

## A global three-dimensional study of the fate of HCFCs and HFC-134a in the troposphere

Maria Kanakidou

Centre des Faibles Radioactivités, Laboratoire mixte CNRS/CEA, Gif-sur-Yvette, France

Frank J. Dentener

Department of Air Quality, Biotechnion, Wageningen, Netherlands

Paul J. Crutzen

Max Planck Institute for Chemistry, Atmospheric Chemistry Division, Mainz, Germany

**Abstract.** We present the first attempt to use a global three-dimensional model of the troposphere to study the degradation chemistry of the alternative chlorofluoro- and fluorohydrocarbons HCFC-22, HCFC-123, HCFC-124, HFC-134a, HCFC-141b, and HCFC-142b and the main removal processes from the troposphere of these halogenated hydrocarbons and their oxidation products. Lifetimes of the parent hydrochlorofluorocarbons (HCFCs) and HFC-134a range from 1.3 to 20 years, with oxidation by the OH radical being the dominant removal process. Using the emission scenarios of McCulloch (1993), we calculate that HCFC-22 volume mixing ratios will reach a maximum of 190 parts per trillion by volume (pptv) around the year 2005, the mixing ratios of all other HCFCs remaining below 100 pptv. The chlorine loading potentials (CLP) of these HCFCs range from 0.014 for HCFC-123 to 0.166 for HCFC-142b, whereas HFC-134a has a zero CLP. Based on recent kinetic information, it is calculated that none of the relatively stable intermediate oxidation products such as COF<sub>2</sub>, COFCl, CF<sub>3</sub>COF, and CF<sub>3</sub>COCl will substantially build up in the atmosphere, the global abundances of these compounds being generally less than 1% those of the parent compounds. A possible exception is HCOF for which the heterogeneous removal parameters have not been experimentally determined. Hydrolysis in clouds, and to a lesser extent in seawater, is the process efficiently removing these species. Organic nitrates from all HCFCs studied will not reach substantial concentrations and will not contribute to chlorine delivery to the stratosphere. The deposition fluxes of the very stable trifluoroacetic acid (TFA), derived from the oxidation of HFC-134a and HCFCs-123 and 124, will reach in the year 2020 maximum levels of 2 μmol/m<sup>2</sup>/yr (about 1 nmol/L rainwater). Maximum deposition occurs in tropical regions, associated with high oxidation rates of the parent compounds, and high rainfall. These predicted concentrations and deposition fluxes are orders of magnitude smaller than what is thought to be toxic for humans, for the fauna, and for the flora.

### 1. Introduction

Hydrochlorofluorocarbons (HCFCs) have substantially shorter atmospheric lifetimes due to oxidation by hydroxyl (OH) radicals and they are therefore less aggressive toward stratospheric ozone (O<sub>3</sub>) than chlorofluorocarbons (CFCs). Hydrofluorocarbons (HFCs) contain no chlorine and therefore have no effect on stratospheric ozone. Furthermore, the global warming potentials (GWP) of the HCFCs and HFCs are significantly lower than those of the CFCs. To fully evaluate the chemical and climatic effects of HCFC and HFC usage, information on the atmospheric lifetime and the distribution of HCFCs, HFCs, and their oxidation products is needed.

Chlorodifluoromethane HCFC-22 (CHClF<sub>2</sub>) is already extensively used as a substitute for the more harmful CFCs. The amount released to the atmosphere increased by a factor of 5

