V. TROPOSPHERIC OH AND HCFC/HFC LIFETIMES

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The Tropospheric Lifetimes of Halocarbons and their Reactions with OH Radicals: An Assessment Based on the Concentration of ^{14}CO

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Tropospheric Hydroxyl Concentrations and the Lifetimes of Hydrochlorofluorocarbons (HCFCs)

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COMBINED SUMMARY AND CONCLUSIONS

The atmospheric lifetime of HCFCs is determined predominantly by reaction with tropospheric OH. Stratospheric loss is secondary and may contribute at most 10% of the total budget.

The lifetimes of HCFCs are determined here by three separate approaches:

(1) 2-D chemical transport model with semi-empirical fit to ^{14}CO;
(2) photochemical calculation of 3-D OH fields and integrated loss;
(3) scaling of the inferred CH_3 CCl_3 lifetime by rate coefficients.

Resulting lifetimes from all three independent approaches generally agree within 15%, as shown in the table below. The integrated losses calculated from the global OH fields in the models (1 & 2) are constrained by modelling of the observations and budgets for ^{14}CO and CH_3CDCl_3 (respectively). Method (3) may be expressed simply as

$$\text{lifetime (HCFC)} = 6.3 \text{ yr} \times k(CH_3\ CCl_3 \text{ at } 277\text{ K}) \ /\ k(\text{HCFC at } 277\text{ K}),$$

where the current estimate of the lifetime for methyl chloroform (6.3 yr) is based on the ALE/GAGE analysis (Prinn et al., 1987). Some of the errors associated with this scaling have been tested with the 3-D OH fields from method (2); method (3) should be reliable for calculating HCFC lifetimes in the range 1 to 30 years.

The calculated local concentrations of OH in these models (1 & 2) are not well tested since there are few observations of OH with which to compare. Based on method (2), the middle tropical troposphere (2-6 km) dominates the atmospheric loss and would be an important region in which to make observations of OH.

Estimated uncertainties in the HCFC lifetimes between 1 and 30 years are ±50% for (1) and ±40% for (2) & (3). Global OH values that give lifetimes outside of these ranges of uncertainty are inconsistent with detailed analyses of the observed distributions for ^{14}CO and CH_3CCl_3. The expected spatial and seasonal variations in the global distribution of HCFCs with lifetimes of 1 to 30 yr have been examined with methods (1) & (2) and found to have insignificant effect on the calculated lifetimes. Larger uncertainties apply to gases with lifetimes shorter than one year; however, for these species our concern is for destruction on a regional scale rather than global accumulation.

Future changes in the oxidative capacity of the troposphere, due to changing atmospheric composition, will affect HCFC lifetimes and introduce additional uncertainties of order ±20%.

Atmospheric Lifetimes for HCFCs

HCFC	k (cm^3 $molec^{-1}$ s^{-1})		lifetime (yr) for method* (1)	(2)	(3)
CH_3CCl_3	5.0×10^{-13}	exp(-1800/T)	5	5.4	6.3
(range)			(3-7)	(4-7)	(5.4-7.5)
CH_3F	5.4×10^{-12}	exp(-1700/T)	3.3	3.8	4.1
CH_2F_2	2.5×10^{-12}	exp(-1650/T)	6.0	6.8	7.3
CHF_3	7.4×10^{-13}	exp(-2350/T)	635.	289.	310.
CH_2FCl	3.0×10^{-12}	exp(-1250/T)	1.26	1.33	1.44
$CHFCl_2$	1.2×10^{-12}	exp(-1100/T)	1.80	1.89	2.10
CHF_2Cl (22)	1.2×10^{-12}	exp(-1650/T)	13.0	14.2	15.3
CH_3CH_2F	1.3×10^{-11}	exp(-1200/T)	0.31	0.25	0.28
CH_2FCH_2F (152a)	1.7×10^{-11}	exp(-1500/T)	0.60	0.58	0.63
CH_3CHF_2	1.5×10^{-12}	exp(-1100/T)	1.46	1.53	1.68
CH_2FCHF_2	2.8×10^{-12}	exp(-1500/T)	3.2	3.5	3.8
CH_3CF_3	2.6×10^{-13}	exp(-1500/T)	40.	38.	41.
CHF_2CHF_2	8.7×10^{-13}	exp(-1500/T)	10.4	11.4	12.3
CH_2FCF_3 (134a)	1.7×10^{-12}	exp(-1750/T)	13.1	14.4	15.5
CHF_2CF_3 (125)	3.8×10^{-13}	exp(-1500/T)	24.9	26.1	28.1
CH_3CFCl_2 (141b)	2.7×10^{-13}	exp(-1050/T)	6.7	6.7	7.8
CH_3CF_2Cl (142b)	9.6×10^{-13}	exp(-1650/T)	16.6	17.8	19.1
CH_2ClCF_2Cl	3.6×10^{-12}	exp(-1600/T)	3.5	4.0	4.2
CH_2ClCF_3	5.2×10^{-13}	exp(-1100/T)	4.1	4.4	4.8
$CHCl_2CF_3$ (123)	6.4×10^{-13}	exp(-850/T)	1.40	1.42	1.59
$CHFClCF_3$ (124)	6.6×10^{-13}	exp(-1250/T)	5.5	6.0	6.6

*Lifetimes from method (1) do not include stratospheric loss; those from method (2) include small additional stratospheric loss. Method (3) is based on scaling the methylchloroform lifetime of 6.3 yrs from Prinn et al. (Science, 238, 945-950, 1988) by the ratio of the rate coefficients at 277 K.

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THE TROPOSPHERIC LIFETIMES OF HALOCARBONS AND THEIR REACTIONS WITH OH RADICALS: AN ASSESSMENT BASED ON THE CONCENTRATION OF ^{14}CO

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EXECUTIVE SUMMARY

Chemical reaction with hydroxyl radicals formed in the troposphere from ozone photolysis in the presence of methane, carbon monoxide and nitrogen oxides provides an important removal mechanism for halocarbons containing C-H and C = C double bonds. The isotopic distribution in atmospheric carbon monoxide has been used to quantify the tropospheric hydroxyl radical distribution. This review reevaluates this methodology in the light of recent chemical kinetic data evaluations and new understanding gained in the life cycles of methane and carbon monoxide. None of these changes has forced a significant revision of the ^{14}CO approach. However, it is now somewhat more clearly apparent how important basic chemical kinetic data are to the accurate establishment of the tropospheric hydroxyl radical distribution.

The two-dimensional (altitude-latitude) time-dependent (seasonal) hydroxyl radical distribution obtained by the ^{14}CO approach has then been used in the Harwell model to estimate halocarbon lifetimes together with their confidence limits. A simple graphical procedure suffices to relate halocarbon lifetime to the pre-exponential factors and activation energy parameters which describe the temperature dependent OH + halocarbon rate coefficients. Lifetimes and their 1-sigma confidence limits are calculated using the Harwell two-dimensional model for a range of alternative fluorocarbons.

1. INTRODUCTION

The role of homogeneous gas phase reaction in the lower atmosphere was first investigated in the 1950's, in attempts to understand the phenomenon of photochemical smog and the chemistry involved in its formation (Leighton, 1961). It was Levy (1971) who first suggested that free-radical chemistry, driven by photochemical dissociation of ozone and nitrogen oxides, might be important in the background troposphere. He proposed that relatively high concentrations of the reactive hydroxyl radicals could be maintained in steady state in the background sunlit troposphere and that this steady state could provide an efficient scavenging mechanism for both natural and man-made trace constituents on a global scale.

Since then attempts have been made to unravel the free-radical chemistry of the troposphere and to quantify its role in the trace gas cycles. The reactions of the hydroxyl radical in the troposphere have been linked to a growing list of trace gases including ozone and NO (Levy 1971; Crutzen 1974), carbon monoxide (Weinstock and Niki 1972), methane (Ehhalt 1974), hydrogen (Seiler and Schmidt 1974) followed somewhat later by the sulphur compounds (Crutzen 1976) and halocarbons (Cox et al 1976). This review concerns the distributions of tropospheric hydroxyl radicals and their role in determining the lifetimes of halocarbons. Figure 1 shows some of the species and some of the atmospheric chemical reactions of importance in the global troposphere.

Interest in tropospheric chemistry has been stimulated by the problem of depletion of stratospheric ozone by chlorofluoromethanes and other chlorine-containing species (HMSO 1976; NAS 1977). The extent to which chlorine compounds injected at the earth's surface reach the stratosphere depends on the efficiency with which they are scavenged in the troposphere. Quantitative determination of the sink strength is required to assess the impact of various chlorine-containing species, both natural and man-made, on stratospheric ozone.

The scavenging processes acting in the troposphere may be divided into physical removal processes, in which species are absorbed irreversibly at the earth's surface or in precipitation elements (cloud and rain droplets, aerosols) and chemical removal processes which involve reactions in the atmosphere. Physical removal is often referred to as wet and dry deposition and may be highly efficient for some trace constituents such as ozone, sulphur dioxide and nitric acid. However for halocarbons it is not generally a particularly efficient process and it may be neglected for most species.

Chemical removal of halocarbons by destruction with tropospheric hydroxyl radicals has been shown to be an important sink for those halocarbons which contain H atoms and C = C double bonds, (Cox et al 1976). This sink process may be represented simply by the equation (1), below:

$$\mathrm{OH} + \mathrm{Halocarbon} \xrightarrow{k} \mathrm{sink} \qquad (1)$$

where k is some temperature dependent OH rate coefficient and OH is some form of globally averaged concentration of hydroxyl radicals.

Early two-dimensional model studies (Derwent and Eggleton 1978) have shown that because of the covariance of the temperature dependent value of k, the hydroxyl radical concentration [OH] and the halocarbon concentration itself [Hal], the lifetime due to OH reaction, τ, cannot be adequately represented by the simple box model equation (2), below:

$$\text{lifetime due to OH reaction} = \frac{\overline{[\mathrm{Hal}]}}{\overline{\mathrm{k}\ [\mathrm{OH}]\ [\mathrm{Hal}]}} = \frac{1}{\bar{\mathrm{k}}\ \overline{[\mathrm{OH}]}} \tag{2}$$

The more reactive halocarbons are not distributed uniformly throughout the troposphere and the sink strength reflects only the OH distribution close to the source, normally close to the surface in midlatitudes of the northern hemisphere. The more reactive the halocarbon, the larger the discrepancy between the "true" average OH concentration and that derived from the box model approach. The less reactive halocarbons often exhibit a more marked temperature dependence in their rate coefficients for OH radical attack. This concentrates oxidation close to the surface and makes chemical removal in the middle and upper troposphere relatively unimportant. The less reactive the halocarbon therefore the lower the tropospheric mean temperature required to calculate the mean reaction rate coefficient in equation (2).

For halocarbons of low reactivity with respect to hydroxyl radicals, mean lifetimes may extend to several years. Under these conditions, inter-hemispheric exchange will give a much more uniform distribution between the two hemispheres. As the halocarbon lifetime increases, then fraction of the surface injection which can reach the stratosphere will also increase. For a halocarbon with a lifetime of 10 years, up to 20% of the surface injection could be transported into the stratosphere. On this basis, methyl chloride and methyl chloroform have been identified as significant chlorine carriers to the stratosphere from natural and man made sources, respectively.

An accurate, quantitative assessment of the impact of a given halocarbon on stratospheric ozone, therefore requires a thorough understanding of tropospheric OH destruction. Such an understanding requires information on the following aspects:

- the reaction rate coefficient of the halocarbon with OH radicals, and its variations throughout the troposphere driven by temperature and pressure,
- the tropospheric distribution of OH radicals,
- the transport mechanisms of halocarbons within the troposphere,
- the halocarbon source strength and its spatial distribution,
- the nature and behaviour of any longer-lived degradation products,
- the transport mechanisms of halocarbons to the stratosphere.

