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Chlorine partitioning in the stratosphere based on in situ measurements

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ABSTRACT

Balloon-borne cryogenic air sampler experiments have been conducted from a tropical (Hyderabad, 17.5°N) and a midlatitude (GAP, southern France, 44°N) station since 1987 in the altitude range of about 8–35 km. Air samples are analysed at the Max Planck Institute for Aeronomy (MPAE) and Physical Research Laboratory (PRL) using various gas chromatographic techniques to obtain the vertical distributions of several halogenated source gases and long-lived dynamical tracers. These observations are used to determine the stratospheric partitioning of the chlorine species into their organic and inorganic forms for the altitude range of 20 to 35 km. Distributions of inorganic chlorine indicate increase in their abundances with altitude, latitude and time. Mixing ratio correlations of organic and inorganic chlorine with N_2O have been obtained which also suggest that the rate of increase in inorganic halogens component in the stratosphere is larger than the increase rate of total organic halogen. This supports previous assessments that halogen-induced ozone depletion will continue to be observed for a few more years, despite the decrease of halocarbon loading into the stratosphere since 1994.

1. Introduction

Large stratospheric ozone depletion, observed particularly at very high latitudes in the winter and at mid-latitudes at almost all seasons, is primarily due to increase in reactive chlorine content in the stratosphere (WMO, 1995; Jackman et al., 1996; Brasseur et al., 1997). Most of the reactive chlorine compounds are produced from man-made halocarbons such as chlorofluorocarbons (CFCs), hydrogenated CFCs (HCFCs — used as CFC substitutes), and methyl chloride, all of which are also called source gases. In the stratosphere, source gases are photodissociated to release highly reactive chlorine atoms, which are in turn converted into many other intermediate species. The chlorine that is not in the form of a source gas is defined as *inorganic* chlorine (Cl_y). This constituent is the sum of the concentrations of HCl, $ClONO_2$, and ClO_x (where ClO_x is a combination of Cl, ClO, Cl_2, Cl_2O_2 and HOCl). The total abundance of Cl atom weighted source gases is referred to as *organic* chlorine (CCl_y). A detailed overview of these definitions and processes involved in chlorine partitioning in the stratosphere is given in Dessler et al. (1998). A list

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Table 1. *List of trace constituents used in this work*

No.	Molecule	Chemical formula	Mixing ratio (pptv)	Approximate % contribution to inorganic chlorine
1	sulfur hexafluoride	SF_6	3.1 ± 0.07	–
2	methane	CH_4	1.7 ± 0.02 (ppmv)	—
3	nitrous oxide	N_2O	313 ± 0.6 (ppbv)	—
4	carbon tetrachloride	CCl_4	104 ± 4*	12.2
5	CFC-11	$CFCl_3$	277.7 ± 3	22.1
6	CFC-12	CF_2Cl_2	523.6 ± 5	27.6
7	CFC-113	CF_3CCl_3	83.3 ± 1	6.2
8	CFC-114	CF_4CCl_2	19.1 ± 0.3	0.9
9	CFC-140	CH_3CCl_3	131.9 ± 2*	12.1
10	HCFC-22	$CHClF_2$	110.5 ± 1	2.7
11	methyl chloride (MC)	CH_3Cl	548.0 ± 10*	14.8

The tropospheric concentrations (average ± standard deviation) are estimated as the average of the tropospheric measurements in the vertical distributions during 16 April 1994 from Hyderabad. Typically there are 2–3 samples collected in the free tropospheric altitude range (8–17 km). Errors in analysis of individual samples varies widely; e.g., 1% (1σ) for SF_6, 2% for CH_4 and about 5–10% for the CFCs. The percentage contributions to the inorganic chlorine in the stratosphere are taken from Daniel et al. (1996) and are appropriate for the year 1991/1992.

* These vertical profiles were not measured, but calculated from their mixing ratio correlations (Subsection 2.2 for this calculation).

of source gases and their relative importance in producing inorganic chlorine in the stratosphere is given in Table 1.

Though protocols have been signed since 1987 to phase out the ozone depleting halocarbons, chlorine loading in the stratosphere has continued till the middle of this decade. This is because the amount of inorganic chlorine released in the stratosphere has been found to be comparable to that which can be estimated from the abundances of organic chlorine (CCl_y) in the troposphere 3 to 5 years before (Montzka et al., 1996). Such delayed response essentially arises because of the time lag that an air parcel experiences, ranging from about 3 to 5 years (depending on the latitude and altitude), to reach a specific stratospheric region from the tropical tropopause. This transport time is often referred to as "age" which is currently being used extensively as a diagnostic tool to study the dynamical properties of the stratosphere (Boering et al., 1996; Volk et al., 1997; Patra et al., 1997; Hall and Waugh, 1998). However, it has always been a difficult task to choose a suitable species for estimating the age of stratospheric air, ideally with well established tropospheric trends and no measurable loss due to photochemical reactions in the stratosphere. With the availability of vertical distributions of sulfur hexafluoride (SF_6), "age" of air is being estimated more accurately and unambiguously (Harnisch et al., 1996; Patra et al., 1997).

Estimations of total chlorine (Cl_{total}) in the stratosphere and further assessments of their partitioning into organic and inorganic chlorine can be obtained from simultaneous measurements of vertical profiles of halocarbons, a dynamical tracer (to determine "age" of stratospheric air), and their time-series observations near the ground. Recently such estimates have been made for the lower stratosphere (up to about 20 km) using halocarbon distributions obtained during Airborne Arctic Stratospheric Expeditions (AASE) (Woodbridge et al., 1995; Daniel et al., 1996) and using data from Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) mission. However, so far no estimates have been made in the region of altitude from 20 to 30 km where the bulk of the ozone resides and which lies above the altitude probed by airborne platforms.

In this article, we calculate the amount of inorganic chlorine released from source gases in the tropical stratosphere which contribute more than 98% to the total inorganic chlorine (Table 1).