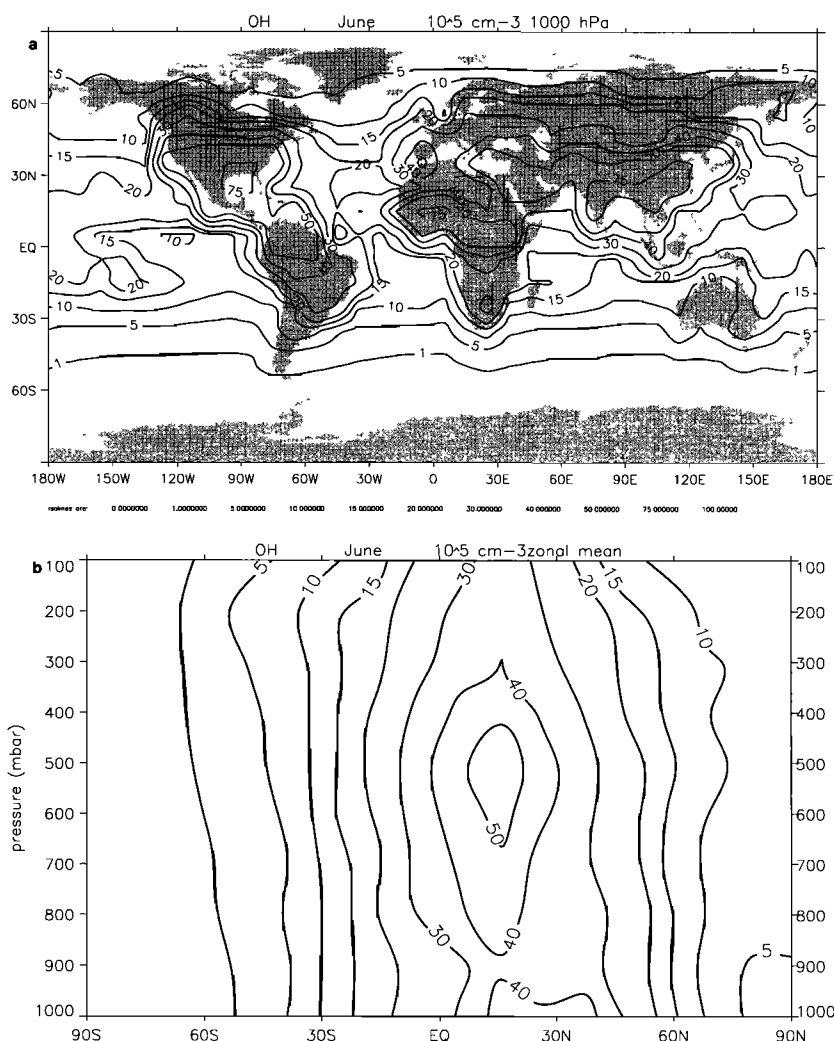
between 1970 and 1990, from about 45 × 10<sup>9</sup> g/yr to almost 220 × 10<sup>9</sup> g/yr. According to observations by *Khalil and Rasmussen* [1987] the HCFC-22 global mixing ratio has doubled over the period 1979–1987 in both hemispheres. A rapid global increase in its atmospheric abundance by 7% per year is currently observed [*Zander et al.*, 1994].

Other preferred substitutes for the CFCs are HFC-134a (CF<sub>3</sub>CH<sub>2</sub>F) and, to a lesser degree, HCFC-123 (CF<sub>3</sub>CHCl<sub>2</sub>), HCFC-141b (CH<sub>3</sub>CCl<sub>2</sub>F), HCFC-124 (CF<sub>3</sub>CHClF), and HCFC-142b (CH<sub>3</sub>CClF<sub>2</sub>). Their production has already started and that of HFC-134a is planned to increase rapidly over the coming years.

In the present study, the three-dimensional global tropospheric model MOGUNTIA has been used to describe the fate of HCFC-22, HCFC-123, HCFC-124, HFC-134a, HCFC-141b, and HCFC-142b as well as their oxidation products in the troposphere. We investigate the fate of these compounds in the troposphere for the first time by using a global three-dimensional model. The following discussion focuses mostly on the two substitutes (HCFC-22 and HFC-134a) which are al-

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Paper number 95JD01919.  
0148-0227/95/95JD-01919\$05.00



**Figure 1.** June daytime mean OH concentrations at (a) 1000 hPa and (b) zonal mean ( $10^5 \text{ molecules cm}^{-3}$ ).

ready in use and for which an extensive use is planned in the near future until 2020, when the phaseout of HCFCs will be completed. Comparison of our results with the two-dimensional modeling results of other groups is performed.