Since the 1970s understanding of many of the above areas has grown tremendously as a result of the many field and laboratory investigations which have been carried out, carefully interpreted with theoretical modelling studies. Instrumental techniques and computational models are both areas which have seen impressive and powerful gains in performance which have had repercussions on our understanding on atmospheric composition and the influence of man's activities. It is now clearly understood that man has had and continues to have a significant influence on the global concentrations of many trace constituents. The number of species whose tropospheric concentrations have a significant upwards trend is being continually revised. In addition to carbon dioxide, now must be added the chlorofluoromethanes (CCl_3F, CCl_2F_2), carbon tetrachloride, methyl chloroform, methane and ozone, itself. Man's activities will most certainly have had an additional influence of the tropospheric distribution of hydroxyl radicals, however, it is not yet possible to quantify what this influence has been.

The tropospheric distribution of the hydroxyl radical has yet to be unambiguously defined. Despite the pioneering investigations of the KFA Julich group using long path ultraviolet absorption spectroscopy, a reliable climatology of hydroxyl concentrations with adequate three-dimensional and temporal resolution is unlikely to be available in the near future. To advance the assessment process for halocarbons in the absence of an observed tropospheric hydroxyl distribution, recourse has been made to derived or inferred distributions from the following principal sourcs:

- chemical modelling studies, (Crutzen and Fishman 1977),
- studies of halocarbon behaviour, particularly methyl chloroform, (Singh 1977; Neely and Plonka 1978),
- studies of the isotopic distribution in atmospheric carbon monoxide, (Volz, Ehhalt and Derwent 1981).

The results from all three methods agree relatively well with each other and with the available observations from the KFA Julich group, within their respective estimated confidence limits. It is, however, important to review these different methods and to form a judgement as to whether current understanding is adequate for assessment purposes.

This review addresses the isotopic distribution in atmospheric carbon monoxide with a view to quantifying the tropospheric hydroxyl distribution. The aim is to examine its potential role in removing from the atmospheric circulation, the proposed alternative aerosol propellants, foam blowing agents, solvents and refridgerants which are currently under consideration as replacements for those halocarbons containing chlorine which may reach the stratosphere. This review has been commissioned within the framework of the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS).

2. THE ISOTOPIC DISTRIBUTION IN ATMOSPHERIC CARBON MONOXIDE

The first attempts to calculate the global mean tropospheric hydroxyl concentration from isotopic distribution in atmospheric carbon monoxide were made by Weinstock 1969 and by Weinstock and Niki (1972). They used the three available ^{14}CO measurements by McKay et al (1963), an estimate of the global source strength for ^{14}CO from the well-known cosmic ray bombardment of atmospheric nitrogen molecules, the OH + CO rate coefficient and derived an estimate for the atmospheric turnover time for ^{12}CO of the order of 1 month. Furthermore, they suggested that OH radicals were responsible for the CO removal and obtained an estimate of their global mean abundance. Seiler (1974) argued that these early measurements of ^{14}CO might be too low and thus have given rise to too short a lifetime and too high a mean tropospheric hydroxyl radical concentration.

Volz, Ehhalt and Derwent (1981) repeated the methodology and obtained a mean tropospheric hydroxyl radical concentration of ($6.5\ ^{+3}_{-2}$) x 10^5 molecule cm^{-3} based on four refinements, viz:

- additional measurements of ^{14}CO in the lower troposphere,
- evaluated chemical kinetic data for the OH + CO reaction,
- improved life cycle data for ^{14}C and ^{12}C in the troposphere,
- a global two-dimensional time-dependent model to investigate the coupled CH_4-H_2-CO-NO_x-O_3 life cycles, replacing the box model approach.

In the intervening years since the publication of these early studies (Weinstock and Niki 1972; Volz, Ehhalt and Derwent 1981), understanding of the oxidizing capacity of the troposphere has developed significantly. The paragraphs which follow have therefore been devoted to a reevaluation of some of the measurements, data and assumptions which were essential in the Volz, Ehhalt and Derwent (1981) study. The general impression gained from this reevaluation is that subsequent research does appear to have neither undermined nor found the ^{14}CO method seriously flawed. It therefore remains a viable method for determining the tropospheric hydroxyl distribution. Nevertheless, some of the input assumptions could now be questioned in detail and these areas are highlighted and their impact on the determination of the tropospheric hydroxyl distribution assessed.

The Methodology Used

The methodology adopted by Volz, Ehhalt and Derwent (1981) was to take a precalculated two-dimensional (altitude, latitude), time-dependent (monthly) field of tropospheric hydroxyl radicals and linearly scale it until it generated surface ^{14}CO and ^{12}CO concentrations which balanced observations. At the point of balance, the methodology simultaneously determined the tropospheric hydroxyl distribution and the biogenic source strength of ^{12}CO, both of which are coupled unknowns.

The estimated tropospheric hydroxyl distribution contains uncertainties which derive directly from the uncertain ^{14}CO measurements, the uncertainties in the ^{14}CO and ^{12}CO life cycles, the uncertainties in the parameters used in the two-dimensional model and the uncertainties inherent all the assumptions made in the model formulation itself. The uncertainty analysis treatment in Volz, Ehhalt and Derwent (1981) considered the contributions from the likely errors in:

- the ^{14}CO production from cosmic rays, (Lingenfelter 1963),
- the ^{12}CO emission from fossil fuel burning, (Seiler 1974; Logan et al 1981),
- the ^{14}CO measurements, (McKay et al 1963; Volz, Ehhalt and Derwent 1981),
- the ^{12}CO latitudinal distribution, (Seiler and Schmidt 1974),
- the transport and chemistry schemes employed in the two-dimensional model, (Derwent and Curtis 1977).

Experimental Techniques

The measurement of the concentration of ^{14}CO is essential to the ^{14}CO approach. The early measurements of McKay et al 1963 relied on the isotopic ratio viz. $^{14}CO/^{12}CO$ in air samples obtained from an air liquefaction plant. McKay et al however failed to determine simultaneously the ^{12}CO concentration and this led to the introduction of uncertainties in using the ^{14}CO approach. A major challenge in the study by Volz, Ehhalt, Derwent and Khedim (1979) was therefore the measurement of the ^{14}CO concentration.

Volz, Ehhalt, Derwent and Khedim (1979) have described their experimental procedures in some detail and only a brief outline is given in the paragraphs below. The procedure consists of two steps,

- the quantitative separation and the collection of the CO from ambient air,
- the determination of its isotopic ratios, $R_{\infty} = [^{14}CO]/[^{12}CO]$.

The ^{14}CO concentration is then given by:

$$[^{14}CO] = R_{\infty} \cdot [^{12}CO]$$

The separation of the CO from ambient air was achieved by quantitative oxidation to CO_2 on a hot platinum catalyst, followed by absorption in CO_2-free aqueous NaOH. Prior to this the atmospheric CO_2 was removed from the air sample by absorption in NaOH. Interferences from any remaining CO_2 were determined by gas chromatography and were found to be less than 5%. The CO concentration in the air was measured by gas chromatography and, in addition, calculated from the amount of CO collected and the volume of air sampled, (100-200 m^3).

The isotopic ratio of the sampled CO was measured in a low-level counting system, similar to those used for ^{14}C dating, with an accuracy of ± 3-5%. The counting system was calibrated against the ^{14}CO standard of the Institut für Umweltphysik, Universitat Heidelberg. The overall accuracy in the determination of the ^{14}CO concentration was largely determined by uncertainties associated with the sampling procedure as discussed by Volz, Ehhalt, Derwent and Khedim (1979), and was generally on the order of $\pm 10\%$ (1σ), including any possible systematic bias.

Measured ^{14}CO Concentrations

So far measurements of the ^{14}CO concentration have been reported only for the northern hemisphere, (Volz, Ehhalt and Derwent 1981). Most of the samples were collected during 1977 and 1978 at a remote, rural site in the Eifel mountains (51°N 2°W) in the Federal Republic of Germany. In addition, three samples were collected during a cruise of the RV Knorr over the Mediterranean Sea and the Atlantic (36° to 46°N) in April 1976 and two samples at Miami, Florida (27°N) in September 1977, (Volz, Ehhalt, Derwent and Khedim 1979).

The ^{14}CO concentration data exhibit a well-defined seasonal cycle with a winter maximum of about 20 molecule cm^{-3} and a summer minimum of 10 molecule cm^{-3}. The annual cycle in ^{14}CO reflects the influence of the chemical sink due to destruction by tropospheric OH radicals.

The ^{14}CO concentration data also show evidence of a latitudinal gradient increasing from the equator to the North Pole. The concentrations at Miami (27°N) in September 1972, 4.2 ± 0.7 molecule cm^{-3} are almost a factor of three smaller than those found at 51°N for the same time of year. Similarly, the concentrations measured over the Atlantic Ocean show an increase from 15 molecule cm^{-3} at 36°N to 19 molecule cm^{-3} at 43°N. This latitudinal distribution in ^{14}CO reflects the influence of the tropospheric OH distribution increasing from the North Pole towards the equator.

Evaluated Rate Coefficient Data

An important aspect of the two-dimensional model used to calculate the tropospheric distribution of hydroxyl radicals, is the chemical kinetic input data adopted. Figure 1 illustrates the main free radical reactions which are believed to be occurring in the sunlit free troposphere. To a degree, the OH distribution estimated by Volz, Ehhalt and Derwent (1981) is sensitive to all the chemical kinetic assumptions. However, some of the chemical kinetic input parameters exert a more significant influence on the OH concentrations than others and it is upon these that we have concentrated upon in the paragraphs below. The Volz, Ehhalt and Derwent (1981) paper drew much of its chemical kinetic input data from the 1979 CODATA review (Baulch et al 1980). This can be directly compared with the 1988 IUPAC evaluation (Atkinson et al 1989).

OH to HO_2 interconversion reactions

The conversion of hydroxyl to hydroperoxyl radicals is driven largely by the reaction of OH radicals with carbon monoxide, methane and hydrogen. There has been an important revision in the OH + CO rate coefficient over the intervening years from 1.4×10^{-13} $(1 + p_{atm})$ cm^3 $molecule^{-1}$ s^{-1} to 1.5×10^{-13} $(1 + 0.6\ p_{atm})$ cm^3 $molecule^{-1}$ s^{-1}. This reevaluation reduces the rate coefficient by 14% at 1 atmosphere pressure and increases it by about 3% under the conditions in the upper troposphere. There have been revisions to the OH + CH_4 and OH + H_2 rate coefficients. Under the conditions approproate to the lower troposphere, the OH + CH_4 rate coefficient has been increased by about 6%, whereas the OH + H_2 rate coefficient has decreased by about 4%. Overall, these latter reevaluations are not likely to be significant compared with that of the OH + CO reaction.

In the two-dimensional model study, the concentration fields of CO, CH_4 and H_2 were taken from the available measurements and sufficient CO, CH_4 and H_2 were injected into the model at every time step to balance removal by all processes in the surface layer including the reaction with hydroxyl radicals. If a lower OH + CO rate coefficient had been employed then, to maintain the same $OH \rightarrow HO_2$ flux, a 10-15% higher OH concentration would be required.

HO_2 to OH interconversion reactions

The conversion of HO_2 radicals to OH radicals is largely driven by the reactions of HO_2 radicals with ozone and nitric oxide. The rate coefficients of these two reactions under conditions appropriate to lower troposphere have not changed by more than 1-7%. These reevaluations are of negligible importance.

