

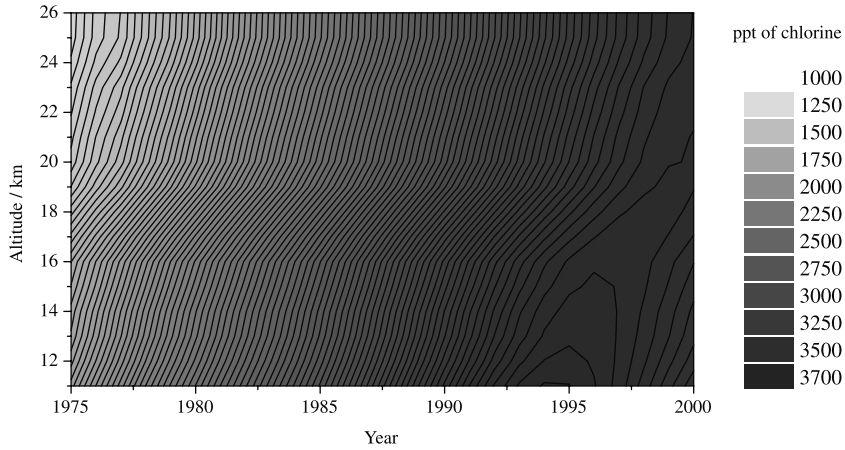

Figure 6a. Reconstructed trend of ΣCl, derived from the tropospheric trend of the mixing ratios of the seven most important chlorine source gases (see text for detail). The calculation of the vertical propagation is based on the average mean age profile determined from the combination of SF_6 and CO_2 measurements. See color version of this figure at back of this issue.

[21] Also shown in Figure 7 are the stratospheric total chlorine levels for the 20 km altitude levels inside the vortex in 1980, and the horizontal line shows when the same amount of total chlorine is expected to appear again in the stratosphere. In 1980 there were about 1770 ppt of total chlorine around 20 km. The same total chlorine level is expected to be reached again in 2062 at 20 km altitude. For the 15 km altitude level the total chlorine was at about 2050 ppt in 1980, and this value should be reached again in about 2049. At 25 km altitude the total chlorine loading was at about 1730 ppt in 1980, a level which should be reached again in 2065.

[22] It is difficult to assess the uncertainty in these estimates. The error in the mean age determination itself is expected to be less than a year (the error solely due to measurement uncertainties is below 6 months). The additional effect of changing stratospheric dynamics may influence stratospheric residence times and is not considered here. The largest uncertainty is, in any case, due to the future development of tropospheric chlorine. This uncertainty arises from both the emissions scenarios and errors or temporal changes in the assumed lifetimes of the chlorine compounds. It is also important to notice that the return to pre-ozone-hole levels of total chlorine does not have to agree with the date of ozone recovery. At the lower altitudes the partitioning between inorganic and organic chlorine is expected to change significantly, as discussed in section 7, so that ΣCl is actually not a good proxy for Cl_y at altitudes below 20 km even inside the polar vortices.

7. Inorganic Fraction

[23] Chemical destruction of ozone is not caused by total chlorine ΣCl, but by inorganic chlorine compounds (Cl_y). As inorganic chlorine is, however, not a conserved species such as SF_6 or CO_2, the mean age derived from these cannot be used directly for the calculation of inorganic chlorine. In fact, as total stratospheric chlorine around 2050 will be composed of longer-lived compounds than it was in 1980, a larger fraction of chlorine may still reside in the organic