## 2. Model Description

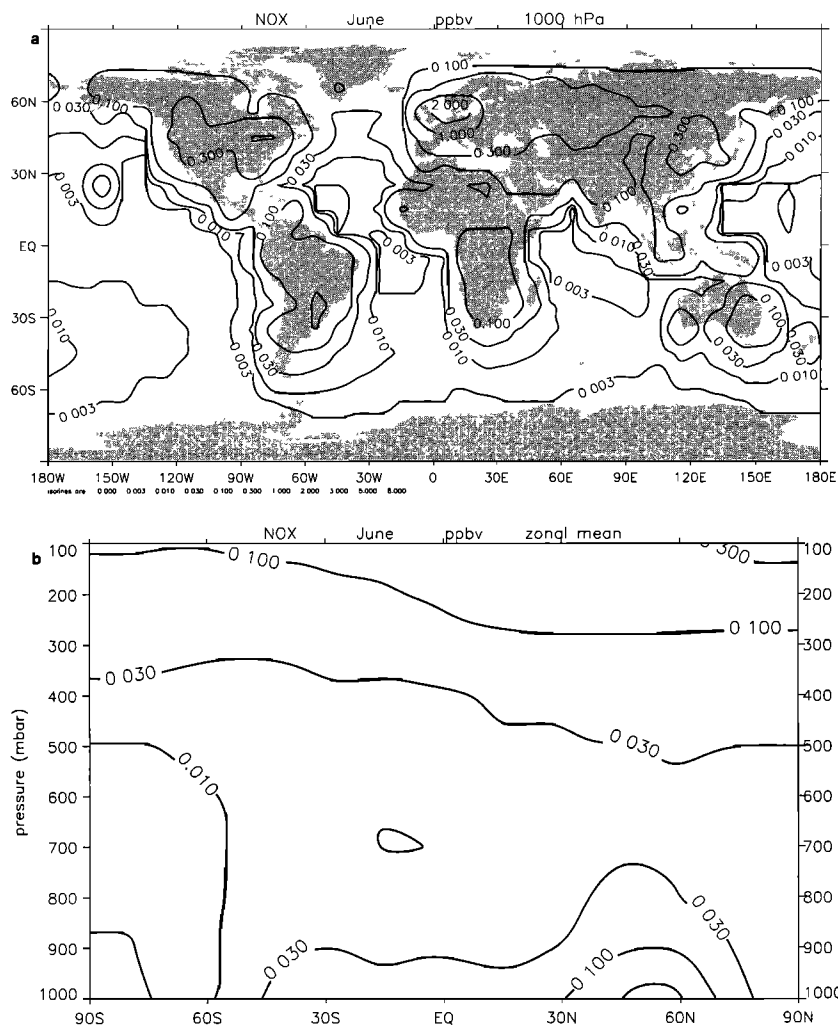
The model used is the global three-dimensional photochemistry/transport model of the troposphere MOGUNTIA, which has been developed at the Max Planck Institute in Mainz. It has a spatial resolution of  $10^\circ$  latitude  $\times$   $10^\circ$  longitude  $\times$  100 hPa [Crutzen and Zimmermann, 1991] from the surface to 100 hPa. Tracer transport in the model is based on monthly means of observed wind fields from 1963 to 1973, compiled by Oort [1983], and an eddy diffusion parameterization based on standard deviations of the winds. The model interhemispheric exchange time and the stratospheric loss parameterization have been successfully tested using  $^{85}\text{Kr}$  [Zimmermann et al., 1989] and CFC-11 ( $\text{CFCl}_3$ ). The deep convection which is of importance for the transport of short-lived species from the surface to the higher troposphere has been parameterized by Feichter and Crutzen [1990] and tested using  $^{222}\text{Rn}$ . The vertical exchange of mass by the clouds is derived from the conservation of water given the convective amount of precipitation and

average large-scale temperature and humidity distribution [Feichter and Crutzen, 1990].

### 2.1. Photooxidant Distributions Calculated by the Full Chemistry Version of MOGUNTIA

To study the fate of HCFC-22, HCFC-123, HCFC-124, HFC-134a, HCFC-141b, HCFC-142b, and their oxidation products in the troposphere, we used model-calculated monthly mean daytime concentrations of OH, NO,  $\text{NO}_2$ , and  $\text{HO}_2$ .

The latter species are needed for “off-line” calculations of intermediate products and were calculated using a version of the model describing  $\text{O}_3/\text{OH}/\text{NO}_x/\text{CH}_4/\text{CO}/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$  photochemistry [Kanakidou and Crutzen, 1993] and heterogeneous chemistry of the nitrate radical ( $\text{NO}_3$ ) and  $\text{N}_2\text{O}_5$  on sulfate and sea-salt aerosol [Dentener and Crutzen, 1993]. Inclusion of more reactive nonmethane hydrocarbons (NMHCs) in the model is leading to reductions in the OH concentrations. The largest part of this effect has been taken into account in the present study by introducing “pseudo” CO emissions from oceans, vegetation, and anthropogenic sources, representing CO formation from NMHC oxidation. The remaining uncertainties on the OH concentrations are evaluated to be lower than 10% in the boundary layer and even less in the free



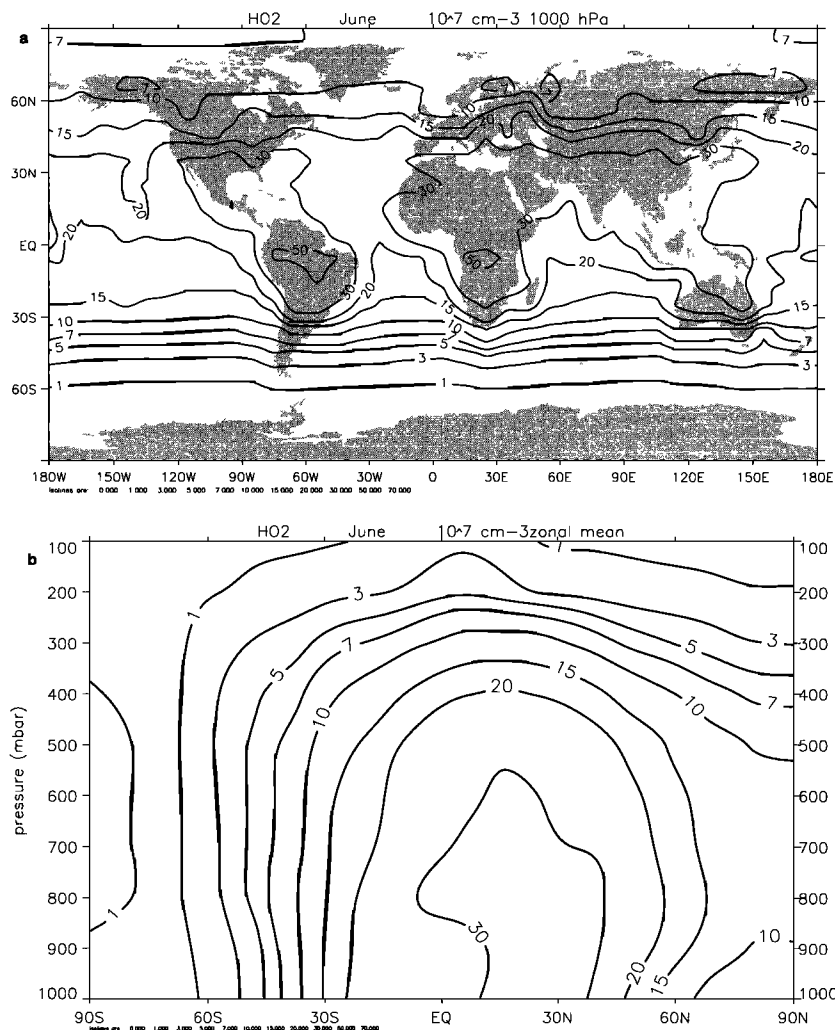
**Figure 2.** June NO<sub>x</sub> volume mixing ratios at (a) 1000 hPa and (b) zonal mean ( $10^{-9}$  v/v).