HO_2 recombination to form hydrogen peroxide

The recombination of HO_2 radicals to form hydrogen peroxide dominates free radical termination in the free troposphere at all heights and latitudes where NO_x levels are low. The reaction has generally

Free Radical Production

O_3 = radiation (280 nm $<\lambda<$ 310 nm) = $O(^1D) + O_2$
$O(^1D) + H_2 = OH + OH$

RCHO + radiation (280 nm $<\lambda<$ 360 nm) = R + HCO
$HCO + O_2 = HO_2 + CO$

HO to HO_2 Interconversion

$OH + CO = H + CH_2$
$OH + CH_4 = CH_3 + H_2O$
$OH + H_2 = H + H_2O$
$OH + O_3 = HO_2 + O_2$
$OH + RCHO = RCO + H_2O$

HO_2 to OH Interconversion

$HO_2 + NO = OH + NO_2$
NO_2 + radiation (280 nm $<\lambda<$ 430 nm) = O + NO
$O + O_2 + M = O_3 + M$
$HO_2 + O_3 = OH\ O_2 + O_2$

Free Radical Loss Processes

$HO_2 + HO_2 + M = H_2O_2 + M$
$OH + NO_2 + M = HNO_3 + M$

Temporary Reservoir Formation

$RCO(O_2) + NO_2 = RCO(O_2)NO_2$
$RCO(O_2)NO_2 = RCO(O_2) + NO_2$
$RCO(O_2) + NO = R + CO_2 + NO_2$

Nighttime Chemistry

$NO_2 + O_3 = NO_3 + O_2$
$NO_3 + NO_2 + M = N_2O_5 + M$
$N_2O_5 + M = NO_3 + NO_2 + M$

Heterogeneous Processes

$HNO_3 + NaCl = NaNO_3 + HCl$
N_2O_5 = aerosol nitrate

Figure 1. The main species and atmospheric chemical reactions of importance in the global troposphere.

not been intensively investigated in laboratory chemistry studies and evaluations have had only a few studies to draw upon. It is not surprising to find that this reaction has undergone a dramatic reevaluation between the 1979 CODATA (Baulch et al 1980) and 1988 IUPAC (Atkinson et al 1989) studies. The unusually large negative activation energy reported previously has been replaced by a significantly smaller but nevertheless still negative value. The effect of the reevaluations is to produce a HO_2 + HO_2 rate coefficient which is about a factor of 1.7 lower in the lower troposphere and a factor of 4 lower in the upper troposphere.

Because of the square dependence of the free radical destruction rate on the HO_2 radical concentration, the reevaluation of the HO_2 + HO_2 rate data should lead to OH and HO_2 radical concentrations about a factor of two higher in the upper troposphere and about thirty percent higher in the lower troposphere.

The reevaluations in the chemical kinetic data indeed strengthen the results of Volz, Ehhalt and Derwent, 1981: at the time of their evaluation, the OH concentrations required to balance the budgets of both ^{12}CO and ^{14}CO were a factor of 1.7 greater than those derived from photochemical models. It appears now that inadequacies in the chemical kinetic data, most important the rate coefficients for the OH +

Table 1. The budget for atmospheric carbon monoxide (^{12}CO) as estimated by Volz, Ehhalt and Derwent (1981) and compared with a more recent assessment (Seiler and Conrad 1987)

Source Strength, g yr^{-1}	**^{14}CO Methodology**	**Present View**
Terpenes and isoprene	1150×10^{12}[a]	1000×10^{12}
Ocean[b]	100×10^{12}	100×10^{12}
Methane oxidation	880×10^{12}[c]	600×10^{12}
Man made sources[c]	640×10^{12}	640×10^{12}
Biomass burning	-	1000×10^{12}
Sink Strength, g yr^{-1}		
OH oxidation	2450×10^{12}[d]	2000×10^{12}
Surface removal	320×10^{12}[e]	390×10^{12}
Stratospheric removal	-	110×10^{12}
Total Source Strength, g yr^{-1}	2770×10^{12}	3300×10^{12}
Total Atmospheric Mass, g	480×10^{12}	550×10^{12}
Lifetime, yrs	0.17	0.17

Notes:
a. calculated assuming mass balance.
b. Seiler (1974). Logan (1981).
c. Seiler (1974).
d. from Derwent and Curtis (1977).
e. Liebl and Seiler (1976).

CO and HO_2 + HO_2 reactions, indeed resulted in too low OH concentrations in the photochemical models at that time. With the revised rate coefficients, the OH distributions from ^{14}CO and from photochemical models are in much better agreement.

Life Cycle Data

Inherent in the methodology were some basic assumptions concerning the methane, carbon monoxide, hydrogen, nitrogen oxides and ozone life cycles in the two-dimensional model of ^{14}CO and in the two-dimensional model used to estimate the hydroxyl radical concentrations, themselves. At the point where the ^{12}CO and ^{14}CO distributions balanced, the methodology returned the biospheric source strength of ^{12}CO allowing a solution to the ^{12}CO budget.

In Table 1, this budget is examined in some detail and compared with a more recent evaluation by Seiler and Conrad (1987). The overall conclusion is that the broad features of the carbon monoxide budget have remained unchanged. In detail, though, there is a major difference in the significance given to biomass burning. The Volz, Ehhalt and Derwent (1981) study was unable to resolve the difference between biomass burning, on the one hand, and terpene and isoprene oxidation on the other, as both are sources of ^{14}CO and ^{12}CO. Subsequently, field campaigns in the tropical regions of South America have led to a quantification of this source as shown in Table 1.

The inclusion of the biomass burning source would have an impact on the Volz, Ehhalt and Derwent (1981) analysis because of the different latitudinal distributions of the ^{12}CO and ^{14}CO source strengths.

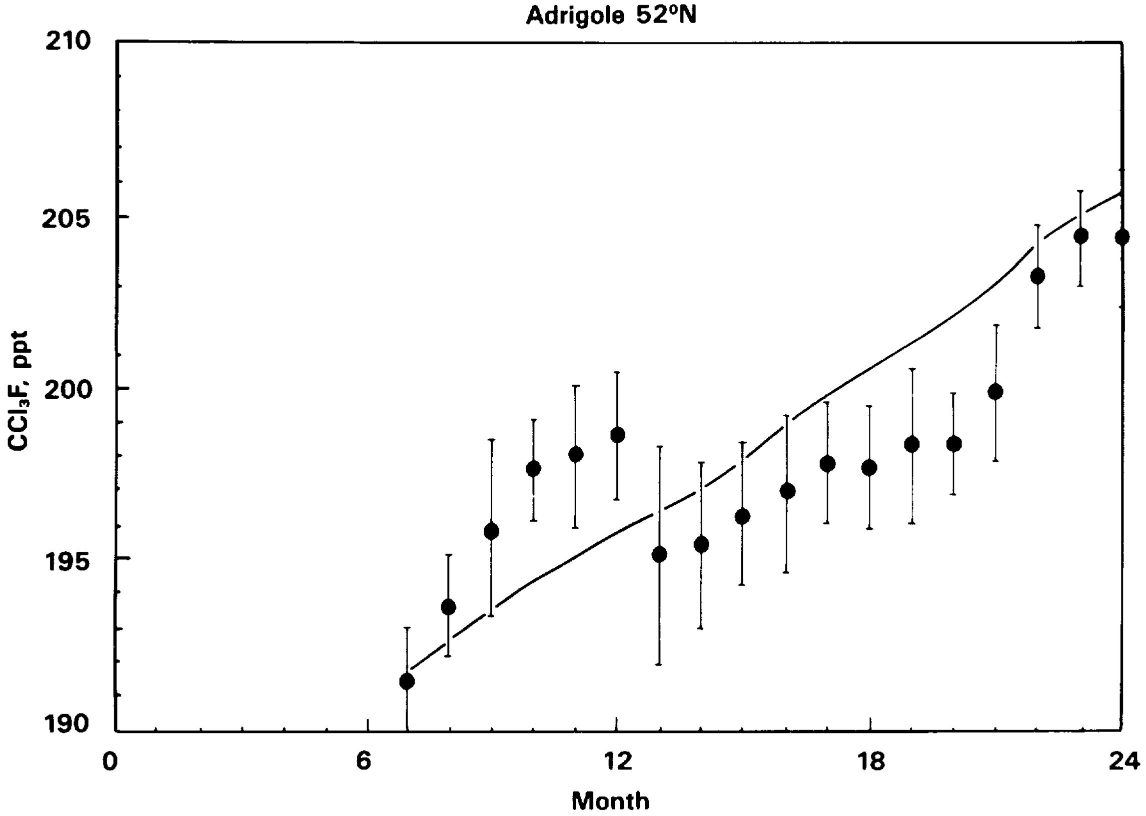

Figure 2. The time series of CCl_3F concentrations at Adrigole 52°N (Cunnold et al. 1986) and the two-dimensional model results.

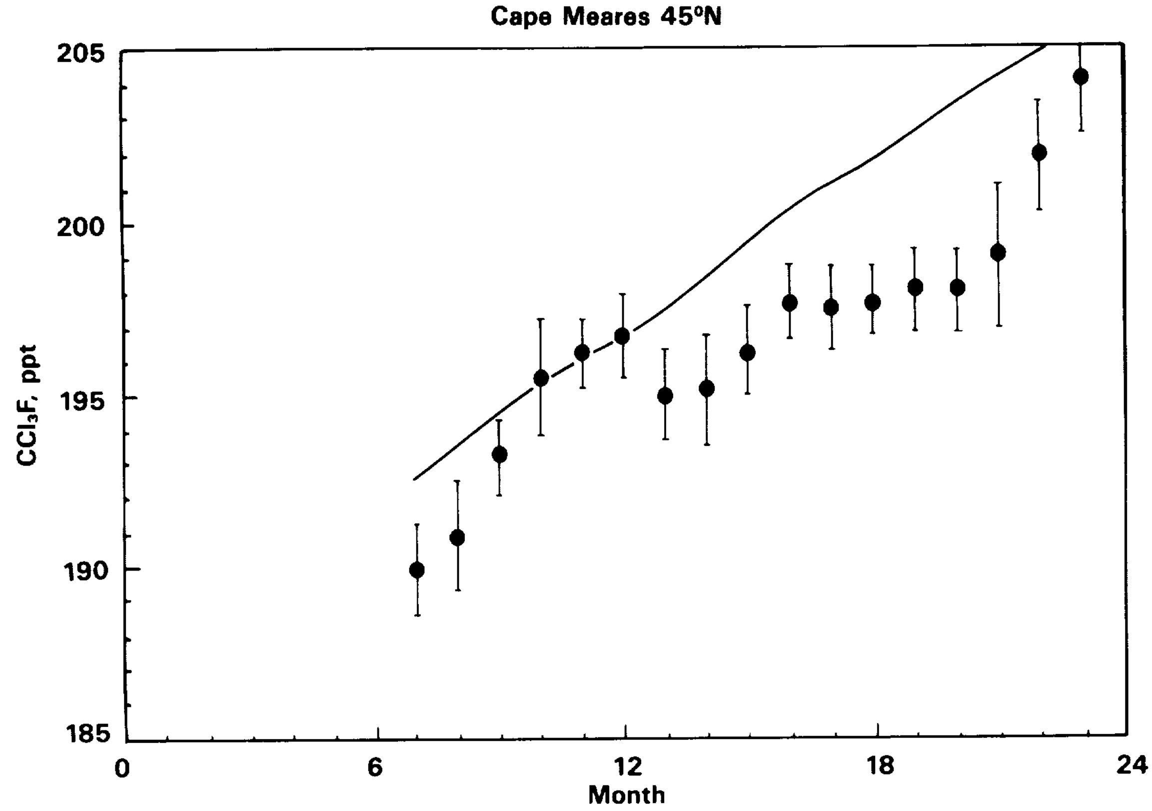

Figure 3. The time series of CCl$_3$F concentrations at Cape Meares 45°N (Cunnold et al. 1986) and the two-dimensional model results.

The difference is minor because ^{14}CO is rather insensitive to this source and is unlikely to have seriously distorted the 2-D model study.

The revised OH + CO rate coefficient has a direct influence on the evaluation of the tropospheric OH distribution through the ^{14}CO life cycle. An important source of ^{14}CO is located in the upper troposphere where the OH + CO rate coefficient has been reevaluated. A fixed ^{14}CO injection was assumed so that the increase in OH + CO rate coefficient would lead to a decreased ^{14}CO penetration into the free troposphere. The reduced OH + CO rate coefficient at the surface would reduce ^{14}CO fluxes there. Overall the OH + CO rate coefficient reevaluation would induce small changes in the tropospheric OH distribution of the order of ± 7%, downwards. The biospheric source strength of ^{12}CO would accordingly require downwards revision to about 1000 x 10^{12} g yr^{-1}. This latter estimate of the ^{12}CO source strength is identical with the more recent assessment of Seiler and Conrad (1987) quoted in Table 1.

Two-dimensional model transport data

The version of the Harwell two-dimensional model used by Volz, Ehhalt and Derwent (1981) had 7 vertical layers of 2.5 km depth and 18 latitude ranges weighted equally by the sine of latitude. Transfer between the boxes both horizontally and vertically was driven by advection and turbulent mixing. The zonally averaged wind fields were taken from Newell et al (1972) and the eddy diffusion coefficients from Louis (1975).