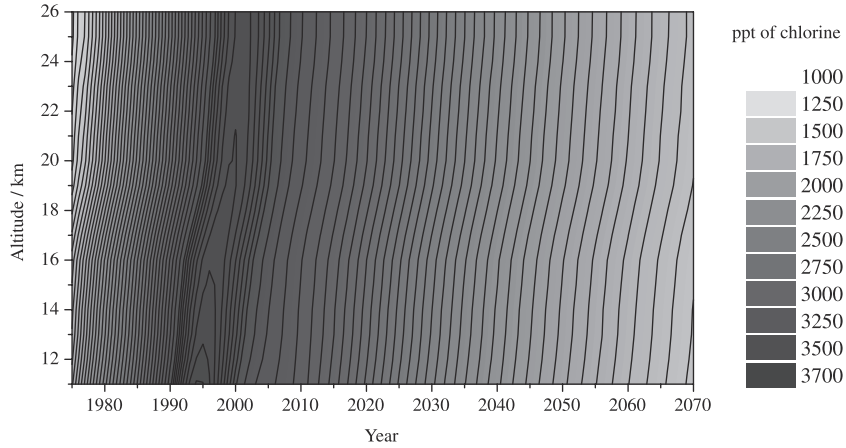

Figure 6b. Same as Figure 6a but extended into the future based on the lifetimes of the chlorine compounds and assumptions about future emissions (see text). Pre-ozone-hole values at 20 km altitude are expected to be reached again in about 2060. See color version of this figure at back of this issue.

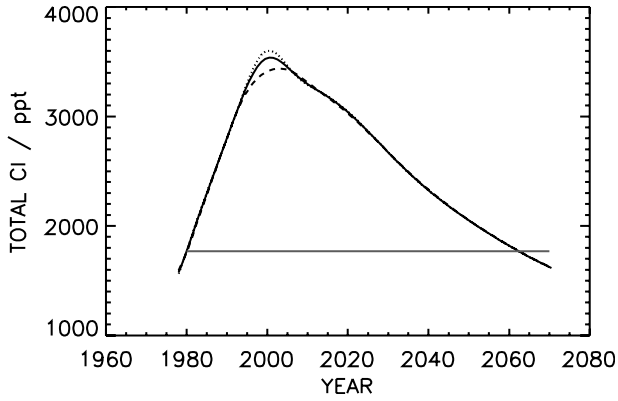

Figure 7. Total chlorine loading at 20 km altitude calculated using different parameterizations of the width of the age spectrum (solid line, $\Delta^2/\Gamma = 0.7$; dashed line, $\Delta^2/\Gamma = 1.25$; dotted line, sharp age, i.e., no age distribution, see text for details). The nonlinearity of chlorine trends during the 1990s was quite pronounced, so that the different parameterizations give significant differences. The "smearing out" of the maximum in the tropospheric chlorine loading is stronger if a wider age spectrum is assumed. There is no effect of the parameterization if the trends are linear, as was the case before 1990 and as is expected for the period from 2010 onward.

fraction which does not react with ozone. Table 3 compares the relative contribution of the six major chlorine species considered in this study for tropospheric conditions in the late 1970s with those around the middle of the 21st century, based on the future evolution of tropospheric chlorine calculated using the base scenario. CFC-12 will still be the strongest contributor to tropospheric chlorine in 2050 and have a larger fractional contribution, while the contribution of CH_3CCl_3 and CCl_4 will be much lower than during the late 1970s. The fractional contribution to total chlorine of CFC-11 and CH_3Cl will be about equal. The two compounds which will be less important in 2050 (CH_3CCl_3 and CCl_4) both have rather short stratospheric lifetimes and will thus release their chlorine in the stratosphere more readily. At a given altitude the fraction of ΣCl already converted to the inorganic form will thus be somewhat smaller in 2050 than in 2000, which will lead to less inorganic chlorine, Cl_y, and an earlier return to pre-ozone-hole values.