troposphere. These uncertainties in the calculated OH field are not expected to significantly affect the calculated concentrations of HCFCs and their oxidation products.

The daytime and monthly mean OH concentrations, calculated for June at 1000 hPa (Figure 1a), show maxima in the tropical regions where both the water vapor concentrations and the intensity of solar UV radiation maximize. Over the continental tropical areas, O<sub>3</sub> concentrations are higher due to emissions of its precursors by biomass burning, soils, and vegetation. Thus O(<sup>1</sup>D) production from O<sub>3</sub> photodissociation and subsequent reaction with water vapor yielding OH radicals are enhanced over these areas. As expected, the regions of highest OH concentrations are shifted to the north in June (summer northern hemisphere (NH), Figures 1a and 1b). High OH concentrations are found in the middle tropical troposphere, corresponding to high O<sub>3</sub> photodissociation rates, enhanced by reflection and scattering of UV radiation by tropical clouds (Figure 1b). To our knowledge the only modeled three-dimensional OH distribution, to compare MOGUNTIA model results with, was published by Spivakovsky *et al.* [1990]. The zonal mean OH radical fields of the two models compare within 20%. The difference may be attributed to updates in the reaction and photolysis rates after 1990, applied in our model.

The computed monthly mean NO<sub>x</sub> distributions at 1000 hPa for June are depicted in Figure 2a. They reflect the NO<sub>x</sub>

emission distributions with well-pronounced maxima in the industrialized regions of the NH and in the areas of tropical biomass burning. The calculated sharp decrease in NO<sub>x</sub> concentrations from the continents to the oceans reflects the short lifetime of NO<sub>x</sub> in the troposphere (of the order of a day) and small sources over the oceans. The seasonal variation in the NO<sub>x</sub> emissions from biomass burning and from soils can also be seen in the calculated distributions. For instance, the NO<sub>x</sub> maxima in the tropics in January occur over northern tropical Africa and over northern tropical America and are located more toward the south in June. The vertical distribution of NO<sub>x</sub> in June (Figure 2b) reflects transport and chemical transformation in the atmosphere of surface emissions, production at various altitudes by lightning, and a small NO<sub>x</sub> influx from the stratosphere. The general pattern of NO<sub>x</sub> distribution calculated by the MOGUNTIA model for NH is in very good agreement with other published three-dimensional modeling results [Penner *et al.*, 1991; Kasibhatla *et al.*, 1993]. In the southern hemisphere (SH) the maximum mixing ratios calculated by the coarse resolution three-dimensional model MOGUNTIA are about 30% lower than those computed by the higher-resolution three-dimensional model of Penner *et al.* [1991] and of the same order of magnitude with those calculated by Kasibhatla *et al.* [1993]. The accuracy of the NO<sub>x</sub> distribution calculated by MOGUNTIA has been evaluated by



**Figure 3.** June daytime mean  $\text{HO}_2$  concentrations at (a) 1000 hPa and (b) zonal mean ( $10^7$  molecules  $\text{cm}^{-3}$ ).

comparisons with measurements [Dentener and Crutzen, 1993; Gallardo and Rodhe, 1995].