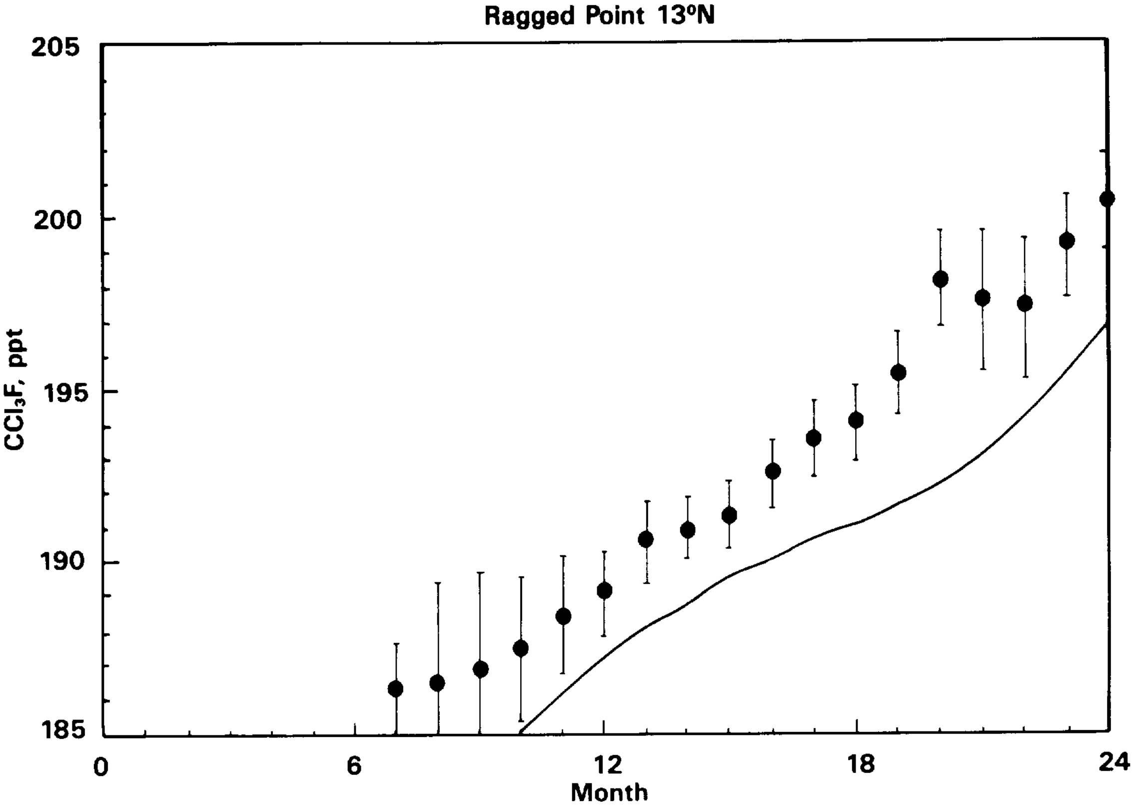

Figure 4. The time series of CCl_3F concentrations at Ragged Point 13°N (Cunnold et al. 1986) and the two-dimensional model results.

The sensitivity of the tropospheric OH distribution derived from the ^{14}CO approach to changes in the transport parameters was investigated by Volz, Ehhalt and Derwent (1981). They concluded that large changes in the transport coefficients of up to a factor of two increase or decrease made little difference to the tropospheric OH distribution required to balance the ^{12}CO and ^{14}CO life cycles. The estimated tropospheric OH distributions changed by less than ± 20%.

In the intervening years since the first studies with the Harwell two-dimensional model, the ALE experiment has made available high quality halocarbon emissions and time series concentration data for a wide latitude range covering both hemispheres (Cunnold et al 1986). These halocarbon measurements provide an excellent database to validate the transport schemes in two-dimensional models.

The CCl_3F emissions for the period 1931-1982 (Chemical Manufacturers Association 1983, 1988) were used in the Harwell two-dimensional model and an upper boundary condition was applied representing stratospheric photolysis, adjusted to give a CCl_3F lifetime in the range 50-75 years.

Figures 2-6 illustrate the model calculated and measured concentrations of CC_3F at Adrigole, Republic of Ireland (52°N 10°W) Cape Meares, Oregon (45°N, 124°W), Ragged Point, Barbados (13°N 59°W), Point Matatula, American Samoa (14°S, 171°W) and Cape Grim, Tasmania (41°S, 145°E) for the eight-

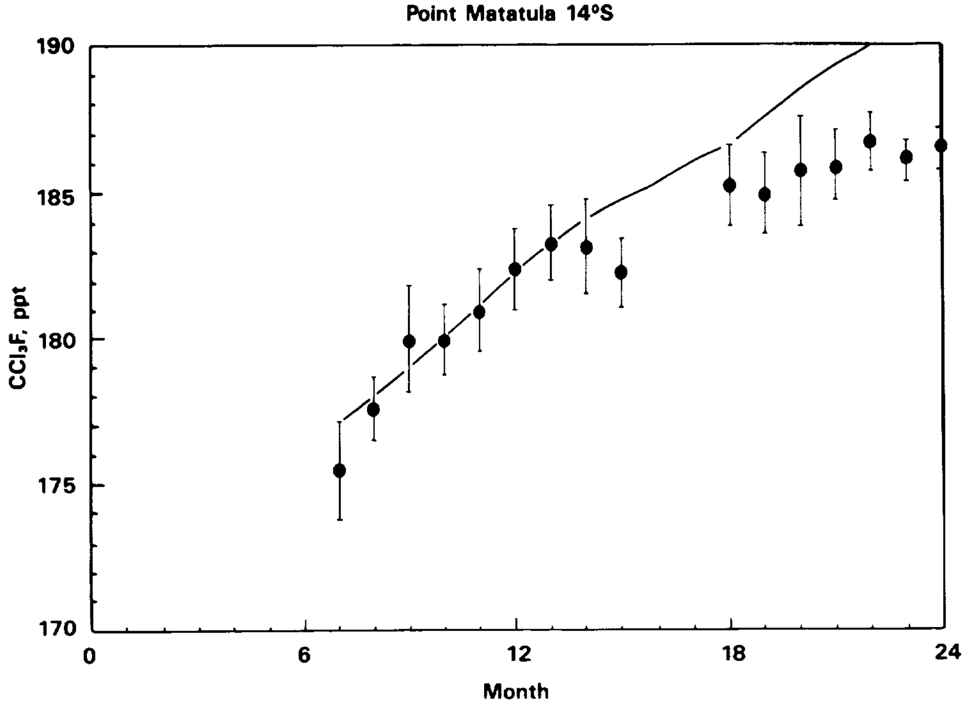

Figure 5. The time series of CCl_3F concentrations at Point Matatula 14°S (Cunnold et al. 1986) and the two-dimensional model results.

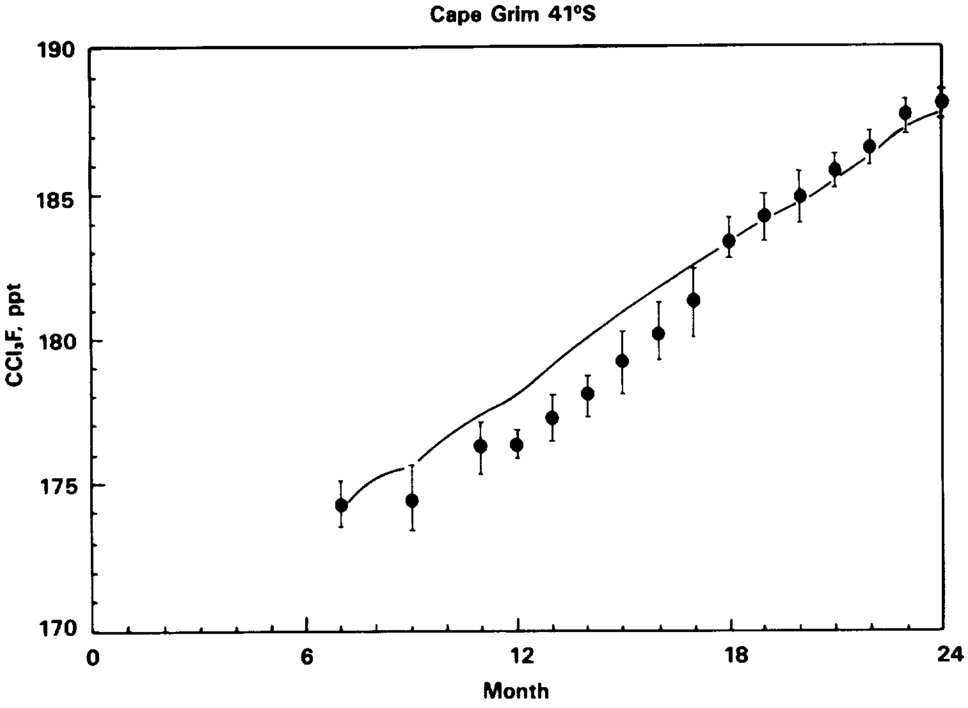

Figure 6. The time series of CCl_3F concentrations at Cape Grim 41°S (Cunnold et al. 1986) and the two-dimensional model results.

een month period from July 1981 to December 1982 (Cunnold et al 1986). Viewed against the ALE measurements, the transport scheme in the Harwell two-dimensional model is clearly performing adequately and without systematic bias.

The conclusion is that the transport scheme adopted in the Volz, Ehhalt and Derwent (1981) study represents adequately the gross features of halocarbon transport and this is an important model validation. Furthermore, the sensitivity of the estimated tropospheric OH distribution to the magnitudes of the transport coefficients is not strong. It is unlikely therefore that inadequacies in present understanding of global transport have seriously influenced the uncertainty in the estimated tropospheric OH distribution using the ^{14}CO method.

3. THE TROPOSPHERIC DISTRIBUTION OF OH RADICALS AND HALOCARBON LIFETIMES

Halocarbon Lifetimes

The behaviour of a halocarbon in a two-dimensional (altitude-latitude) atmosphere injected at the earth's surface, subject to stratospheric destruction and oxidation by hydroxyl radicals can be described by the differential equation:

$$\frac{d}{dt}[\mathrm{Hal}] + \mathrm{div}\,([\mathrm{Hal}]\,.\,\mathrm{U}) - \mathrm{div}\,(\mathrm{K.N.}\ \mathrm{grad}\,([\mathrm{Hal}]/\mathrm{N})$$

$$= \mathrm{E} - \mathrm{k}[\mathrm{OH}][\mathrm{Hal}] - \mathrm{SL}[\mathrm{Hal}] \qquad (3)$$

The time behaviour of the halocarbon concentration [Hal] in molecule cm^{-3} was computed by solving the above continuity equation over a 6 x 18 mesh point grid extending vertically in 2.5 km steps and in 18 steps latitudinally with equal spacing in sine ϕ where ϕ is the latitude angle. The two-dimensional wind field, U, and the eddy diffusion tensor, K, were taken from Newell et al (1972) and Louis (1975), respectively. The detailed procedures used in the finite-differencing scheme have been described elsewhere (Derwent and Curtis 1977). The finite difference form of the above equation was integrated numerically using the Harwell program FACSIMILE (Curtis and Sweetenham 1987). For a 100 year model simulation, 15 minutes computer time were required using an IBM compatible 80386/80387-based microcomputer (Dell System 310).

The terms in the above continuity equation describing the halocarbon behaviour were derived as follows:

- E: a time-independent halocarbon injection was assumed with a spatial distribution which closely followed the population distribution between the hemispheres,
- SL: stratospheric loss coefficient, which was set to give a lifetime due to stratospheric removal, acting on its own, of 50-100 years,
- [OH]: this is the time dependent two-dimensional distribution of tropospheric hydroxyl radicals determined by Volz, Ehhalt and Derwent (1981) and illustrated in figure 7,
- k: this is the temperature dependent rate coefficient for hydroxyl radical attack on the halocarbon of interest.