[24] We have estimated the difference between Cl_y and ΣCl at 20 km altitude and above inside the Arctic vortex on the basis of the simultaneous observations of the chlorine source gases and N_2O. We have used the parameterization suggested by *Plumb et al.* [1999] to detrend observed tracer mixing ratios and have derived fractional dissociation rates for the six most abundant chlorine gases, CFC-12, CFC-11, CFC-113, HCFC-22, CH_3CCl_3, CCl_4, and CH_3Cl based on our observations performed in 1997 and 2000 [*Müller et al.*, 1998, 2000]. Deep inside the polar vortex at altitudes at and above 20 km the chlorine from most compounds is nearly completely released and in the inorganic fraction [see, e.g., *Schmidt et al.*, 1991]. Even a rather long lived compound like CFC-12 is already converted to inorganic chlorine by more than 90%. The only source gas which still carries a significant amount of organic bound chlorine under these circumstances is HCFC-22, of which only about half has been photolyzed in air masses typical of 20 km altitude inside the vortex. As HCFC-22 will contribute a little less than 5% to total chlorine around the expected time of chlorine recovery (compared to about 1% around 1980), this would result in inorganic chlorine levels which are about 2–3% lower during the middle of the 21st century when compared to 1980. As chlorine levels are expected to fall at a rate of a little over 1% by the middle of the century, this would mean that at about 20 km altitude inside the polar vortices the inorganic chlorine might reach pre-ozone-hole values about 2–3 years earlier than the total chlorine. In this part of the stratosphere, total chlorine is thus expected to be a rather good proxy for inorganic chlorine. At altitudes below 20 km, however, the fraction of ΣCl still residing in the organic form is larger and will increase in the future as the chlorine budget will be shifted toward longer-lived compounds. This may actually lead to a faster return of inorganic chlorine levels to pre-ozone-hole values than predicted based on total chlorine. A detailed analysis of this effect needs to consider not only correlations between the individual chlorine species and a reference compound like, e.g., N_2O but also the effect of a changing distribution of residence times (tracer transience) for species with chemical loss and is beyond the scope of this paper.

8. Conclusions

[25] Mean age is an important atmospheric parameter, which needs to be studied in detail. Mean age can be derived from the observations of suitable long-lived tracers but is very sensitive to the assumptions made in its calculation, like the tropospheric trend and the assumptions about the age spectrum. SF_6-derived and CO_2-derived mean ages show a compact correlation, but SF_6-derived mean ages appear to be systematically larger than CO_2-derived mean ages in air masses with mean ages above 5 years. This difference seems to increase with increasing mean age. It will be interesting to compare SF_6 observations in future winters in order to find out whether this was a special feature of the 1999/2000 winter or whether this occurs more often in the polar stratosphere. As SF_6 may thus have a sink in the mesosphere which would influence the mean age determination for rather old air, we suggest that for mean ages larger than 5 years the CO_2-derived mean age may be

Table 3. Comparison of Relative Contribution of Chlorine Species to Total Chlorine Between 1976 (Representative of the Late 1970s) and 2050 (Representative of the Time When Total Stratospheric Chlorine Levels Are Expected to Return to Pre-ozone-hole Values)

Compound	Relative Contribution 1976, %	Relative Contribution 2050, %
CCl_3F	17.9	16.6
CCl_2F_2	22.6	34.3
$C_2Cl_3F_3$	2.1	8.5
CCl_4	17.7	4.3
CH_3CCl_3	9.4	0.0
$CHClF_2$	1.2	4.6
CH_3Cl	29.1	31.7

more representative. The mean ages derived for the higher levels of our analysis are in good agreement with previous observations by *Schmidt and Khedim* [1991], indicating that there has been little or no change in the average mean age over the past 20 years.

[26] The average profiles of N_2O which we have derived from our observations were used to calculate reference profiles of mean age based on a correlation between mean age and N_2O. It was shown that the values of our high-latitude Arctic reference profile are in rather good agreement with mean values observed in the Antarctic vortex.

[27] While tropospheric chlorine levels are decreasing and will very likely continue to do so in the future, the propagation of these tropospheric chlorine levels into the stratosphere is not described by a simple time lag. The concepts of mean age and the age spectrum need to be considered when deriving stratospheric chlorine levels. This is of particular importance under conditions when tropospheric trends are nonlinear. A typical distribution of mean age has been derived for polar winter deep inside vortex conditions, and this has been used to derive stratospheric total chlorine levels at different altitudes for the year 1980, which is (somewhat arbitrarily) chosen as the year of the onset of severe chemical destruction of ozone in the Antarctic polar vortex (ozone hole). At this time there were about 1770 ppt of total chlorine around 20 km, while at around 25 km the total chlorine loading was at about 1730 ppt. The same total chlorine levels are expected to occur again in 2062 and 2065 for the 20 and 25 km altitude levels, respectively. The different partitioning of total chlorine into organic and inorganic fractions in the future, which is due to the changing mixture of chlorine compounds, is not expected to change this temporal evolution very strongly at altitudes above 20 km, where most of the chlorine is in the inorganic fraction already. At 20 km altitude, inorganic chlorine levels (Cl_y) could recover to pre-ozone-hole values about 3 years earlier. For lower altitudes this may, however, be a major factor which needs to be considered in future studies.