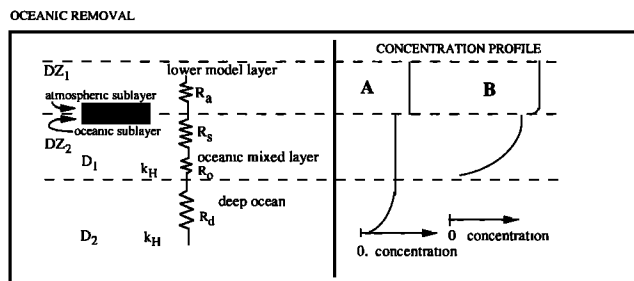
As for OH, the calculated daytime and monthly mean  $\text{HO}_2$  distribution (Figures 3a and 3b) is mainly determined by the incoming solar UV radiation. Thus the highest  $\text{HO}_2$  concentrations are found in the tropical regions and, in particular, in places of low  $\text{NO}_x$  concentrations, where  $\text{HO}_2$  chemical loss by reaction with NO leading to OH and  $\text{NO}_2$  is not dominant. The  $\text{HO}_2$  vertical distribution (Figure 3b) also features the enhanced photolytic production in the tropics.

## 2.2. Evaluation of Uncertainties on Calculated OH Field and Stratospheric Loss Parameterization; Tests on Methylchloroform and CFC-11

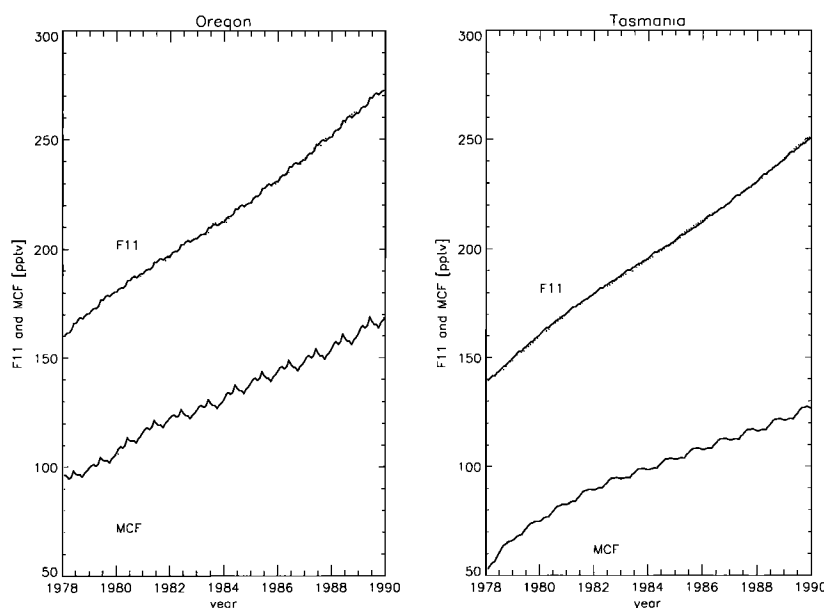
The calculated hydroxyl radical concentration distribution has been tested for its capability to reproduce the observed methylchloroform ( $\text{CH}_3\text{CCl}_3$ ) mixing ratios at the ALE/GAGE Stations [Prinn et al., 1992, 1994].  $\text{CH}_3\text{CCl}_3$  is emitted by industry in amounts known with an uncertainty of about 10% [Midgley, 1989]. To simulate the spatial pattern of the emissions, we scale the  $\text{CH}_3\text{CCl}_3$  emissions, reported for five global areas for the year 1986 (P. Midgley, personal communication, 1993), with the production by country of CFC-113 [McCulloch et al., 1994] and, within the countries, with the  $1^\circ \times 1^\circ$  population distribution given by Fung et al. [1991].

In the troposphere,  $\text{CH}_3\text{CCl}_3$  is mainly oxidized by the OH radical. The rate of this reaction has been recently reevaluated [Talukdar et al., 1992] resulting in 15–20% lower rate constants than previously. A small fraction (about 5%) is removed by hydrolysis in the oceans [Butler et al., 1991].

For this study, the oceanic loss of  $\text{CH}_3\text{CCl}_3$  has been parameterized by considering a simple resistance model (Figure 4) [Butler et al., 1991; Kindler et al., 1992]. The first resistance is at the ocean-atmosphere interface in the atmospheric marine



**Figure 4.** Parameterization of oceanic loss processes A low solubility and reactivity (see equation (1)) and B higher solubility and reactivity (see equations (1) and (3)).



**Figure 5.** Calculated and measured methyl chloroform (MCF) and CFC-11 volume mixing ratios at (a) Oregon and (b) Tasmania ( $\text{pptv} = 10^{-12} \text{ v/v}$ ). Dotted lines represent the measurements, solid lines the calculations.