This is done for the height range up to 35 km in which no work has been done earlier. The importance of the tropical region lies in transporting the source gases from the troposphere to the stratosphere, and yet there are not many measurements to estimate the amount of organic and inorganic chlorine explicitly for this region. The main advantage of this study is that simultaneous measurements of source gases including SF_6 (for "age" determination) up to about 35 km in 1987, 1990, and 1994 are available, which cover the time of high chlorine loading.

2. Estimation of vertical distributions

2.1. In situ measurements

Balloon flights were conducted from Hyderabad (17.5°N, 78.6°E) carrying a cryogenic air sampler on 27 March 1987, 9 April 1990, and 16 April 1994. During each flight, about 14 air samples were collected at the predetermined altitudes in the height range of about 8 to 35 km. These air samples have been analysed in the laboratory using gas chromatographs (GCs) equipped with flame ionization detector (FID), electron capture detector (ECD), and quadrupole mass spectrometer (MS) for hydrocarbons, halocarbons, and hydrohalocarbons, respectively. Details of these experiments as well as the results obtained can be found in Lal et al. (1994, 1994a), Fabian and Gömer (1984) and Patra (1997). However, a brief description of the analysis procedure is given here. CH_4 was separated on a molecular sieve 13X filled stainless steel column and detected using a FID. Similarly, N_2O was separated on a Porapak-Q packed column and measured using an ECD. SF_6, CFCs, and Halons were separated together using a Porasil-L packed column. The temperature of the GC column was varied from -10°C to 225°C. An ECD was used for their detection. GC-MS analysis of HCFCs and methyl halides were made by using a capillary column type DB-1 of length 60 m × with OD of 0.32 μm. Accuracies of these measurements are given in Table 1. Another set of vertical profiles measured using similar techniques from GAP, France (44°N) on 23 June 1987 (Borchers et al., 1989) and a set of reference profiles suggested for midlatitude based on a number of vertical profiles obtained from the same location (Fabian et al., 1996), are used to find the mixing ratio inter-correlations. These data sets are also used to study the latitudinal variations of chlorine loading and its partitioning in the stratosphere. The locations and available profiles for various species are given in Table 2.

2.2. Empirical approach

Since the vertical profiles of a few source gases required to calculate the Cl loading are not available in some sets of measurements (Table 2), an empirical approach (Plumb and Ko, 1992) has been adopted to construct the missing profiles from their mixing ratio correlations with CH_4, or CFC-11 (selected based on their simpler and compact relationships) using the measured distributions in other sets. Measurements of the long-lived gases on 27 March 1987 and 9 April 1990 indicate that the Quasi-Biannual Oscillation (QBO) of the lower stratospheric zonal winds has a large effect on the vertical tracer distributions (Fig. 1). The observations of SF_6, N_2O, and CFC-12 show a kink at around 25 km altitude on 27 March 1987 at approximately the altitude where the Singapore zonal winds change from west to east. On 9 April 1990, where the QBO is just in the other phase with easterlies in the lower and westerlies in the upper parts, the profiles for N_2O and CFC-12 show a sharper gradient above about 25 km. The profiles obtained on 16 April 1994 are very similar to the observations of March 1987 because the vertical distribution of zonal wind (or the QBO-phase) was similar. The Max Planck Institute of Chemistry (MPIC) 2D model profiles (Patra, 1997) agree better with these profiles where the region between 40 and 10 hPa has easterly winds. This feature is typical also for 3-dimensional models. For profiles of shorter lived gases like CFC-11, the effect of QBO dynamics is even larger as the chemical lifetime of CFC-11 at 25 km level is too less compared to that of CFC-12 or N_2O.

To eliminate the tropospheric trend we normalised the profiles to their average tropospheric mixing ratio for all the data sets. Correlations were then established for CH_3Cl vs. CH_4 from the 1987 Hyderabad profiles and for CCl_4 vs. CFC-11 and CH_3CCl_3 (CFC-140) vs. CFC-11 from the 1990 Hyderabad profiles. Analogous correlations were obtained from the reference profiles of southern France. The correlations (Fig. 2) exhibited

Table 2. *Details of the chemical species used in this calculation*

Flight details	Species measured	Species estimated using an empirical approach
Hyderabad (17.5°N) — 27 March 1987 (14 air samples in 10–33 km altitude range*)	SF_6, CH_4, N_2O, CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, HCFC-22, CH_3Cl	CCl_4, CFC-140
Hyderabad (17.5°N) — 9 April 1990 (14 air samples in 11–33 km altitude range*)	CH_4, N_2O, CCl_4, CFC-11, CFC-12, CFC-113, CFC-114, HCFC-22, CFC-140	SF_6, CH_3Cl
Hyderabad (17.5°N) — 16 April 1994 (14 air samples in 8–37 km altitude range*)	SF_6, CH_4, N_2O, CFC-11, CFC-12, CFC-113, CFC-114	CCl_4, CFC-140, CH_3Cl
GAP, France (44°N) — 23 June 1987 (14 air samples in 8–33 km altitude range*)	CH_4, N_2O, CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, HCFC-22	CCl_4, CH_3Cl, CFC-140
GAP, France (44°N) — Reference 1990	CH_4, N_2O, CCl_4, CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, HCFC-22, CFC-140, CH_3Cl, CFC-115	SF_6

Species which are not measured have been estimated using an empirical approach (discussed in the text).
* Each air sample was collected within about 1 km height range.

compact relations which could be fitted by polynomials up to 2nd order in the altitudes of lower and middle stratosphere.

These relations for Hyderabad are

$$(CH_3Cl) = 2.27554(CH_4) - 1.245944 \quad (1)$$

$$(CCl_4) = 0.9368859(CFC11) + 0.1089776 \quad (2)$$

$$(CH_3CCl_3) = 0.7761508(CFC11)^2 + 0.2669933(CFC11) + 0.0423582; \quad (3)$$

and for southern France are

$$(CH_3Cl) = 2.3153903(CH_4)^2 - 2.0988853(CH_4) + 0.5188277 \quad (4)$$

$$(CCl_4) = 1.022228(CFC11) - 0.02345964 \quad (5)$$

$$(CH_3CCl_3) = 0.9790653(CFC11) - 0.02342109. \quad (6)$$

The above relations are used to calculate the normalised profiles for CH_3Cl, CCl_4 and CH_3CCl_3 for the flights on which they are not measured. Finally all the profiles are scaled by the tropospheric concentrations for a particular year to obtain the actual profiles for that year. The idea to use correlations of normalised profiles is to account for the changing tropospheric trends of some of these gases.