[28] It should be emphasised at this point that because of the declining temperatures in the stratosphere and also because of changes of the bromine loading of the stratosphere, stratospheric ozone values will not necessarily recover to pre-ozone-hole values at the same time as total chlorine levels [e.g., *Shindell et al.*, 1998; *Waibel et al.*, 1999; *Dameris et al.*, 1998]. It must also be pointed out that an increase in the water vapor content of the stratosphere will, in addition, lead to substantial cooling, which would favor heterogeneous chlorine activation and hence ozone destruction under polar winter conditions [*Kirk-Davidoff et al.*, 1999]. Possible changes in stratospheric dynamics are not at all considered in this study and may change the system because of changing transport, which could lead to longer or shorter residence times of an air parcel in the stratosphere. The by far largest uncertainty in predicting future stratospheric chlorine levels is, however, the tropospheric chlorine loading, which is dependent on international adherence to the regulations enforced by the Montreal Protocol and its subsequent amendments. Another uncertainty in these calculations is the atmospheric lifetimes. The emissions of other chlorine and bromine gases such as HCFCs and Halons, which are not considered in this study (with the exception of HCFC-22), would further retard the recovery of stratospheric ozone, too. As most of the HCFCs have shorter atmospheric lifetimes than most CFCs and as HCFCs and are also banned under the Montreal Protocol, they are, however, expected to be at quite low levels by the middle of the century when the chlorine from the CFCs and the organic solvents is expected to reach pre-ozone-hole levels again. Taking into account all these uncertainties, the dates derived for chlorine recovery should be considered as a best estimate based on the given set of lifetimes and emissions and assuming that there will be no major changes in stratospheric circulation.

[29] **Acknowledgments.** We would like to acknowledge the good cooperation with our colleagues at the Institute for Stratospheric Chemistry of the Forschungszentrum Jülich and, in particular, the help of Erich Klein and Cornelius Schiller. We thank Pierre Faucon and his team of the French CNES for the continuous excellent balloon launch operation. We would also like to thank Jim Elkins and Steve Montzka of NOAA CMDL for the permission to use their tropospheric trend data for this study and Michael Volk for discussions on the calculation of mean age. We thank Pieter Tans from NOAA CMDL for the permission to use unpublished CO_2 data. Financial support for the balloon observations by the German Ministry of Research and Technology (BMBF), the European Commission (DG XII), and the Forschungszentrum Jülich is gratefully acknowledged. We would also like to thank the reviewers for their valuable and constructive comments.

References

Anderson, J., J. M. Russell, S. Solomon, and L. Deaver, HALOE confirmation of stratospheric chlorine decreases in accordance with the Montreal Protocol, *J. Geophys. Res.*, *105*, 4483–4490, 2000.

Andrews, A. E., K. A. Boering, B. C. Daube, S. C. Wofsy, E. J. Hintsa, E. M. Weinstock, and T. P. Bui, Empirical age spectra for the lower tropical stratosphere from in situ observations of CO_2: Implications for stratospheric transport, *J. Geophys. Res.*, *104*, 26,581–26,595, 1999.

Andrews, A. E., K. A. Boering, S. C. Wofsy, B. C. Daube, D. B. Jones, S. Alex, M. Loewenstein, J. R. Podolske, and S. E. Strahan, Empirical age spectra for the midlatitude lower stratosphere from in-situ observations of CO_2: Quantitative evidence of a subtropical "barrier" to horizontal transport, *J. Geophys. Res.*, *106*, 10,257–10,274, 2001.

Conway, T. J., P. P. Tans, 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.

Cunnold, D. M., P. J. Fraser, R. F. Weiss, R. G. Prinn, P. G. Simmonds, B. R. Miller, F. N. Alyea, and A. J. Crawford, Global trends and annual releases of $CFCl_3$ and CF_2Cl_2 estimated from ALE/GAGE measurements from July 1978 to June 1991, *J. Geophys. Res.*, *99*, 1107–1126, 1994.