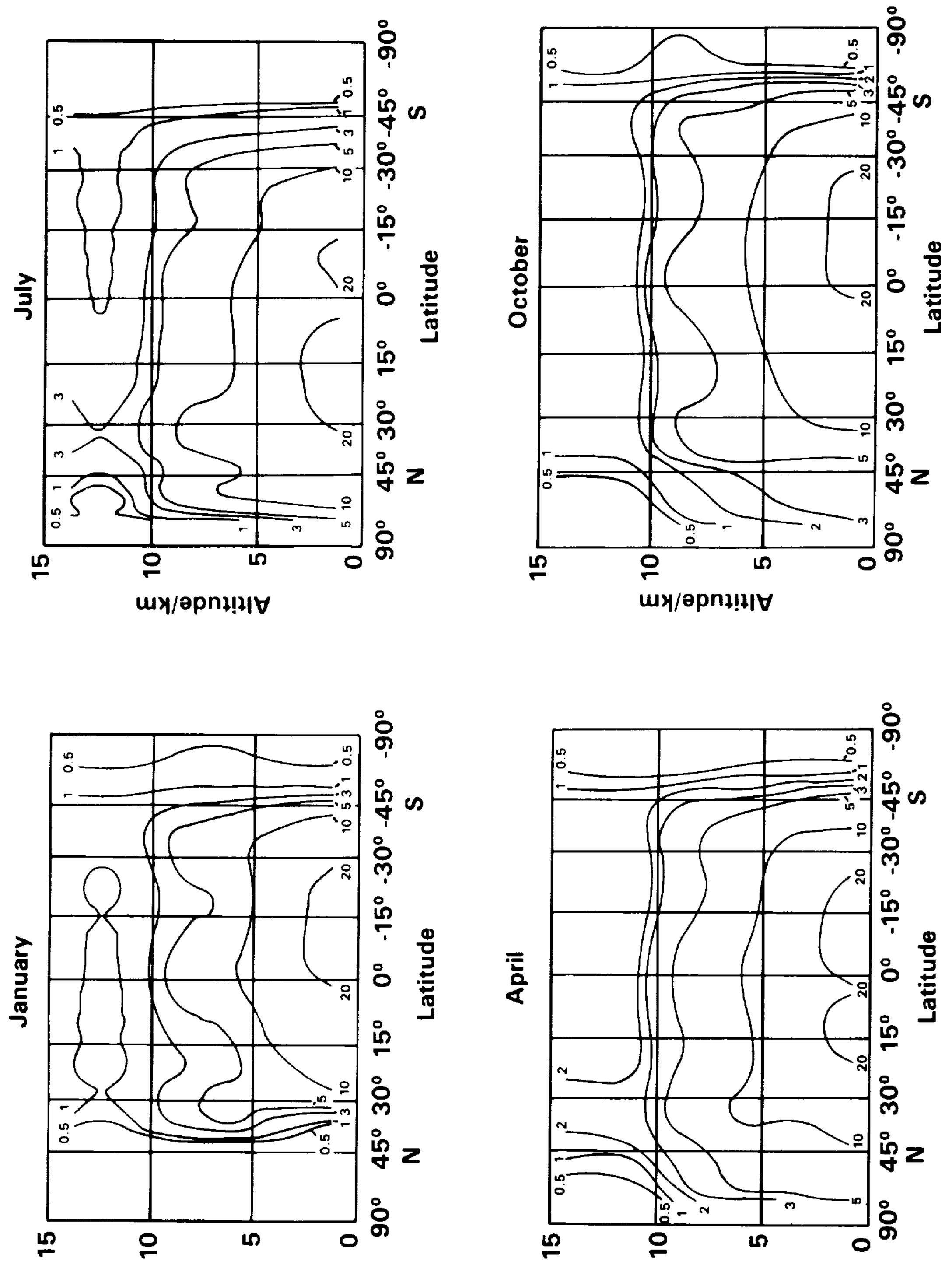

Figure 7. Distribution of hydroxyl radicals ^{14}CO method in 10^5 molecule cm^{-3}

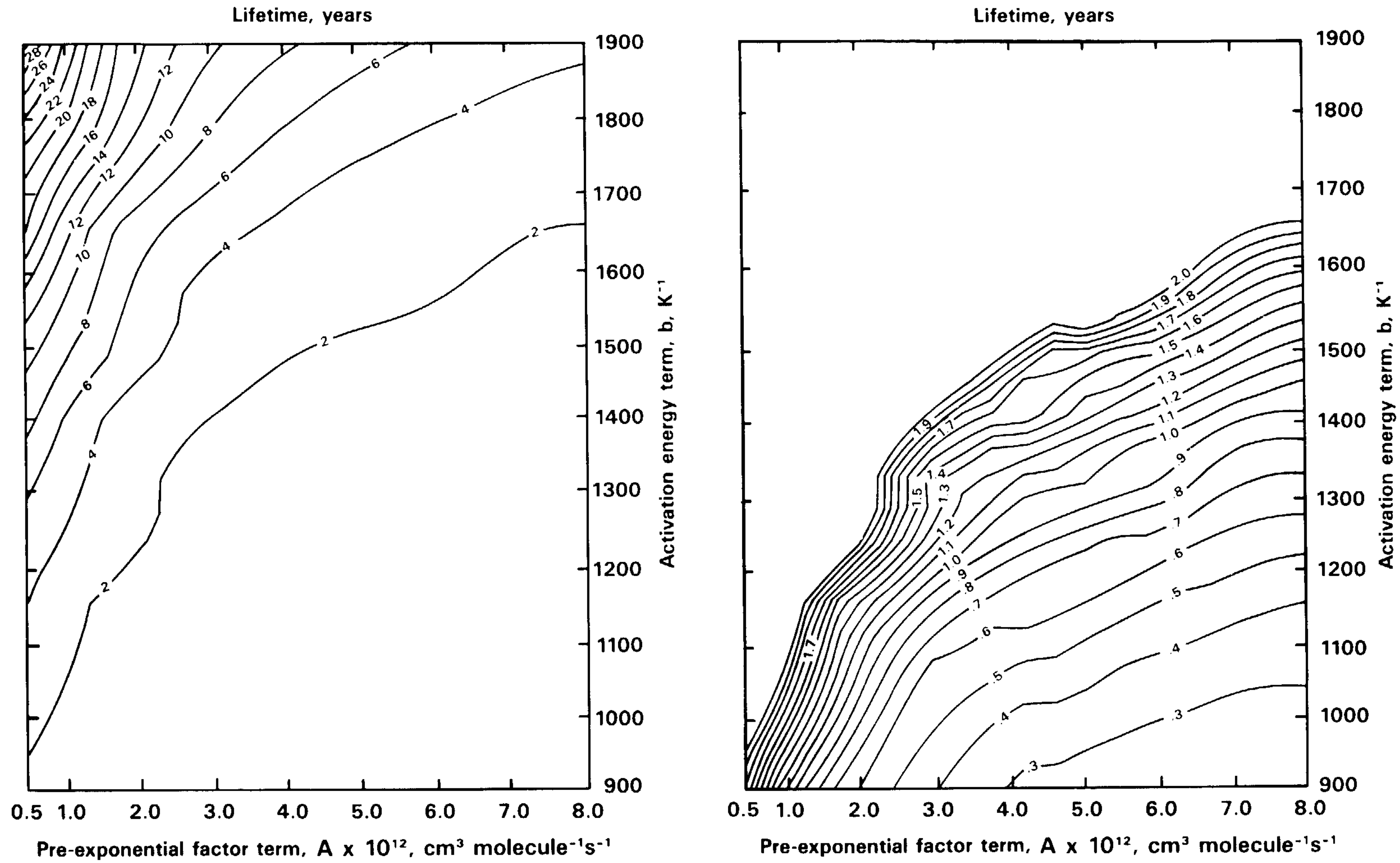

Figure 8. Halocarbon lifetimes in years determined by the ^{14}CO method for halocarbons reacting with OH radicals with a rate coefficient of A exp (-b/T) where T is the temperature in K.

At the end of the 100 year model experiment, the total model halocarbon inventory was divided by the total halocarbon injection rate to determine the halocarbon lifetime. The assumption of fixed tropospheric hydroxyl radical concentrations implies low tropospheric halocarbon loadings so as not to perturb the tropospheric hydroxyl radical concentrations. For reactive halocarbons, this implies that halocarbon concentrations are not more than 1 ppb at the most.

Figure 8 shows the total lifetimes including both tropospheric OH oxidation and stratospheric removal calculated for various assumptions concerning the form of the temperature dependent OH + halocarbon rate coefficient. Clearly, this temperature dependent parameter exerts a dominant influence on halocarbon lifetime, with lifetimes covering 0.2 - 30 years for reasonable ranges in expected values of preexponential factors and activation energies.

However the ^{14}CO method is not uncertainty-free and its accuracy and precision as a means of determining halocarbon lifetime is dependent on a whole range of experimental, life cycle and modelling assumptions which may be called into question. Volz, Ehhalt and Derwent (1981) gave some thought to uncertainty limits on their tropospheric OH distribution which this reevaluation has not changed. They recommended a mean tropospheric OH concentration of $6.5\ ^{+3}_{-2}$ molecule cm^{-3}. Assuming that the kinetic parameters defining the OH + halocarbon rate coefficient are described with complete certainty, we can use the 1-sigma confidence limits for the tropospheric OH distribution to determine the confidence limits of the halocarbon lifetime. The Harwell two-dimensional model was therefore rerun with the entire tropospheric OH distribution scaled upwards and downwards to the 1-sigma confidence limits. The resulting upper and lower 1-sigma confidence limits of the halocarbon lifetimes encompassed the range of a factor of two for all the halocarbons examined. Lifetimes were apparently slightly more accurately determined for the longer-lived halocarbons, reflecting the influence of the assumed constant stratospheric removal.

Lifetimes of Alternative Fluorocarbons

For some of the candidate alternative fluorocarbons evaluated chemical kinetic data for the OH + halocarbon degradation reactions are already available, Table 2. The lifetimes of these halocarbons due to stratospheric removal and tropospheric OH radical degradation can therefore be determined using the Harwell two-dimensional model. Table 2 gives the atmospheric lifetimes calculated for a constant injection in mid-latitudes of the northern hemisphere from a 100 year model calculation. The tropospheric OH distribution calculated with the ^{14}CO method gives lifetimes for the alternative fluorocarbons in the range 0.3-635 years. For most of the alternative halocarbons, these lifetimes are considerably shorter than the corresponding lifetimes for the fully halogenated halocarbons.

To complete the environmental acceptability work, modelling studies are required following up the behaviour of any chlorine-containing molecular fragments produced by the halocarbon degradation. The behaviour of the fragments could readily be incorporated into the two-dimensional model to determine the magnitude of any stratospheric fluxes of species such as $COCl_2$, $COHCl$, CF_3COCl, $CFCl_2CHO$, $CFCl_2CO(O_2)NO_2$, CF_2ClCHO, $CF_2ClCO(O_2)NO_2$, $COFCl$ and so on. Competing processes for these chlorine-containing fragments would include tropospheric degradation, dry deposition, photolysis and wet scavenging.