3. "Age" of air

The average "age" of air essentially indicates the time taken by an air parcel to travel from the surface to a particular height in the stratosphere. Much has been written about the average age of air and its distributions, based on numerical experiments, and the most recent work (Hall and Waugh, 1998) further highlights the significance of finding an ideal dynamical tracer (without any loss in the middle atmosphere) for the determination of age of stratospheric air, particularly in the high latitudes. Fortunately, our measurements of source gases are in the tropical and midlatitude region where the age of air can be calculated from the vertical profiles of SF_6 relatively unambigu-

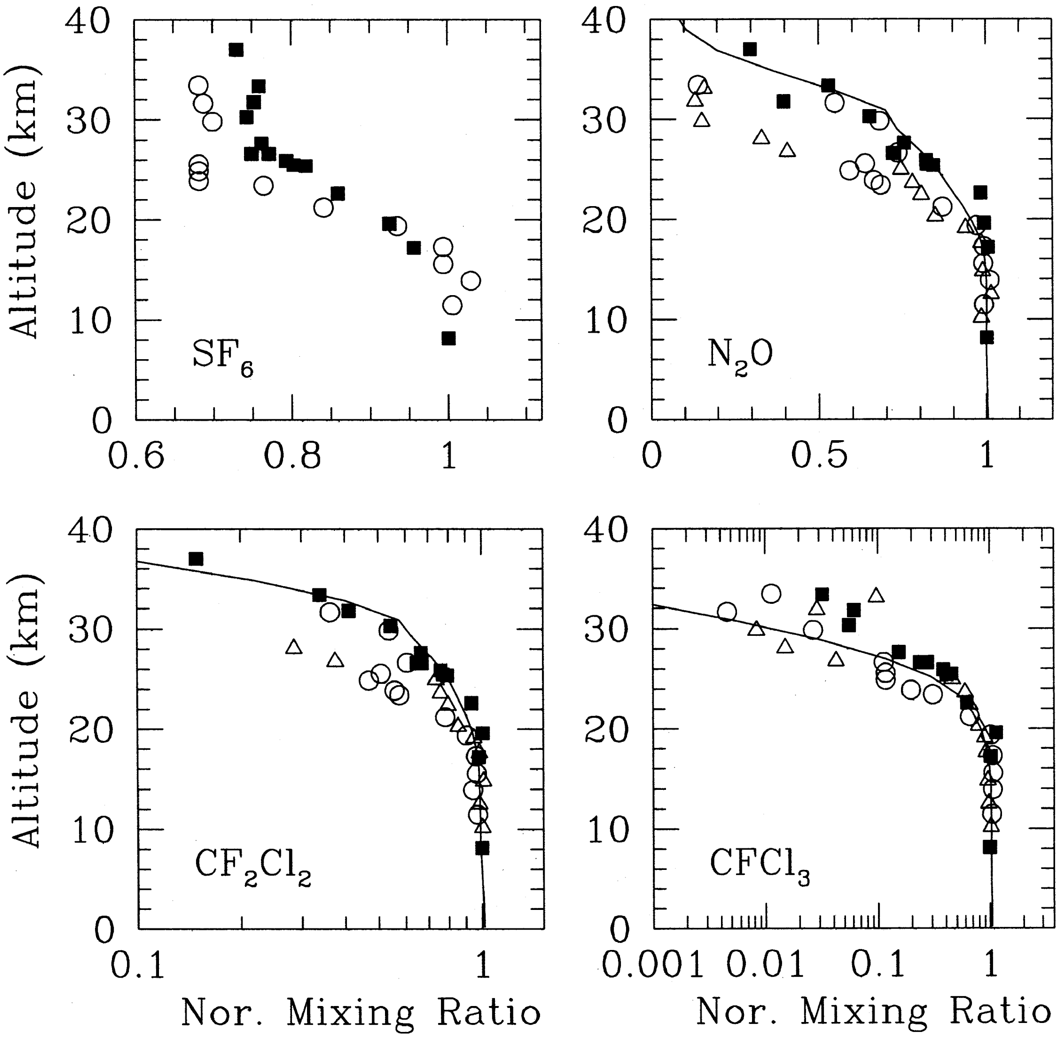

Fig. 1. Vertical distributions of SF_6, N_2O, CFC-12, and CFC-11, depicting various dynamical disturbances observed on 27 March 1987 (open circle), and 16 April 1994 (filled square) over Hyderabad. These profiles belong to the QBO-east-phase above about 40 hPa. The MPIC model simulated profile (continuous line) and the observed profile on 9 April 1990 over Hyderabad (open triangle, QBO-west-phase above 40 hPa) are shown for a comparison. The stratospheric profiles of SF_6 are known to be controlled by primarily the dynamics, those of of N_2O and CFC-12 are controlled by both chemistry and dynamics, and that of CFC-11 are mainly controlled by chemistry (attains photochemical equilibrium).

ously (Patra et al., 1997). Therefore, in this article we will discuss mainly the selection of vertical profiles of age which are derived from the measurements of SF_6.