boundary layer ( $r_a$ ); two others are in the oceanic sublayer ( $r_s$ ) and in the oceanic mixed layer ( $r_o$ ), respectively; and the last one is in the deep ocean ( $r_d$ ). As  $\text{CH}_3\text{CCl}_3$  hydrolyzes rather slowly in seawater, the main loss is expected to occur in the deep ocean. Thus the first three resistances can be neglected, and the oceanic loss rate ( $L_o$ ) can be given by

$$L_o = \varepsilon \frac{\text{HRT}}{\Delta Z_1} \Delta Z_2 k_H \sqrt{D_2 k_H} \quad (1)$$

where  $\varepsilon$  is the ocean surface fraction;  $\Delta Z_1$  is the height of the atmospheric mixed layer and  $\Delta Z_2$  is the height of the oceanic mixed layer (on average 80 m);  $H$  is the Henry's law coefficient ( $\text{M atm}^{-1}$ );  $R$  is the gas constant ( $0.083 \text{ atm M}^{-1} \text{ K}^{-1}$ );  $T$  is the oceanic temperature (K);  $k_H$  is the hydrolysis rate ( $\text{s}^{-1}$ ) and  $D_2$  is the diffusion coefficient in the deep (nonmixed layer) ocean ( $1.7 \text{ cm}^2 \text{ s}^{-1}$ ). This loss rate ( $L_o$ ) applied to  $\text{CH}_3\text{CCl}_3$  resulted in a turnover time of 63 years due to removal into the oceans.

A net outflux to the stratosphere has been applied at the upper boundary layer of the model for  $\text{CH}_3\text{CCl}_3$ . It is parameterized by a hemispheric mean and monthly varying loss rate applied at the 100-hPa level. It corresponds to a turnover time of 54 years, close to the value calculated by a stratospheric two-dimensional model (C. Brühl, private communication, 1992). The loss at the upper model layer represents the net effect of an outflux (loss) in the Intertropical Convergence Zone (ITCZ), a gain during downward transport at midlatitudes and latitudinal transport. As there are significant differences in the transport parameterizations in the two-dimensional stratospheric model and the MOGUNTIA three-dimensional model, the use of a latitudinally varying outflux and influx in MOGUNTIA would not be realistic. The stratospheric loss parameterization used in this study has been tested by simulating CFC-11 mixing ratios and trends in the atmosphere. Similarly to  $\text{CH}_3\text{CCl}_3$ , a hemispheric mean and monthly vary-

ing stratospheric loss term was applied at the upper boundary of MOGUNTIA for CFC-11. This corresponds to a turnover time of 53 years, as calculated by the two-dimensional stratospheric model (C. Brühl, private communication, 1992). The historical emissions (strength and distribution) given by Hartley and Prinn [1993] were used. According to these statistics, 95% of the emissions occur in the northern hemisphere (NH) and about 10% of the CFC-11 is emitted over the former USSR and Asia. Figures 5a and 5b show a very good agreement between calculated and measured CFC-11 mixing ratios at the ALE stations of Oregon and Tasmania, with a maximum deviation of less than 5%. The corresponding model interhemispheric exchange time is 1.02 years.

Using the OH field computed by the full photochemistry version of MOGUNTIA, we calculated the  $\text{CH}_3\text{CCl}_3$  distribution in the troposphere. The comparison between observed and calculated mixing ratios is shown in Figures 5a and 5b.  $\text{CH}_3\text{CCl}_3$  mixing ratios were measured at the ALE/GAGE network surface stations [Prinn *et al.*, 1992]. Note that very recently, the measured  $\text{CH}_3\text{CCl}_3$  concentrations were recalibrated to be 17% lower than previously [Prinn *et al.*, 1994]. The observed concentrations plotted in Figures 5a and 5b are corrected using the new calibration factor. Both the trend and the seasonality of the measurements are reasonably well reproduced by the model. The slopes of the calculated and measured  $\text{CH}_3\text{CCl}_3$  mixing ratios indicate that our calculated OH concentrations may be low by 20%. With respect to oxidation by tropospheric OH the turnover time of  $\text{CH}_3\text{CCl}_3$  is calculated to be 6.5 years. The overall atmospheric lifetime of  $\text{CH}_3\text{CCl}_3$ , including a loss to the oceans and to the stratosphere, is calculated to be 5.3 years.

Considering the uncertainties in the measurements, rate constants, and emissions, we conclude that the calculated OH concentrations, without any correction, can be safely adopted for the purpose of the present study.

**Table 1.** Henry's Law Coefficients and Hydrolysis Rates Adopted in This Study

Species	$H$ (M atm <sup>-1</sup> )	Reference
HCFC-22	exp [-8.689 + 205.9/( $T - 255.1$ )]*	McLinden [1989]
HCFC-123	exp [-14.06 + 2570/ $T$ ]*	McLinden [1989]
HCFC-124	exp [-17.39 + 3229/ $T$ ]*	McLinden [1989]
HCFC-141b	exp [-24.61 + 5248/ $T$ ]*	McLinden [1989]
HCFC-142b	exp [-15.11 + 2544/ $T$ ]*	McLinden [1989]
Methylchloroform	exp [-20.29 + 4655/ $T$ ]*	McLinden [1989]
ROOH	300	with $R$ = haloalkylgroup [Wine and Chameides, 1989]
CClF <sub>2</sub> OONO <sub>2</sub>	2.9 exp [5910 · (1/ $T - 1/298$ )]	taken equal to that of PAN [Wine and Chameides, 1989]
COF <sub>2</sub>	20	George et al. [1993]
COFCl	10	average of COF <sub>2</sub> and COCl <sub>2</sub> George et al. [1993]
CF <sub>3</sub> COCl	2.5	George et al. [1993]
CF <sub>3</sub> COF	3	George et al. [1993]
HCOF	3	taken equal to CF <sub>3</sub> COF
CClF <sub>2</sub> C(O)OOH	3000	assumed as suggested by [Wine and Chameides, 1989]
CCl <sub>2</sub> FC(O)OOH	3000	assumed as suggested by [Wine and Chameides, 1989]