Dameris, M., V. Grewe, R. Hein, C. Schnadt, C. Brühl, and B. Steil, Assessment of the future development of the ozone layer, *Geophys. Res. Lett.*, *25*, 3579–3582, 1998.

Daniel, J. S., S. M. Schauffler, W. H. Pollock, S. Solomon, A. Weaver, L. E. Heidt, R. R. Garcia, E. L. Atlas, and J. F. Vedder, On the age of stratospheric air and inorganic chlorine and bromine release, *J. Geophys. Res.*, *101*, 16,757–16,770, 1996.

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

Engel, A.,U. Schmidt, and R. A. Stachnik, Partitioning between chlorine reservoir species deduced from observations in the Arctic winter stratosphere, *J. Atmos. Chem*, *27*, 107–126, 1997.

Engel, A., U. Schmidt, and D. McKenna, Stratospheric trends of CFC-12 over the past two decades: Recent observational evidence for declining growth rates, *Geophys. Res. Lett.*, *25*, 3319–3322, 1998.

Farman, J. C., B. G. Gardiner, and J. D. Shanklin, Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction, *Nature*, *315*, 207–210, 1985.

Geller, L. S., Tropospheric SF_6: Observed latitudinal distribution and trends, derived emissions and interhemispheric exchange time, *Geophys. Res. Lett.*, *24*, 675–678,1997.

Greschner, B., Gas chromatographic measurements of the atmospheric concentration of carbon dioxide, methane and nitrous oxide in Heidelberg (in German), Diploma thesis, Inst. für Umweltphysik, Univ. of Heidelberg,Heidelberg, Germany, 1995.

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

Hall, T. M., and D. W. Waugh, The influence of nonlocal chemistry on tracer distributions: Inferring the mean age of air from SF_6, *J. Geophys. Res.*, *103*, 13,327–13,336, 1998.

Hall, T. M., D. W. Waugh, K. A. Boering, and R. A. Plumb, Evaluation of transport in stratospheric models, *J. Geophys. Res.*, *104*, 18,815–18,839, 1999.

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

Keeling, C. D., J. F. S. Chine, and T. P. Whorf, Increased activity of northern vegetation inferred from atmospheric CO_2 measurements, *Nature*, *382*, 146–149, 1996.

Kida, H., General circulation of air parcels and transport characteristics from a hemispheric GCM, part 2. Very long-term motions of air parcels in the troposphere and stratosphere, *J. Meteorol. Soc. Jpn.*, *61*, 510–523, 1983.

Kirk-Davidoff, D. B., E. J. Hintsa, J. G. Anderson, and D. W. Keith, The effect of climate change on ozone depletion through changes in stratospheric water vapour, *Nature*, *402*, 399–401, 1999.

Montzka, S. A., J. H. Butler, R. C. Myers, T. M. Thompson, T. H. Swanson, S. D. Clarke, L. T. Lock, and J. W. Elkins, Decline in the tropospheric abundance of halogen from halocarbons: Implications for stratospheric ozone depletion, *Science*, *272*, 1318–1322, 1996.

Montzka, S. A., J. H. Butler, J. W. Elkins, T. M. Thompson, T. H. Swanson, A. D. Clarke, and L. T. Lock, Present and future trends in the atmospheric burden of ozone-depleting halogens, *Nature*, *398*, 690–694, 1999.

Müller, M., A. Engel, and U. Schmidt, Observations of vertical profiles for long lived trace gases in the arctic vortex during the ADEOS/ILAS validation campaign, in *Proceedings of the 4th European Symposium on Polar Stratospheric Ozone, Schliersee, Bavaria, 22-26 September 1997, Air Pollut. Res. Rep. 66,* edited by N. R. P. Harris, I. Kilbane-Dawe, and G. Amanatidis, pp. 366–369, Eur. Comm., Brussels, 1998.

Müller, M., A. Engel, and U. Schmidt, Investigation of stratospheric dynamics in the Arctic polar region derived from tracer measurements during the winter 1999/2000, paper presented at THESEO 2000-SOLVE Science Meeting, Eur. Comm., Palermo, Italy, 25–29 Sept. 2000.