The age of stratospheric air increases with height and is estimated to be about 4 years in the altitude region of about 27 to 37 km in the tropical stratosphere (Patra et al., 1997). It also increases significantly with latitude (found to be up to 8–10 years in the polar regions at 30 km (Harnisch et al., 1996; Volk et al., 1997). Hence, it is important to account for the concentration of the gas

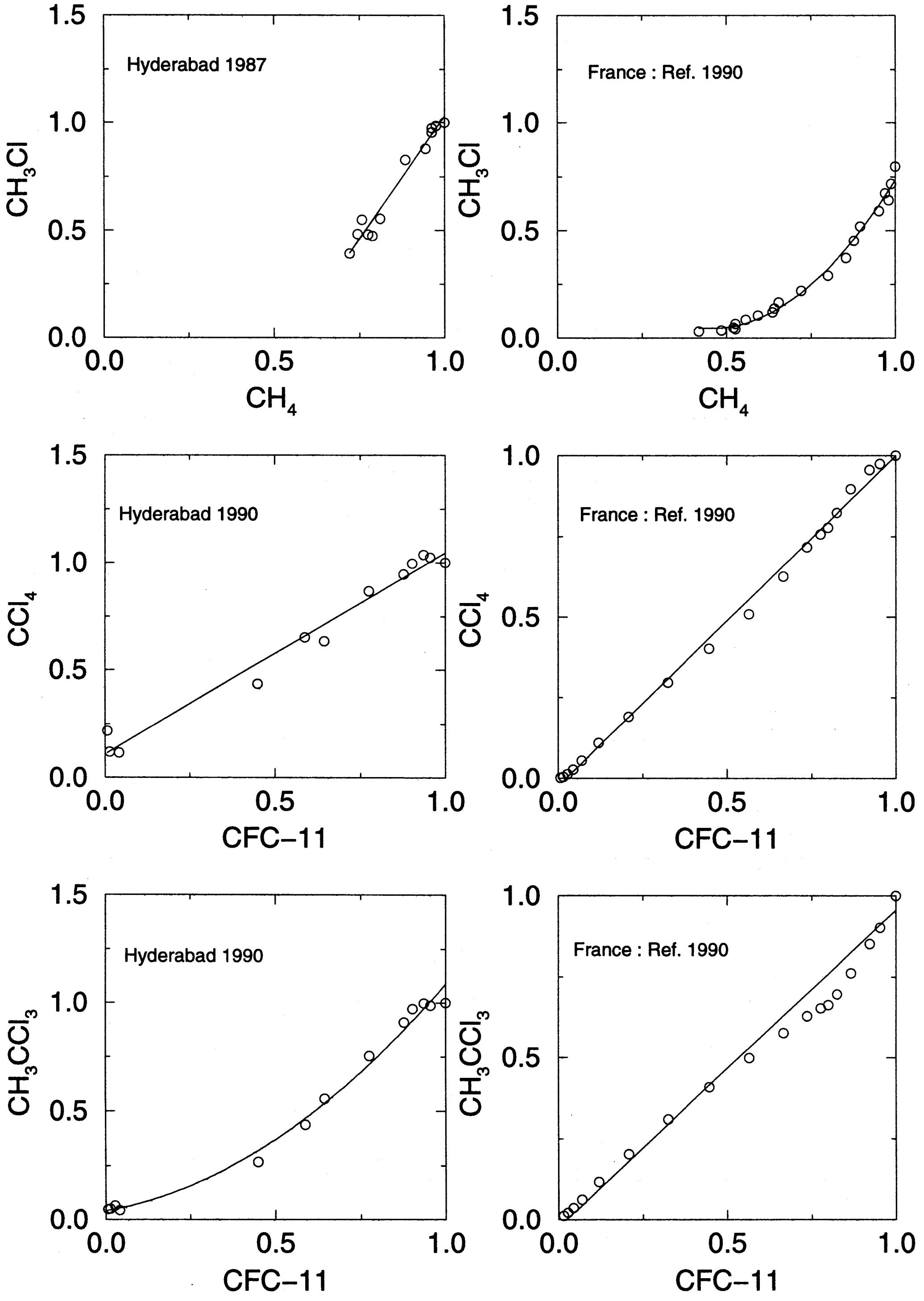

Fig. 2. Mixing ratio correlations of species measured during balloon flights for the years shown. These have been used to calculate the vertical distributions of trace gases which are not measured during balloon flights for the remaining years. The compact relations seen are due to the existence of slope equilibrium.

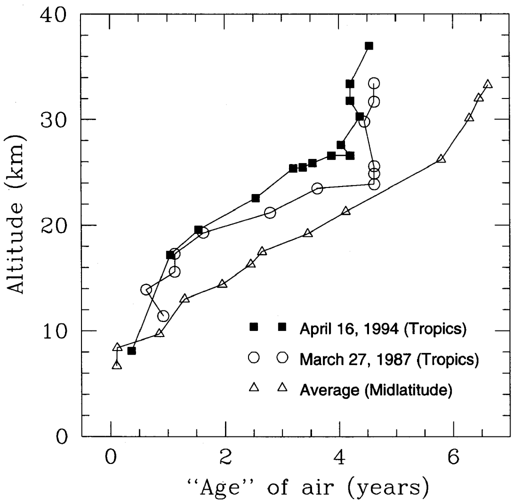

Fig. 3. A comparison of "age" of air estimated from the measured vertical profiles of SF_6 on 27 March 1987 (from Harnisch et al., 1996) and on 16 April 1994 (from Patra et al., 1997), both over Hyderabad (tropics). An average profile for midlatitude is also shown for comparison (constructed using the data from Harnisch et al., 1996).

under study in an air parcel during its entry to the stratosphere ("age" years before). However, the effect due to this correction on a species with near zero growth rate (e.g., methyl chloride) will be negligible. This correction will be more significant for the chemical species with rapidly changing tropospheric abundances such as CFCs, HCFCs (introduced as substitutes for the CFCs) etc. In this calculation, the correction for such time lag is incorporated using the "age" profiles derived from the vertical distributions of SF_6. Simultaneous "age" profiles are available for 27 March 1987 (Harnisch et al., 1996) and 16 April 1994 (Patra et al., 1997) from Hyderabad (Fig. 3). An "age" profile similar to 27 March 1987 has been used for 9 April 1990 as the mixing ratio correlations of many long-lived trace species revealed similar behaviour during 1987 and 1990. An average "age" profile (Fig. 3) is obtained for midlatitude (GAP, southern France) based on the reported age distributions (Harnisch et al., 1996). In general, the stratospheric air over midlatitudes is about 1.5 years older when compared to the tropical stratosphere at a given altitude above 25 km and varies from a year to months near the tropopause (Fig. 3 for details).