Table 2. OH + halocarbon rate coefficients and atmospheric lifetimes for a range of alternative fluorocarbons

Formulae	OH + halocarbon rate coefficient, cm^3 $molecule^{-1}$ s^{-1}	Lifetime,[c] yrs	
		Stratospheric loss	None
CH_3F	$5.4 \times 10^{-12} \exp(-1700/T)$	3.12	3.33
CH_2F_2	$2.5 \times 10^{-12} \exp(-1650/T)$	5.40	6.0
CHF_3	$7.4 \times 10^{-13} \exp(-2350/T)$	46.35	635.0
CH_2FCl	$3.0 \times 10^{-12} \exp(-1250/T)$	1.23	1.26
$CHFCl_2$	$1.2 \times 10^{-12} \exp(-1100/T)$	1.74	.80
CHF_2Cl	$1.2 \times 10^{-12} \exp(-1650/T)$	10.35	13.0
CH_3CH_2F	$1.3 \times 10^{-11} \exp(-1200/T)$	0.31	0.31
CH_2FCH_2F	$1.7 \times 10^{-11} \exp(-1500/T)$	0.59	0.60
CH_3CHF_2	$1.5 \times 10^{-12} \exp(-1100/T)$	1.42	1.46
CH_2FCHF_2	$2.8 \times 10^{-12} \exp(-1500/T)$	2.98	3.17
CH_3CF_3	$2.6 \times 10^{-13} \exp(-1500/T)$	22.29	40.2
CHF_2CHF_2	$8.7 \times 10^{-13} \exp(-1500/T)$	8.64	10.4
CH_2FCF_3	$1.7 \times 10^{-12} \exp(-1750/T)$	10.40	13.1
CHF_2CF_3	$3.8 \times 10^{-13} \exp(-1500/T)$	17.06	25.9
CH_3CFCl_2	$2.7 \times 10^{-13} \exp(-1050/T)$	5.89	6.68
CH_3CF_2Cl	$9.6 \times 10^{-13} \exp(-1650/T)$	12.49	16.6
CH_2ClCF_2Cl	$3.6 \times 10^{-12} \exp(-1600/T)$	3.28	3.51
CH_2ClCF_3	$5.2 \times 10^{-13} \exp(-1100/T)$	3.80	4.11
$CHCl_2CF_3$	$6.4 \times 10^{-13} \exp(-850/T)$	1.36	1.40
$CHFClCF_3$	$6.6 \times 10^{-13} \exp(-1250/T)$	4.99	5.54

Notes:

a. Chemical kinetic data from Hampson, Kurylo and Sander (1989)
b. T is absolute temperature in K
c. Lifetimes in steady state have been determined in a two-dimensional model assuming a northern hemispheric and constant injection rate, allowing for either 2% yr stratospheric removal or not
d. The 1-sigma confidence limits on the lifetimes encompass a range of a factor of two.

4. CONCLUSIONS

A review of the ^{14}CO method for determining the tropospheric hydroxyl radical distribution has revealed a number of areas where changes have occurred since the original publication of Volz, Ehhalt and Derwent (1981). None of these changes has however forced a revision of the approach. They have served to complete our understanding of areas which were difficult to understand in the early work. The chemical kinetic data is notable in this regard. It is now much easier to understand why the early hydroxyl radical concentrations may have been under-estimated in the photochemical models as compared to the ^{14}CO evaluation.

For the expected OH + halocarbon chemical rate coefficient parameters defined in terms of preexponential factors and activation energies, it is possible to estimate resulting halocarbon lifetimes using a simple graphical procedure. The ^{14}CO approach allows the determination of tropospheric halocarbons lifetimes, halocarbons with reasonable precision, 1-sigma confidence limits spanning about a factor of two.

It is important to remember that OH + halocarbon rate coefficients, hydroxyl distributions and halocarbon concentrations exhibit important covariance terms so that halocarbon lifetimes are not well-determined quantities. The lifetimes determined in this review are valid only for halocarbons injected at the northern hemisphere surface over the latitude range of the major continental land masses and population centres.

To illustrate the ^{14}CO method, the graphically determined lifetimes for methane and methyl chloroform are found to be $7\,^{+3}_{-2}$ and 5 ± 2 years, respectively, which are in close accord with our two-dimensional model studies (Cox and Derwent 1981; Derwent and Eggleton 1978), and current literature evaluations (Ehhalt 1988; Prinn 1988). The current methyl chloroform lifetime overlaps the ALE/GAGE evaluation, $6.3\,^{+1.2}_{-0.9}$ years and confirms both estimates since they are completely independent.

Lifetimes of some candidate alternative fluorocarbons have been tabulated in Table 2 based on detailed studies using the Harwell two-dimensional model. These studies should be readily extended to include the subsequent transport and fate of the secondary degradation products liberated by OH attack on the parent halocarbon.

There is mounting evidence that man's activities are inducing changes in the composition of the global atmosphere (Rowland and Isaksen 1988). Some of the trace gases for which global trends are beginning to become characterised play an important role in global tropospheric chemistry, as described in figure 1. In considering the environmental acceptability of alternative fluorocarbons, an attempt should be made to investigate their tropospheric sinks in future scenarios in which the composition of the global troposphere has been grossly perturbed by man's activities. For example, future subsonic aircraft operations may increase local tropospheric OH concentrations (Derwent 1982) and other perturbations can be put forward that would decrease tropospheric OH concentrations. A scenario approach could help to put upper and lower bounds on the lifetimes of alternative fluorocarbons over the next 50 years.

5. ACKNOWLEDGEMENTS

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TROPOSPHERIC HYDROXYL CONCENTRATIONS AND THE LIFETIMES OF HYDROCHLOROFLUOROCARBONS (HCFCs)

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ABSTRACT

Three-dimensional fields of modeled tropospheric OH concentrations are used to calculate lifetimes against destruction by OH for many hydrogenated halocarbons, including the CFC alternatives (hydrochlorofluorocarbons or HCFCs). The OH fields are taken from a 3-D chemical transport model (Spivakovsky et al., 1989) that accurately simulates the global measurements of methyl chloroform (derived lifetime of 5.5 yr). The lifetimes of various hydro-halocarbons are shown to be insensitive to possible spatial variations and seasonal cycles. It is possible to scale the HCFC lifetimes to that of methyl chloroform or methane by using a ratio of the rate coefficients for reaction with OH at an appropriate temperature, about 277 K.

1. INTRODUCTION

Synthetically produced halocarbons that contain chlorine and bromine, often called chlorofluorocarbons (CFCs) and halons, pose a direct threat to the stratospheric ozone layer (e.g., NASA/WMO, 1986; Watson et al., 1988) and also contribute substantially to the greenhouse forcing of the climate (Ramanathan, 1975; Lacis et al., 1981). A single characteristic of CFCs and halons that aggravates these environmental problems is their long atmospheric lifetimes; most are destroyed only by ultraviolet sunlight in the stratosphere. As a result of these environmental concerns, there will soon be international restrictions on CFC growth as agreed upon in the Montreal Protocol, and there is now a search for alternative fluorocarbons, environmentally acceptable substitutes (AFEAS Workshop, 16-17 May 1989, Boulder Colorado). One key property of these alternative compounds must be a short atmospheric residence time, implying efficient loss in the troposphere or at the Earth's surface.

Many of the suggested alternative fluorocarbons contain hydrogen (hydrochlorofluorocarbons or HCFCs), and atmospheric loss of these HCFCs is dominated by reaction with tropospheric OH. Their buildup in the atmosphere (units: kg) will be controlled by the ratio of emissions (kg yr^{-1}) to atmospheric destruction (yr^{-1}). The globally averaged, annual mean lifetime (yr) of the HCFCs (against atmospheric loss) is defined as the global atmospheric content (kg) divided by the total annual loss (kg yr^{-1}).

In this report we derive the lifetime of HCFCs and other hydrogenated halocarbons in two ways. The primary method involves modelling the OH distribution from first principles, specifying or predicting the HCFC distribution, and then integrating the HCFC loss over the globe (e.g., Logan et al., 1981). The tropospheric OH fields are calculated from a global 3-D climatology of sunlight, temperature, O_3, H_2O, NO_x, CO, CH_4 and other hydrocarbons (see Spivakovsky et al., 1989). Uncertainties in the calculated OH concentrations occur not only with the kinetic model, but also with the global climatologies of the other trace gases and cloud-cover needed as input to the photochemical model.

The OH fields used here were developed and applied to study methyl chloroform in a 3-D Chemical Transport Model (CTM). With the CTM, we specified sources, global transport and chemical losses of CH_3CCl_3 in order to simulate the latitudinal and seasonal patterns, and the global trends (see Spivakovsky et al., 1989). Similar CTM modelling of all the HCFCs is impractical and would require also a history and geographical location of emissions. Instead, the four-dimensional OH field (latitude x longitude x altitude x time) is applied here to test various hypotheses on the sensitivity of HCFC lifetimes to their tropospheric distribution; it is used also to test the accuracy of scaling the HCFC lifetimes to an assumed methyl chloroform lifetime.

The second method for deriving HCFC lifetimes selects a reference species with a global budget and atmospheric lifetime (against OH destruction) that is thought to be well understood (see Makide and Rowland, 1981). The lifetime of methyl chloroform, CH_3CCl_3, derived from the ALE/GAGE analysis is often used (Prinn et al., 1987) and is then scaled by the ratio of the rate coefficients for reaction with OH (Hampson, Kurylo and Sander, AFEAS, 1989), $k(OH + CH_3CCl_3)/k(OH + HCFC)$, to calculate the HCFC lifetime. Possible errors in this approach are associated with the assumed lifetime for CH_3CCl_3, and with the use of a single scaling factor that does not reflect the different spatial distribution of the HCFCs. This scaling approximation is tested here for plausible global patterns in the HCFC concentration and for different temperature dependence of the rate coefficients.

The tropospheric chemistry model for OH is described in Section 2. We calculate the global losses for methane and methyl chloroform in Section 3, and then compare the results for methyl chloroform with other published values. The integrated losses for a range of possible distributions of an HCFC are given in Section 4. HCFC lifetimes and uncertainties are discussed in Section 5.

2. THE CHEMICAL MODEL

The lifetimes calculated here for the HCFCs, as well as for CH_3CCl_3, CH_3Cl, CH_3Br and CH_4, use global distributions of OH from the photochemical model developed for the 3-D Chemical Transport Model (CTM developed at GISS & Harvard). The model for tropospheric OH is based on a 1-D photochemical model (an updated version of Logan et al., 1981; DeMore et al., 1987) that has been used to parameterize OH concentrations as a function of sunlight and other background gases (see Spivakovsky et al., 1989). This parameterized chemistry has been used to calculate a three-dimensional set of mean OH concentrations for the CTM grid over one year: the diurnally averaged OH concentrations are stored at 5-day intervals with a spatial resolution of 8 degrees latitude by 10 degrees longitude over 9 vertical layers (see Prather et al., 1987 for CTM documentation) for a total of more than 1/2 million values, even at this coarse resolution. The 5-day average temperatures at each grid point are also stored.

The local independent variables needed to derive OH concentrations are taken from the parent General Circulation Model (5-day averages of pressure, temperature, water vapor and cloud cover; see Hansen et al., 1983) and from observed climatologies (CO, O_3, CH_4, NO_x, H_2O above 500 mbar and stratospheric ozone column). The observational database for most of these species is insufficient to define the necessary 4-D fields, and we have assumed zonally uniform distributions with smooth variations over latitude, altitude and season for most species. One exception is that from the available data we are able to differentiate between the continental and the maritime troposphere up to 3 km altitude. See Spivakovsky et al. (1989) for details of the assumed trace-gas climatology and the chemical parameterization.

The annual averages of the zonal mean OH concentrations are shown in Table 1a; Table 1b gives the corresponding annual average temperatures. Hydroxyl concentrations are highest in the middle troposphere over the tropics. The OH density peaks at 700-800 mbar because cloud cover and Rayleigh scattering reduce solar ultraviolet light below 800 mbar.