Nakazawa, T., T. Machida, S. Sugawara, S. Murayama, S. Morimoto, G. Hashida, H. Honda, and T. Itoh, Measurements of the stratospheric carbon dioxide concentration over Japan using a balloon-borne cryogenic sampler, *Geophys. Res. Lett.*, *22*, 1229–1232, 1995.

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

Plumb, I. C., P. F. Vohralik, and K. R. Ryan, Normalization of correlations for atmospheric species with chemical loss, *J. Geophys. Res.*, *104*, 11,723–11,732, 1999.

Podolske, J. R., M. Loewenstein, S. E. Strahan, and K. R. Chan, Stratospheric nitrous oxide distribution in the Southern Hemisphere, *J. Geophys. Res.*, *94*, 16,767–16,772, 1989.

Prinn,, R. G., et al., A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *J. Geophys. Res.*, 17,751–17,792, 2000.

Russell, J. M., M. Luo, R. J. Cicerone, and L. E. Deaver, Satellite confirmation of the dominance of chlorofluorocarbons in the global stratospheric chlorine budget, *Nature*, *329*, 526–529,1996.

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

Schmidt, U., G. Kulessa, E. Klein, E.-P. Röth, P. Fabian, and R. Borchers, Intercomparison of balloon-borne cryogenic whole air samplers during the MAP/GLOBUS 1983 campaign, *Planet. Space Sci.*, *35*, 647–656, 1987.

Schmidt,, U., R. Bauer, A. Khedim,E. Klein,G. Kulessa, and B. Schubert, In-situ observations of long lived trace gases in the Arctic stratosphere during winter, in *Ozone in the Atmosphere*, edited by R. D. Bojkov and P. Fabian, pp. 298–301, A. Deepak, Hampton, Va., 1989.

Schmidt, U., R. Bauer, A. Khedim, E. Klein, G. Kulessa, and C. Schiller, Profile observations of long-lived trace gases in the Arctic vortex, *Geophys. Res. Lett.*, *18*, 767–770, 1991.

Shindell, D. T., D. Rind, and P. Lonergan, Increased polar stratospheric ozone losses and delayed eventual recovery owing to increasing greenhouse-gas concentrations, *Nature*, *392*, 592–598, 1998.

Solomon, S., Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys.*, *37*, 275–316, 1999.

Strunk, M., A. Engel, U. Schmidt, C. M. Volk, T. Wetter, I. Levin, and H. Glatzel-Mattheier, CO_2 and SF_6 as stratospheric age tracers: Consistency and the effect of mesospheric loss, *Geophys. Res. Lett.*, *27*, 341–344,2000.

Volk, C. M., J. W. Elkins, D. W. Fahey, G. S. Dutton, J. M. Gilligan, M. Loewenstein, J. R. Podolske, K. R. Chan, and M. R. Gunson, Evaluation of source gas lifetimes from stratospheric observations, *J. Geophys. Res.*, *102*, 25,543–25,564, 1997.

Waibel, A. E., T. Peter, K. S. Carslaw, H. Oelhaf, G. Wetzel, P. J. Crutzen, U. Pöschl, A. Tsias, E. Reimer, and H. Fischer, Arctic ozone loss due to denitrification, *Science*, *283*, 2064–2068, 1999.

Waugh, D. W., et al., Three-dimensional simulations of long-lived tracers using winds from MACCM2, *J. Geophys. Res.*, *102*, 21,493–21,513, 1997.

Waugh, D. W., D. B. Considine, and E. L. Fleming, Is upper stratospheric chlorine decreasing as expected?, *Geophys. Res. Lett.*, *28*, 1187–1190, 2001.

Woodbridge, E. L., et al., Estimate of total organic and inorganic chlorine in the lower stratosphere from in situ and flask measurements during AASE II, *J. Geophys. Res*, *100*, 3057–3064, 1995.

World Meteorological Organization (WMO), The stratosphere 1981: Theory and measurements, *WMO Rep. 11*, U. N. Environ. Programme, Geneva, 1981.

World Meteorological Organization (WMO), Scientific assessment of stratospheric ozone: 1989, *WMO Rep. 20*, U. N. Environ. Programme, Geneva, 1989.

World Meteorological Organization (WMO), Scientific assessment of ozone depletion: 1998, *WMO Rep. 37*, U. N. Environ. Programme, Geneva, 1999.