4. Tropospheric trends

The need for information on tropospheric growth rates of trace gases has been the focus of a number of global networks such as the Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment (ALE/GAGE)/Advanced GAGE program, and the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) program (Fraser et al., 1994). In this work, tropospheric concentrations (at ground level from a tropical and a midlatitude station in the NH) are taken mostly from Fraser et al. (1994) for 1980–1990 period and from Montzka et al. (1996) for the period of 1991 to 1996. The surface observations of a few key organic chlorine species are shown in Fig. 4. The symbols show the actual concentrations given in Fraser et al. (1994) and Montzka et al. (1996). Agreements are very good (discrepancies well within 1%) in few data sets, such as those for CFC-11, CFC-12, CH_3CCl_3, etc. However, some of the data sets such as for CCl_4 show a large discrepancy which reflects calibration differences. We have normalised the values given by Fraser et al. to match the more recent results of Montzka et. al. Tropospheric growth rates are calculated for each year using these baseline abundances which are to be used in the "age" correction while calculating total chlorine (see eq. (7)).

Tropospheric chlorine loading due to halocarbons is calculated using the tropospheric concentrations of the source gases and compared (Fig. 5) with the scenario 1 of WMO (1995) (the emissions of halocarbons follow the guidelines in the Copenhagen Amendments to the Montreal Protocol). A good match is apparent (disparities are less than 3% for inorganic chlorine), indicating the validity of the assumptions employed in evaluating the growth rates as a whole. The decrease after 1994 is due to the falling-off production of the ozone depleting substances in compliance with the Montreal Protocol and its amendments. However, it is estimated that the highest loading of halocarbons in the stratosphere will be experienced towards the end of this century.

5. Partitioning of total chlorine

Partitioning of organic and inorganic chlorine in the stratosphere can be estimated from the

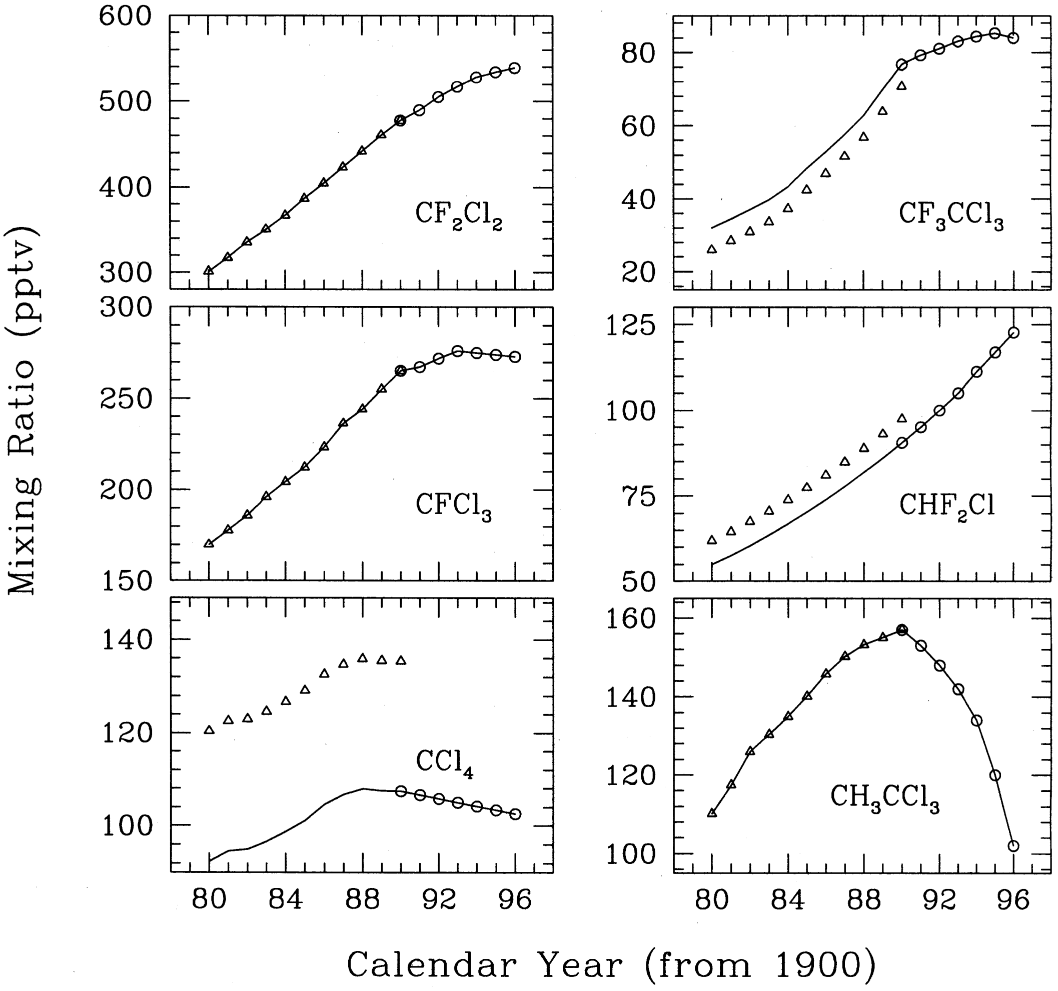

Fig. 4. Observed tropospheric mixing ratio of some of the important chlorine containing gases (continuous line), compiled from Fraser et al. (1994) for the period 1980 to 1990 (△), and from Montzka et al. (1996) during the period of 1991 to 1996 (○) for tropical northern hemisphere. Data obtained from Fraser et al. (1994) are adjusted for a few gases to the later measurements to achieve continuity in the tropospheric trends. These 6 gases constitute about 83% of CCl_y abundance near the tropopause.