Species	$k_H$ (s <sup>-1</sup> )	Product	Reference
HCFC-22	$6 \times 10^{-10}$	HC(O)OH, HCl, HF	Wine and Chameides [1989]
Methylchloroform	$5.4 \times 10^{-9}$	CH <sub>3</sub> C(O)OH, HCl	Wine and Chameides [1989]
HCFC-123	$2 \times 10^{-9}$	CF <sub>3</sub> CHO, HF	suggested by Wine and Chameides [1989]
HCFC-124	$2 \times 10^{-9}$	CF <sub>3</sub> CHO, HF, HCl	suggested by Wine and Chameides [1989]
HCFC-141b	$2 \times 10^{-9}$	CH <sub>3</sub> COOH, HCl, HF	suggested by Wine and Chameides [1989]
HCFC-142b	$2 \times 10^{-9}$	CH <sub>3</sub> COOH, HCl, HF	suggested by Wine and Chameides [1989]
ROOH	$10^{-4}$		Wine and Chameides [1989]
CClF <sub>2</sub> OONO <sub>2</sub>	$10^{-4}$		Wine and Chameides [1989]
COF <sub>2</sub>	8	CO <sub>2</sub> , HF	George et al. [1993]
COFCl	50	CO <sub>2</sub> , HF, HCl	average of COF <sub>2</sub> and COCl <sub>2</sub> [George et al., 1993]
CF <sub>3</sub> COCl	200	CF <sub>3</sub> COOH, HCl	George et al. [1993]
CF <sub>3</sub> COF	147	CF <sub>3</sub> COOH, HF	George et al. [1993]
HCOF	0.01	HF, HCOOH	see text [Bunton and Fendler, 1966]
CClF <sub>2</sub> C(O)OOH	$5 \times 10^{-4}$	CClF <sub>2</sub> COOH, H <sub>2</sub> O <sub>2</sub>	suggested by Wine and Chameides [1989]
CCl <sub>2</sub> FC(O)OOH	$5 \times 10^{-4}$	CCl <sub>2</sub> FCOOH, H <sub>2</sub> O <sub>2</sub>	suggested by Wine and Chameides [1989]

Asterisk,  $H$  in mass %/kPa;  $T$  in Kelvin.

### 2.3. Oxidation of HCFCs and HFC-134a in the Troposphere

As mentioned above, the OH, NO, NO<sub>2</sub>, and HO<sub>2</sub> concentration fields calculated with the full chemistry version of the model have been used to study the temporal and spatial distribution of several HCFCs, HFC-134a, and of their oxidation products in the troposphere. For this we consider a total of more than 100 gas phase reactions involved in the photochemical removal of HCFC-22, HCFC-123, HCFC-124, HFC-134a, HCFC-141b, HCFC-142b, and their oxidation products. We also consider heterogeneous removal processes (oceanic removal, washout, and hydrolysis in clouds) of the HCFCs and some of their oxidation products. The Henry's law coefficients and the hydrolysis rates, used to calculate the heterogeneous loss rates, are given in Table 1. The gas phase chemical reactions describing the HCFCs and HFC-134a oxidation in the troposphere and the corresponding reaction rate coefficients adopted in this study are summarized in Table 2. Simplifications are made concerning the chemistry of the CF<sub>3</sub>O radical. Reaction rates of the CF<sub>3</sub>O radical with NO, NO<sub>2</sub>, CO, hydrocarbons, and CH<sub>2</sub>O have been measured [Saathoff and Zellner, 1993] and there is continuing research on this topic [Franklin, 1993]. COF<sub>2</sub> has been identified as a product from CF<sub>3</sub>O reaction with NO. The CF<sub>3</sub>OH formed from the reaction of CF<sub>3</sub>O with hydrocarbons is also very quickly decomposed to

COF<sub>2</sub> (see detailed discussion by Saathoff and Zellner [1993] and Franklin [1993]). Thus to simplify this complicated CF<sub>3</sub>O chemistry, we assume an instantaneous yield of unity for COF<sub>2</sub> from the CF<sub>3</sub>O radical, justified by the fast reaction rates of the above mentioned reactions. Organic nitrate formation by reaction of halogenated alkylperoxy radicals with nitrogen oxide (RO<sub>2</sub> + NO → RONO<sub>2</sub>) is neglected here because the branching ratio between nitrate production and halogenated alkoxy radical formation (RO<sub>2</sub> + NO → RO + NO<sub>2</sub>) has not yet been determined. Not all of the gas phase reaction rates involved in the chemistry of HCFCs and HFC-134a have been measured at present and thus assumptions on the others have to be made. The results presented here may depend on these assumptions (Table 2) and thus the relative importance of these reactions might change when more measurements become available.