Zander, R., et al., The 1994 northern midlatitude budget of stratospheric chlorine derived from ATMOS/ATLAS-3 observations, *Geophys. Res. Lett.*, *23*, 2357–2360, 1996.

A. Engel, H.-P. Haase, M. Müller, and U. Schmidt, Institut für Meteorologie und Geophysik, Johann Wolfgang Goethe-Universität Frankfurt, Georg Voigt Strasse 14, Frankfurt, D-60325 Germany. (an.engel@meteor.uni-frankfurt.de; h.p.haase@meteor.uni-frankfurt.de; m.mueller@meteor.uni-frankfurt.de; u.schmidt@meteor.uni-frankfurt.de)

I. Levin and C. Poss, Institut für Umweltphysik, University of Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg Germany. (lv@uphys1.uphys.uni-heidelberg.de; christian.poss@iup.uni-heidelberg.de)

M. Strunk, TLC-GmbH, Kleyerstrasse 27, 60325 Frankfurt Germany. (martin.strunk@bku.db.de)

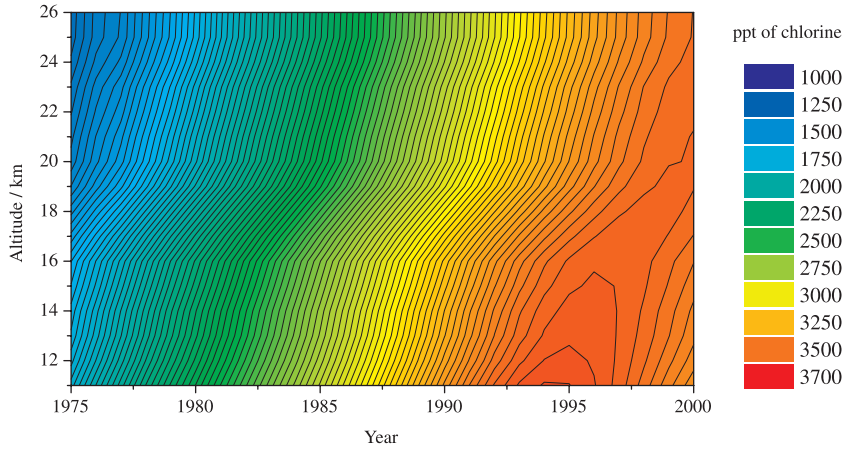

Figure 6a. Reconstructed trend of ΣCl, derived from the tropospheric trend of the mixing ratios of the seven most important chlorine source gases (see text for detail). The calculation of the vertical propagation is based on the average mean age profile determined from the combination of SF_6 and CO_2 measurements.

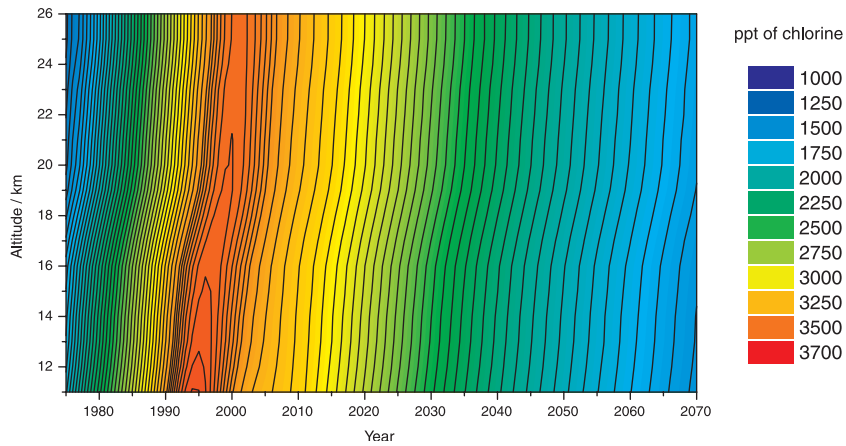

Figure 6b. Same as Figure 6a but extended into the future based on the lifetimes of the chlorine compounds and assumptions about future emissions (see text). Pre-ozone-hole values at 20 km altitude are expected to be reached again in about 2060.