observed vertical distributions of source gases. Total amount of chlorine (Cl_{total}) at the tropopause is transported to the stratosphere in their respective organic forms where they get dissociated either by the solar UV radiation or due to reactions with O^1D and OH in the stratosphere. Dissociation of each compound leads to the formation of inorganic chlorine. Therefore, at any altitude Cl_{total} can simply be represented by the sum of Cl_y and CCl_y in the stratosphere (Woodbridge et al., 1995 and Daniel et al., 1996 for further details). In other words chlorine partitioning can be expressed as

$$Cl_{y,z} = Cl_{total,z} - CCl_{y,z}$$

$$Cl_y = \sum_{i=1}^{N} n_{Cl,i}\mu_{entry,z,i} - \sum_{i=1}^{N} n_{Cl,i}\mu_{z,i}, \qquad (7)$$

where N is the total number of chlorine containing species under study, $n_{Cl,i}$ is the number of chlorine

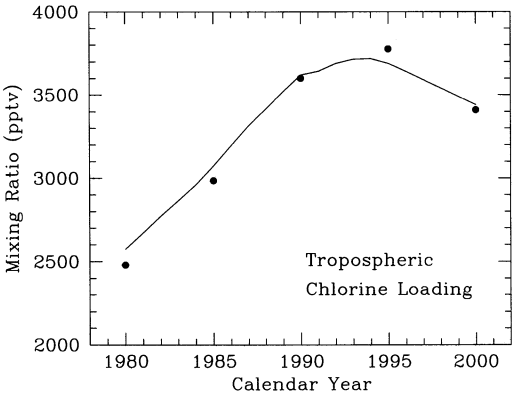

Fig. 5. Estimated change in tropospheric chlorine loading (solid line) using the individual growth rates used in this calculation of chlorine partitioning. The filled circles are chlorine loading calculated using the surface concentrations of halocarbons for scenario 1 as given in WMO (1995).

atoms in species i, $\mu_{\mathrm{entry},z,i}$ is the concentration of a particular species in the air parcel at altitude z while entering the stratosphere, and $\mu_{z,i}$ are the concentration of chlorine containing gases observed at altitude z. Both the terms in RHS of eq. (7) are measurable quantities: first from the known age of stratospheric air parcel and tropospheric trends of halocarbons, and second from the vertical distributions of trace gases.

Vertical distributions of $\mathrm{Cl_{total}}$, CCl_y, and Cl_y are calculated using eq. (7) and shown in Fig. 6. The errors in these parameters are estimated to be about 5% for lower heights and about 15% for upper stratosphere. Total chlorine abundances at different altitudes are calculated as the atom weighted mixing ratios of the chlorine containing gases CCl_y at the tropopause with their appropriate age correction applied at particular altitude. In general, a decrease in mixing ratio of $\mathrm{Cl_{total}}$ with increasing height is observed as the tropospheric concentration of major source gases were lower in the past. However the rates of change in the mixing ratio of the source gases were much faster prior to 1990 (Fig. 4) which is clearly reflected as larger decrease in $\mathrm{Cl_{total}}$ profiles in 1987 and 1990. On the other hand, the rate of increase was approaching zero after 1990, therefore the $\mathrm{Cl_{total}}$ profile estimated for April 1994 does not show any significant decrease with altitude (a case of fairly steady organic chlorine loading into the stratosphere). The mismatch in $\mathrm{Cl_{total}}$ profiles from Hyderabad and GAP in 1987 arises due to the difference in the "age" of air profiles in the lower stratosphere (Fig. 3).

The organic chlorine (CCl_y) in the tropical stratosphere (Figs. 6a, c, d) is considerably higher compared to that in the midlatitude (Fig. 6b), because the tropical upwelling makes the air younger in the tropics. The tropical region transports these constituents most effectively through the strong tropical upwelling from the troposphere to the stratosphere and mesosphere. The concentrations of these gases decrease from low latitudes to high latitudes due to their photochemical loss during meridional transport and downward motion in the mid- and high latitudes. The CCl_y values are about 950 pptv and 770 pptv over Hyderabad and GAP, respectively, at around 25 km altitude. Therefore, the inorganic chlorine (Cl_y) is produced mainly in the tropical stratosphere, due to higher abundances of CCl_y gases, larger availability of solar radiation, and higher abundance of $\mathrm{O^1D}$.

Due to inefficient scavenging of Cl atoms from the stratosphere, these radicals and their subsequent transforms (especially the temporary reservoirs HCl, $\mathrm{ClONO_2}$) are transported to the high latitudes and the polar stratosphere where they efficiently participate in the ozone destruction cycles after activation on polar stratospheric clouds. It is also seen from the estimated Cl_y profiles that their abundances in the midlatitude stratosphere (Fig. 6b) are higher than those in the tropics, particularly in the lower stratosphere (Fig. 6a) due to the combined effect of transport of inorganic Cl compounds from the tropics and in situ production of Cl due to photodissociation and chemical losses of CCl_y gases. Previous estimates of Cl_y abundances based on aircraft measurements of trace gases in the lower stratosphere also indicate an increase with increasing altitude and latitude (Daniel et al., 1996).

The MPIC 2D model results also show fairly good agreement with these calculations. The model simulations are made using the photochemical reaction rates for the source gases as given in DeMore et al. (1992) and applying a family approach. Inorganic chlorine is calculated as $(\mathrm{HCl} + \mathrm{ClONO_2} + \mathrm{ClO}_x)$ abundances (for details of the model see Brühl and Crutzen (1993)). The deviations in 1987 and 1990 in the estimated Cl_y