The global loss of a gas that reacts with OH is the integral over a wide range of conditions in temperature, density and trace gas abundance. The integrand is extremely non-linear, and thus, the average loss

Table 1a. Annual Average OH concentration (10^4 cm^{-3})

	LATITUDE																							
P(mbar)	90S	84S	76S	68S	60S	52S	44S	36S	28S	20S	12S	4S	4N	12N	20N	28N	36N	44N	52N	60N	68N	76N	84N	90N
100									20	26	43	40	35	30	26	19								
150									43	51	68	59	54	49	44	34								
200	33	32	30	25	25	24	30	38	52	57	65	58	52	48	43	36	30	21	17	18	17	20	22	20
300	31	27	24	21	23	26	33	43	62	76	80	77	72	65	59	50	39	28	21	20	21	28	32	33
500	41	36	32	30	36	45	63	81	119	131	135	147	141	124	118	108	80	61	45	40	34	41	46	44
700	51	44	41	42	43	51	68	89	139	154	159	180	182	171	159	139	111	88	64	58	56	53	56	32
800		42	40	44	36	48	65	89	144	157	152	168	168	159	155	140	130	108	79	67	77	52	56	32
900			31	32	14	21	35	65	114	124	123	130	134	135	126	110	116	90	62	53	59	23	26	20
1000				20	11	16	28	52	92	105	103	112	112	112	107	88	86	63	43	40	46	17	21	10

Table 1b. Annual Average Temperature (°K)

	LATITUDE																							
P(mbar)	90S	84S	76S	68S	60S	52S	44S	36S	28S	20S	12S	4S	4N	12N	20N	28N	36N	44N	52N	60N	68N	76N	84N	90N
100									207	204	203	202	202	202	203	206								
150									215	215	215	215	215	216	216	215								
200	206	209	209	211	212	213	214	217	222	225	225	225	226	226	225	223	220	217	215	214	214	214	214	215
300	216	217	216	219	221	224	228	233	239	244	246	246	247	246	245	241	236	231	227	225	223	222	222	217
500	232	236	237	240	244	247	252	257	263	268	270	270	270	270	269	266	260	255	250	248	245	244	242	225
700	247	248	248	254	259	263	267	272	277	282	283	283	283	284	283	280	275	270	265	262	259	258	256	235
800		255	256	258	264	268	273	278	283	287	288	289	289	289	289	286	280	275	270	267	264	262	261	239
900			264	262	268	273	278	283	288	291	293	293	294	294	294	291	285	279	275	270	267	265	263	244
1000				267	271	276	282	287	291	295	297	297	297	298	297	293	289	283	277	272	268	268	267	246

Quantities are the annual zonal average of the 4-D fields described in the text.

No values for OH or T are reported for the extra-tropical stratosphere (above 200 mbar).

At higher pressures over Antarctica the number of points are insufficient to report a zonal average.

Table 2. Global Average OH concentrations

integrating kernel	OH (10^4 cm^{-3})	effective T (K)
dm	80	
exp(-1000/T) dm	96	259
exp(-1700/T) dm	105	262
exp(-1800/T) dm	106	263
exp(-2300/T) dm	111	265
(1 + 0.6/P) dm	91	
dz	65	

Integrals over mass (dm, from the surface to 100 mbar) are weighted by different factors: exponential in temperature (e.g., -1700/T for CH_4), and linear in pressure (i.e., 1 + 0.6/P for CO). Integrals over volume (dz) preferentially weight the lower atmospheric densities in the upper troposphere. Use of the average OH with the effective temperature in the exponential gives the correct global integral.

is not equal simply to the product of averages (Makide and Rowland, 1981). It is misleading to report a single "global average OH concentration" without qualifying it as to the averaging kernel. The global OH concentrations averaged over the atmosphere (100-1000 mbar with no stratospheric contribution) are reported here in Table 2 for a variety of integrating kernels. The average OH is largest, 111×10^4 cm^{-3}, when weighted appropriately (by mass) for loss of an HCFC with a large exponential factor of -2300/T. A larger temperature dependence result in greater average OH because the OH densities are maximal at high temperatures in the tropics (see Table 1). The spatially averaged OH density is smallest, 65×10^4 cm^{-3}, because of the large volumes of air in the upper troposphere with low OH concentrations. The effective temperatures given in Table 2 are those needed to get the correct globally averaged integral, and should not be confused with the optimal scaling temperature in Section 4. (The scaling temperature must also account for the change in mean OH as the temperature dependence varies.)

3. GLOBAL LOSS OF CH_3CCl_3 AND CH_4

The globally integrated losses for methane and for methyl chloroform are calculated by integrating the loss frequency (OH and temperature fields described above) using realistic, but fixed tropospheric distributions for CH_4 and CH_3CCl_3. Tropospheric reactions with OH dominate the loss of both species, but stratospheric losses cannot be ignored and are used in place of OH densities in layer 9 (0-70 mbar) globally and in layer 8 (70-150 mbar) outside the tropics. The stratospheric losses are calculated from a 1-D vertical diffusion model for stratospheric chemistry evaluated at the appropriate latitude and season.

The assumed conditions and resulting atmospheric losses of CH_4 and CH_3CCl_3 are summarized in Table 3. The lifetime of methane is 8.7 yr with about 6% of the loss occurring in the stratosphere and more

Table 3. Global budgets for CH_4 and CH_3CCl_3

	CH_4	CH_3CCl_3
Rate coefficient		
k(X + OH)	$2.3 \times 10^{-12} e^{-1700/T}$	$5.0 \times 10^{-12} e^{-1800/T}$
Concentration		
NH (<28°/>28°)	1700/1700 ppb	140/150 ppt
SH	1600 ppb	110 ppt
Atmospheric content	4580 x 1012g	2930 x 109g
Atmospheric losses		
total	524×10^{12}g	534×10^9g
tropics (2-6 km)	270×10^{12}g	260×10^9g
stratosphere	29×10^{12}g	53×10^9g
Lifetime	8.7 yr	5.5 yr

Budgets based on integration of 4-D tropospheric OH fields with zonally fixed, non-seasonal distributions as noted. Stratospheric profiles and losses are included.

than half in the tropical middle troposphere. The lifetime of methyl chloroform is 5.5 yr. Stratospheric loss for methyl chloroform is about three times more rapid than for methane because photolysis of CH_3CCl_3 becomes important in the stratosphere. Again the tropical middle troposphere accounts for about half of the global loss.

Methyl chloroform is usually chosen as a reference species for tropospheric loss, with a "known" atmospheric lifetime based on the ALE/GAGE analysis of Prinn et al. (1987). We compare the lifetimes in Table 3 for CH_3CCl_3 with those from the ALE/GAGE analysis and the recent 3-D CTM simulations (Spivakovsky et al, 1989). The ALE/GAGE analysis uses observations of CH_3CCl_3 at 5 surface sites, industry data for atmospheric emissions, and a 9-box atmospheric model, to derive an annual average global lifetime of 6.3 yr with a reported 1-sigma range of 5.4-7.5 yr. Errors in the lifetime due to uncertainties in the atmospheric emissions used in the ALE/GAGE study have been reduced by recent analyses of CH_3CCl_3 sources from industry surveys (Midgley, 1989) and from observations (Prather, 1988).

When the same OH and temperature fields are used in the complete CTM simulation of CH_3CCl_3 (Spivakovsky et al., 1989) the integrated loss correctly includes all correlations of OH and temperature with CH_3CCl_3 concentrations. The 3-D CTM simulation showed that the standard OH field (with a resulting lifetime of 5.5 yr) and the OH field scaled by a factor of 0.75 (with a lifetime of 7.1 yr) bracket the observations. This range, however, does not include uncertainties in the observations (i.e., absolute calibration) or in the sources. The observed seasonal cycle of CH_3CCl_3 in the southern hemisphere is not a direct measure of the absolute OH concentrations; however, its accurate simulation in the CTM provides some confirmation of the integrated seasonal variation of the modeled OH fields in the southern hemisphere. Such comparisons emphasize the mid-latitude photochemistry which has the largest seasonal variations, and they are independent of absolute calibration and sources because they depend on the relative (%) changes in CH_3CCl_3.

It is difficult to find other globally distributed trace gases with well defined sources and trends that can be used to test global OH concentrations. For example, Derwent and Volz-Thomas (AFEAS, May, 1989; Volz et al., 1981) have used carbon monoxide, both ^{14}CO and ^{12}CO, to test and recalibrate the OH fields in their 2-D model. Another possibility, HCFC-22 (CHF_2Cl) has limited data on hemispheric abundances, trends and sources. Data for HCFC-22 are sparse and barely able to define the hemispheric ratio and instantaneous trend (N/S = 89/77 ppt, +6.5 ppt/yr in 1985, see NASA/WMO, 1986). Furthermore, significant uncertainties exist currently for the absolute calibration and atmospheric emissions of most HCFCs. HCFC-22 is used as an intermediate chemical in the production of other compounds, and thus its release is only a fraction of production. Recent estimates of HCFC-22 emission (130 Gg/yr in 1985, M. McFarland, personal communication) are twice as large as previous values, and are now barely able to reconcile the current atmospheric budget from the limited observations noted above.

It is not possible at present to put a formal "one-sigma" accuracy on the OH fields used here, either from first principles, or from constraints using the methyl chloroform budget. The uncertainty factor for the OH fields is chosen to be 1.3 and is applied to the lifetimes for HCFCs in Section 5.

4. SENSITIVITY OF HCFC LIFETIME TO GLOBAL DISTRIBUTION

We use the 4-D fields of OH and temperature to understand how to predict the lifetime of one species relative to another. Specifically, how can the lifetime of one species be scaled to another with a different spatial-temporal distribution and loss rate? Idealized tropospheric distributions are used to examine the sensitivity of HCFC lifetime to (a) the temperature dependence of their reaction rates with OH, (b) large interhemispheric gradients, (c) enhanced concentrations in the boundary layer near sources, and (d) seasonal cycles in concentration.

a. Sensitivity to rate coefficient: $k = A \times \exp(-B/T)$

Two species, X and Y, with the same global distribution and with rate coefficients for reaction with OH that differ only by a constant factor, $k(OH+X)/k(OH+Y) = $ constant, will have lifetimes that scale inversely by the same factor. In most cases, however, the rate coefficients have different temperature dependence, B, or pressure dependence (as in the case of CO). We investigate the dependence of HCFC lifetime on values of B ranging from 0 to 2300 K, by integrating the loss for an atmospheric tracer that is uniformly distributed throughout the troposphere and stratosphere. The A coefficient was selected to match the CH_4 rate, $k = 2.3E\text{-}12 \times \exp(-B/T)$ cm^3 s^{-1}, and stratospheric losses were not included.

The integrated global loss rates are given in Table 4a; lifetimes range from 81 yr (B = 2300 K) to 0.02 yr (B = 0 K). In Figure 1 we show the error associated with predicting the lifetime by scaling to a reference lifetime (9.42 yr at B = 1700 K) using an appropriate temperature in the ratio of reaction rates. This scaling temperature is not necessarily the mean temperature of the OH losses, but includes also the shift in the reaction-weighted mean OH as a function of reaction rate (see Section 2 and Table 2). The optimal temperature for scaling the lifetimes is 277 K, and the resulting errors are less than 2% over the range $800 K < B < 2300 K$. Use of a temperature 10 K warmer or colder yields errors in the lifetime of order 10% when scaling the reference case (B = 1700 K) to greater (2300 K) or smaller (1000 K) activation energies.

b. Sensitivity to interhemispheric gradient

HCFCs released predominantly from industrialized countries in the northern mid-latitudes will establish a global distribution similar to that for CFCs (see Prather et al., 1987). The north-to-south latitudinal gradient will have an interhemispheric absolute difference about equal to one year's emissions, and higher concentrations will build up over the presumed continental sources at mid-latitudes. The sensitivity of HCFC lifetimes to their interhemispheric gradient will depend on hemispheric asymmetries in the OH fields (and temperatures in so far as they affect the rate coefficients). The base case described above assumes a uniformly distributed tracer with OH reaction rates appropriate for CH_4, and the perturbed case includes doubling the abundance in either hemisphere uniformly. Results are shown in Table 4b. For a factor of 2 asymmetry in the HCFC distribution, the lifetime changes by only 1.5%. Thus the effective OH loss is about 9% greater in the northern hemisphere. Spivakovsky et al. (1989) note that the higher concentrations of CO in the northern hemisphere (reducing OH) are more than offset by the higher levels of O_3 and NO_x.

Table 4. Lifetime for species x against tropospheric OH

a. Sensitivity to rate coefficient k(OH + X) = A/exp(-B/T)

A ($cm^3\ s^{-1}$)	B (K)	lifetime (yr)
2.3E-12	2300	81.2
2.3E-12	2000	27.7
2.3E-12	1700	9.42
2.3E-12	1500	4.58
2.3E-12	1100	1.08
2.3E-12	500	.120
2.3E-12	0	.019

b. Sensitivity to interhemispheric ratio

NH:SH	lifetime (yr)
2:1	9.28
1:1	9.42
1:2	9.57

c. Sensitivity to boundary layer enhancements

enhancement	lifetime (yr)
none	9.42
+10% (global)	9.33
+10% (global, land)	9.35
+10% (>30°N)	9.42
+10% (>30°N, land)	9.41
+100% (>30°N)	9.37
+100% (>30°N, land)	9.33

d. Sensitivity to seasonal cycle

amplitude	lifetime (yr)
none	9.42
±1%	9.43
±10%	9.52
±50%	9.97

Except where noted X has a uniform mixing ratio throughout the troposphere and stratosphere, but no loss in the stratosphere. Default values are k(OH + X) = 2.3×10^{-12} exp(-1700/T), boundary layer defined as 984-850 mbar, and no seasonal cycle.