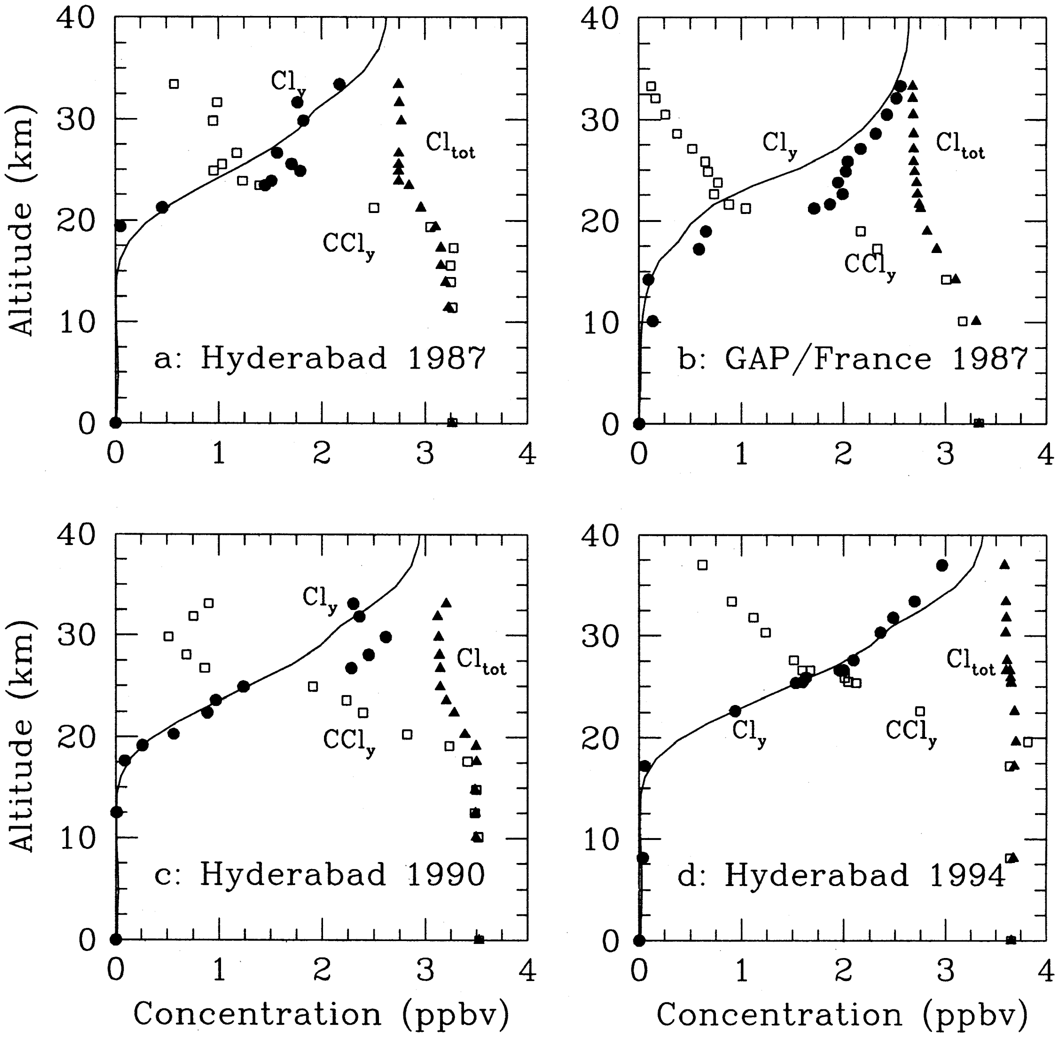

Fig. 6. Vertical distributions of Cl_{total} (filled triangle), CCl_y (open square), Cl_y (filled circle) as calculated using eq. (7). Those calculated using the observations over Hyderabad are for (a) 27 March 1987; (c) 9 April 1990 and (d) 16 April 1994. The distributions estimated using the profiles obtained from GAP, France are shown in (b). Estimated Cl_y from MPIC 2D model derived profiles of HCl, $ClONO_2$ and ClO_x is shown as continuous line.

based on observations and the 2D model derived profiles using boundary conditions of WMO (1995) (Figs. 6a, c), are caused by the dynamical perturbations observed in the vertical profiles of some of the chlorine containing organic compounds since the QBO is not taken into account in the precalculated residual circulation of the model.

6. Correlations of CCl_y and Cl_y with other gases

It has already been seen that the vertical distributions of many chemical species like CH_4, N_2O, CFC-12 are dynamically disturbed if compared to their normal (zonal average) stratospheric distributions (e.g., profiles measured on 16 April 1994 or 2D model results). These deviations have also propagated in the CCl_y and Cl_y profiles. Hence, inter-correlations of these chemical species (as tracers/proxy altitude) with organic and inorganic chlorine species for the individual set of results are expected to eliminate the dynamical influences to a large extent. Compact relations of CCl_y and Cl_y with N_2O are observed in the stratosphere (Figs. 7 and 8, respectively). Correlations of CCl_y with CFC-12 can be treated at the juxtaposition with those obtained using N_2O. More importantly, there is no systematic departure of these estimates of CCl_y (and also their correlations with N_2O) for Hyderabad and GAP compared to the best fit obtained by Woodbridge et al. (1995). In addition, Fig. 7 does not indicate significant increase in chlorine abundances in the stratosphere with time. We calculate organic chlorine abundances to be approximately 3100, 3355, and 3645 pptv, respectively, in March 1987, April 1990, and April 1994 over Hyderabad near the tropopause (~17 km). These results are in fairly good agreement with the CCl_y concentration of 3449 during 1991–1992 near the tropopause (corresponding to $N_2O =$ 310 ppbv) calculated using the "best fit" curve of Woodbridge et al. (1995) and somewhat out of range from that estimated ($CCl_y = 3667$ pptv) by Daniel et al. (1996) for the same period.

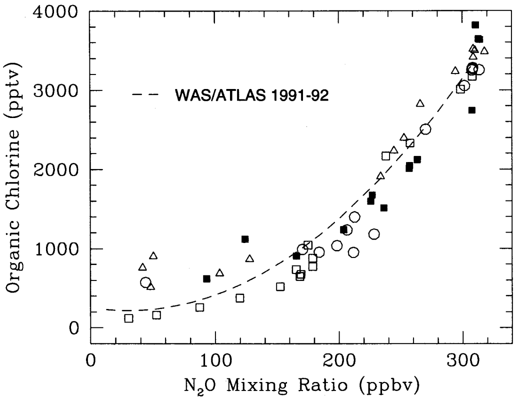

Fig. 7. Estimated organic chlorine abundances versus simultaneously measured N_2O mixing ratio correlations obtained for Hyderabad on 27 March 1987 (○), 9 April 1990 (△) and 16 April 1994 (■) and for GAP on 23 June 1987 (□). The dashed line (WAS/ATLAS 91–92) is from Woodbridge et al. (1995).

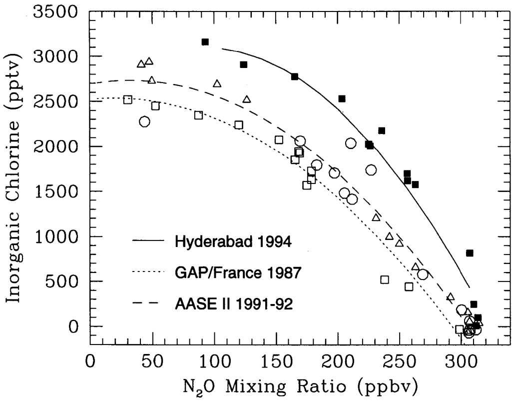

Fig. 8. Cl_y versus N_2O correlation plots showing the quadratic fits: dashed line (AASE II 1991–92) is from Daniel et al. (1996); dotted line is obtained from the southern France reference profiles; continuous line is for the calculations using measurements on 16 April 1994 over Hyderabad. The symbols have the same meaning as in Fig. 7.

However, correlations between Cl_y and N_2O suggest rapid increase with time in the inorganic chlorine mixing ratio in the lower and middle stratosphere, corresponding to N_2O abundance of ≈300–100 ppbv in the tropical region (Fig. 8 for details), neglecting the tropospheric growth rates of N_2O compared to that of the halocarbons. This feature suggests that although there is no distinct growth rate of organic chlorine in the stratosphere (Fig. 7), its inorganic component is accumulating with time (Fig. 8), which implies that the production of Cl_y from the CCl_y gases is higher than the removal rate of the former. The higher the altitude (lower N_2O concentration) the higher is the Cl_y accumulation rate. Therefore, it is suggested that although the tropospheric loading of effective equivalent chlorine to be released as the inorganic chlorine in the stratosphere has peaked during 1994–1995 (Fig. 5) the pure chlorine induced (in absence of enhanced aerosol loading by volcanic eruption) ozone depletion would continue to be greater in the subsequent years.

The correlation of estimated Cl_y with N_2O obtained for GAP shows similar behaviour if compared to that obtained from Airborne Arctic Stratospheric Expedition II (AASE II) flights during 1991–1992 period and the difference in concentrations is apparent. But correlation characteristics appear to differ for the tropical region (Hyderabad), particularly on 16 April 1994 which is assumed to represent the normal stratospheric conditions. A steeper gradient can be seen with decreasing N_2O which suggests larger production of inorganic chlorine in the tropics compared to the midlatitude region. The N_2O correlation with Cl_y on 9 April 1990 also shows similar features. Abundances of Cl_y in the tropical stratosphere (at $N_2O = 100$ pptv corresponding altitude) are estimated to be about 2200, 2700, and 3000 pptv, respectively, on 27 March 1987, 9 April 1990, and 16 April 1994. However, we believe Cl_y concentration on 27 March 1987 was higher than this estimate — the error is associated with inadequate measurements in the altitude region of low N_2O concentration. The increase in loading of CCl_y gases from the troposphere to stratosphere is apparently reflected in the increased Cl_y abundances in the stratosphere. These estimates are again in better agreement with Woodbridge et al. (1995) compared to that estimated by Daniel et al. (1996) for $N_2O = 100$ pptv. The quadratic fits for GAP in 1987, and Hyderabad in 1994 can be expressed as:

$$\begin{aligned} Cl_y &= 2803.3 + 1.51671(N_2O) - 0.0339448(N_2O)^2 \quad \text{GAP 1987} \\ Cl_y &= 2244.3 + 14.3213(N_2O) - 0.0658306(N_2O)^2 \quad \text{Hyderabad 1994} \end{aligned} \tag{8}$$

These relations are compared with those (eq. (9)), obtained by Daniel et al. (1996) using global measurements in the lower stratosphere indicating much higher gradient of Cl_y with first order in N_2O mixing ratio over Hyderabad on April 1994 compared to those which have been obtained for GAP and AASE II.

$$Cl_y = 2691.4 + 2.4359(N_2O) - 0.0368334(N_2O)^2 \quad \text{AASE II.} \tag{9}$$

7. Conclusions

The amount of organic and inorganic chlorine abundances causing stratospheric ozone depletion can be well estimated only if prior information is available on the following: (1) well-established tropospheric trends of CCl_y species from their time-series measurements at a number of ground-based sites; other additional information ("age" of stratospheric air) should ideally be obtained from the vertical profiles of long-lived gases like SF_6; (2) distributions of chemical tracers like CH_4, N_2O, and some of the key organic chlorine-containing gases, e.g., CFC-12, CFC-11 are available (remaining can be empirically obtained).

As expected, it is found that in the lower and middle stratosphere the abundance of organic chlorine is higher in the tropics compared to midlatitudes and the inverse is true for inorganic chlorine species. MPIC 2D model results are also in good agreement with these estimations based on in situ measurements. The amount of CCl_y species is calculated to be about 3100, 3355, and 3645 pptv, respectively on 27 March 1987, 9 April 1990, and 16 April 1994 near the tropopause over Hyderabad, based on observations. It can also be noted that the N_2O–CCl_y correlation plots obtained for Hyderabad, GAP and during AASE II measurements are in fairly good agreement. The inorganic chlorine concentrations are found to be about 2200, 2700, and 3000 pptv on 27 March 1987, 9 April 1990, and 16 April 1994, respectively at 32 km altitude. A comparison with previous observations clearly shows an increase of inorganic chlorine in the middle stratosphere during the period of measurements (1987–1994). These results imply slower removal of inorganic chlorine species from the stratosphere compared to the chlorine containing organic species.

Our results also indicate that even though the loading of chlorinated organic species from the troposphere to the stratosphere has started decreasing since around 1994, the severity of chlorine induced ozone depletion will continue in the later years. This delayed response is caused by the time lag due to transport of source gases from the troposphere to the stratosphere of about 5 years.

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