The assumed seasonal cycle is: positive in winter, (DJF >30°N) & (JJA <30°S), negative in summer, (JJA >30°N) & (DJF <30°S).

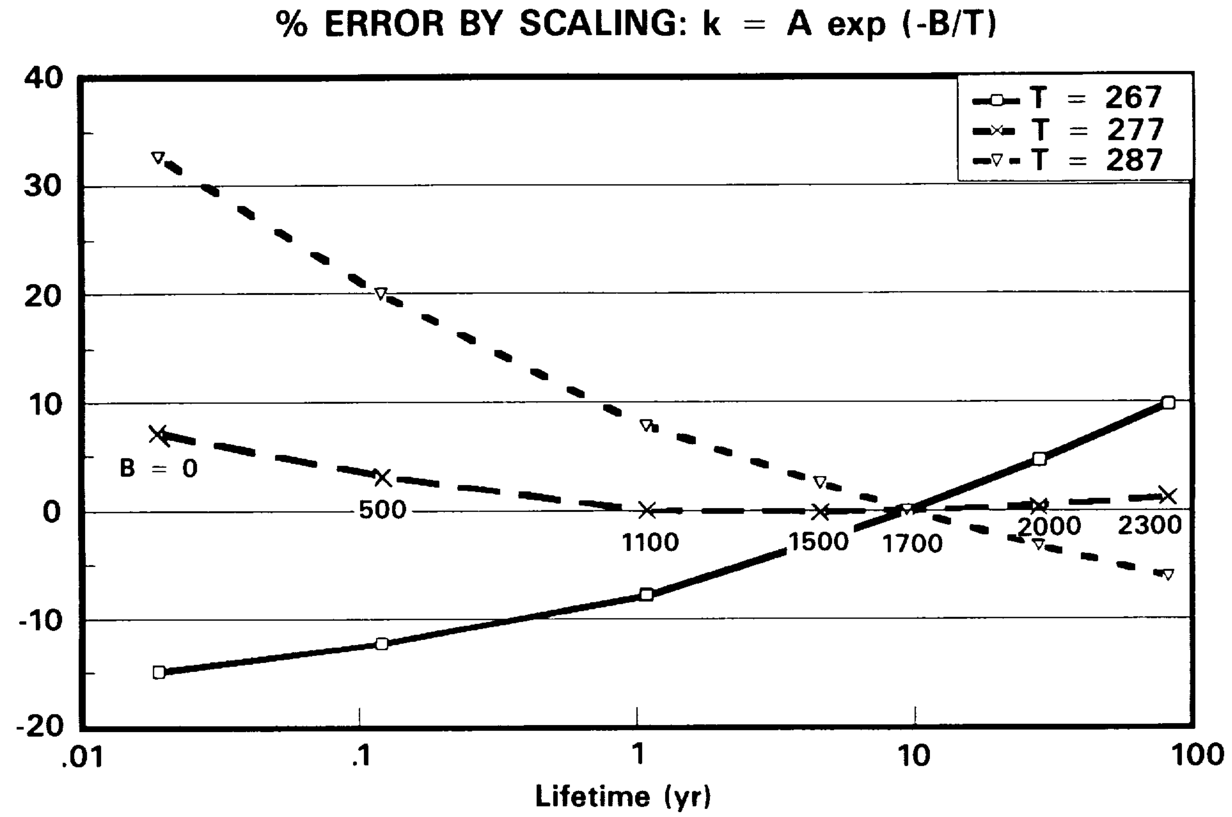

Figure 1. Error (%) in predicting HCFC lifetimes by scaling the rate coefficient for reaction with OH. The lifetime against OH destruction is calculated by integrating the 4-D fields of OH and T with a rate coefficient k = 2.3E-12 exp (-B/T) and a uniformly distributed tracer. The reference case is chosen to be B = 1700 K with a lifetime of 9.42 yr. A range of values for B from 0 K to 2300 K is considered (see Table 4a, noted on graph). Three different effective temperatures (267 K, 277 K and 287 K) have been chosen to predict a lifetimes by scaling the "known" result for B = 1700 K. Minimum error occurs for T = 277 K.

c. Sensitivity to enhancement in the boundary layer

Enhanced abundances of $CFCl_3$ and CF_2Cl_2 are both observed and predicted in the lower troposphere over much of the northern mid-latitudes, especially near continental sources. A similar buildup of HCFCs would be expected. We examine the sensitivity of HCFC lifetimes to boundary layer enhancements in the lowest 1.5 km for several assumptions: northward of 30°N, globally, over land, or over land and ocean. The reference case is that with methane kinetic rates as above. The net effect of boundary layer enhancements, as shown in Table 4c, is negligible ($<1\%$) if they are less than 100% and are restricted to the northern mid-latitudes as expected. If there were a globally uniform source, and hence accumulation in the boundary layer over the tropics also, then a $+10\%$ enhancement in the lowest 1.5 km would increase losses and reduce the lifetime by at most 1%.

d. Sensitivity to seasonal cycles

Seasonal variations in the concentrations of a gas should be included when calculating the OH losses. In most cases the seasonal cycle is driven by the corresponding variations in OH, and, thus, the lowest concentrations of the trace gas occur slightly after the greatest OH levels (i.e., late summer). This anticorrelation of OH and trace gas increases the lifetime of the gas relative to that calculated with a fixed concentration. As shown in Table 4d, this effect is negligible ($<0.2\%$) for a gas like CH_4 with a lifetime of about 9 yr and an observed seasonal amplitude of ±1.5%. Since large seasonal variations occur only in short-lived species, we would not expect the seasonal amplitude for an HCFC to exceed ±10% (corresponding to a 1% increase in lifetime) unless the lifetime were very short, less than 1.5 yr. The seasonal effect is so small because the majority of OH loss occurs in the tropics, as noted above, where OH concentrations do not vary significantly with season.

In summary, a short-lived HCFC with a lifetime of about 0.5 yr might be expected to have a seasonal amplitude of ±25% (lifetime correction: +2.5%), a north:south interhemispheric ratio of 2:1 (lifetime correction: -1.5%), and a boundary layer enhancement north of 30°N over land of 100% (lifetime correction: -1%). The sum of these corrections tend to cancel, or be very small, and thus the lifetime predicted from a uniform distribution should be a reasonably accurate, ±10%, evaluation of the true lifetime.

5. SUMMARY OF HCFC LIFETIMES

The lifetimes of HCFCs and other hydrohalocarbons are reported in Table 5. These lifetimes are calculated directly from the tropospheric OH fields using the recommended rate coefficients (Hampson, Kurylo and Sander, AFEAS, 1989) and a fixed, uniform distribution of trace gas (labelled TROP-OH). They have been augmented (labelled TOTAL) with much smaller stratospheric losses that include estimated destruction by OH and photolysis. Stratospheric OH loss is scaled by rate coefficients at a temperature of 250 K to an assumed methane (stratosphere only) loss rate of 1/160 yr^{-1}; stratospheric photolysis is assumed only for species with a $-CCl_3$ group (1/60 yr^{-1}) or a $-CCl_2$ group (1/120 yr^{-1}) and is based on the lifetimes of $CFCl_3$ and CF_2Cl_2. An additional column of lifetimes in Table 5 (labelled SCALED) has been calculated by ratioing the rate coefficients (scaling temperature of 227 K) and multiplying by the methyl chloroform lifetime of 6.3 yr. As expected from the analyses in this report the two approaches agree very well.

An attempt has been made to estimate uncertainty factors for HCFC lifetimes in the same manner as in the kinetics reviews. We identify the uncertainty in the reaction rate of 277 K and then multiply by the estimated uncertainty factor for the OH fields (1.3). The uncertainty associated with a non-uniform distribution is significant only for HCFCs with lifetimes less than 1 yr, and has been increased. The final uncertainty quoted in Table 5 is representative of the likely range, but cannot be treated as a formal statistical error.

Although the ALE/GAGE analysis of the total atmospheric residence time for CH_3CCl_3 agrees with the chemical model's lifetime for destruction by OH, the combined uncertainties in the two lifetimes cannot rule out another sink, such as hydrolysis (Wine and Chameides, AFEAS, 1989), with a lifetime as short as 25 yr.

There is a clear need for other trace species that can be used to test the tropospheric abundance of OH. Such species must have accurate histories of emissions and good, absolutely calibrated measurements. In situ atmospheric tests of the kinetic model for OH should possibly focus on the tropical middle troposphere where most of the destruction of HCFCs will occur.

Table 5. Atmospheric Lifetimes for the HCFCs & other Halocarbons

			LIFETIME (yr)			uncertainty	
species	A	B	TROP-OH	TOTAL	SCALED	f	(CFC)
CH_3F	5.4E-12	1700	4.0	3.8	4.1	1.8	
CH_2F_2	2.5E-12	1650	7.2	6.8	7.3	1.7	
CHF_3	7.4E-13	2350	302.	289.	310.	2.3	
CH_2FCl	3.0E-12	1250	1.42	1.33	1.44	1.8	
$CHFCl_2$*	1.2E-12	1100	2.10	1.89	2.10	1.6	
CHF_2Cl	1.2E-12	1650	15.1	14.2	15.3	1.6	(22)
CH_3CH_2F	1.3E-11	1200	0.27	0.25	0.28	5.	
CH_2FCH_2F	1.7E-11	1500	0.62	0.58	0.63	5.	
CH_3CHF_2	1.5E-12	1100	1.65	1.53	1.68	1.8	(152a)
CH_2FCHF_2	2.8E-12	1500	3.76	3.54	3.81	3.	
CH_3CF_3	2.6E-13	1500	40.5	38.1	41.	3.	
CHF_2CHF_2	8.7E-13	1500	12.1	11.4	12.3	3.	
CH_2FCF_3	1.7E-12	1750	15.3	14.4	15.5	1.8	(134a)
CHF_2CF_3	3.8E-13	1500	27.7	26.1	28.1	3.	(125)
CH_3CFCl_2*	2.7E-13	1050	7.6	6.7	7.8	1.7	(141b)
CH_3CF_2Cl	9.6E-13	1650	18.8	17.8	19.1	1.7	(142b)
CH_2ClCF_2Cl	3.6E-12	1600	4.2	4.0	4.2	3.	
CH_2ClCF_3	5.2E-13	1100	4.7	4.4	4.8	1.8	
$CHCl_2CF_3$*	6.4E-13	850	1.55	1.42	1.59	2.0	(123)
$CHFClCF_3$	6.6E-13	1250	6.5	6.0	6.6	1.8	(124)
CH_4	2.3E-12	1700	9.4	8.9	9.6		
CH_3Cl	1.7E-12	1100	1.45	1.35	1.48		
CH_3Br	6.0E-13	820	1.48	1.37	1.53		
CH_3CCl_3**	5.0E-12	1800	6.2	5.4	6.3		

Rate coefficients are in units of $cm^3\ s^{-1}$, $k = A \exp(-B/T)$.

TROP-OH lifetimes include only the integrated loss with respect to OH in the troposphere. TOTAL lifetimes include the small additional losses estimated to occur in the stratosphere as described below. SCALED lifetimes are keyed to the CH_3CCl_3 lifetime of 6.3 yr (Prinn et al., 1987) and the ratio of the rate constants at 277 K.

Species marked (*) with 2 Cl's on one C are assumed to have a lifetime of 120 yr with respect to stratospheric photolysis; methyl chloroform (**) is assumed to have a stratospheric lifetime of 60 yr due to photolysis. Stratospheric loss due to reaction with OH is scaled to the CH_4 stratospheric lifetime (160 yr) and rate coefficient at 250 K.

The lifetime uncertainty factor (f) is assumed here to be the product of the kinetic factor (at 277 K), the uncertainty in the OH fields (1.3), and an additional uncertainty factor for HCFCs with short lifetimes.