### 2.4. Nonreactive Rainout

The nonreactive rainout of CClF<sub>2</sub>OONO<sub>2</sub>, CClF<sub>2</sub>OOH, COF<sub>2</sub>, COFCl, HCOF, CF<sub>3</sub>COF, CF<sub>3</sub>COCl, CCl<sub>2</sub>FCOOH, CClF<sub>2</sub>COOH, and trifluoroacetic acid (TFA) is taken into consideration using the parameterization presented by Junge [1957]. The rate of the removal  $L_p$  (s<sup>-1</sup>) is taken to be proportional to the average rate of formation of precipitation  $P$  (g m<sup>-3</sup> s<sup>-1</sup>) and to the dimensionless scavenging efficiency  $\epsilon$

**Table 2.** Gas Phase Reaction Rates and Cross-Section Literature Sources

Reaction	Reaction Rate* $k$	Reference
<i>HCFC-22 Chemistry</i>		
$\text{CHClF}_2 + \text{OH} \rightarrow \text{CClF}_2 + \text{H}_2\text{O}$	$1.2 \times 10^{-12} \exp(-1650/T)$	(a)
$\text{CClF}_2 + \text{O}_2 \rightarrow \text{CClF}_2\text{O}_2$	very fast	
$\text{CClF}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{CClF}_2\text{OOH} + \text{O}_2$	$3.4 \times 10^{-12}$	(o)
$\text{CClF}_2\text{O}_2 + \text{NO} \rightarrow \text{CClF}_2\text{O} + \text{NO}_2$	$3.1 \times 10^{-12} \exp(500/T)$	(a)
$\text{CClF}_2\text{O}_2 + \text{NO}_2 \rightarrow \text{CClF}_2\text{OONO}_2$	$k_0 = 1.4 \times 10^{-28}(T/300)^{-6.4}$ $k_\infty = 7.5 \times 10^{-12}$ $F_c = 0.26$	(c)
$\text{CClF}_2\text{O} \rightarrow \text{COF}_2 + \text{Cl}$	very fast	
$\text{CClF}_2\text{OOH} + \text{OH} \rightarrow \text{CClF}_2\text{O}_2 + \text{H}_2\text{O}$	$1.7 \times 10^{-12} \exp(220/T)$	suggested for ROOH (d)
$\text{CClF}_2\text{OOH} \xrightarrow{h\nu} \text{CClF}_2\text{O} + \text{OH}$	that of $\text{CH}_3\text{OOH}$ is used	(e)
$\text{CClF}_2\text{OONO}_2 \xrightarrow{M} \text{CClF}_2\text{O}_2 + \text{NO}_2$	$k_0 = 1.8 \times 10^{-3} \exp(-10500/T)$ $k_\infty = 1.6 \times 10^{16} \exp(-11990/T)$ $F_c = 0.26$	(c)
$\text{CClF}_2\text{OONO}_2 \xrightarrow{h\nu} \text{CClF}_2\text{O}_2 + \text{NO}_2$	cross-section $\text{CCl}_2\text{FOONO}_2$	(f)
$\text{COF}_2 \xrightarrow{h\nu}$	very slow	
<i>HCFC-123 Chemistry</i>		
$\text{CF}_3\text{CHCl}_2 + \text{OH} \rightarrow \text{CF}_3\text{CCl}_2 + \text{H}_2\text{O}$	$7.7 \times 10^{-13} \exp(-900/T)$	(a)
$\text{CF}_3\text{CCl}_2 + \text{O}_2 \rightarrow \text{CF}_3\text{CCl}_2\text{O}_2$	very fast	
$\text{CF}_3\text{CCl}_2\text{O}_2 + \text{NO} \rightarrow \text{CF}_3\text{CCl}_2\text{O} + \text{NO}_2$	$1.45 \times 10^{-11}$	(p)
$\text{CF}_3\text{CCl}_2\text{O}_2 + \text{NO}_2 \rightarrow \text{CF}_3\text{CCl}_2\text{OONO}_2$	$k_0 = 1.7 \times 10^{-28}(T/300)^{-6.7}$ $k_\infty = 7.8 \times 10^{-12}$ $F_c = 0.23$	that of $\text{CCl}_2\text{FO}_2$ (c)
$\text{CF}_3\text{CCl}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{CF}_3\text{CCl}_2\text{OOH} + \text{O}_2$	$1.3 \times 10^{-13} \exp(790/T)$	(o)
$\text{CF}_3\text{CCl}_2\text{OONO}_2 \xrightarrow{M} \text{CF}_3\text{CCl}_2\text{O}_2 + \text{NO}_2$	$k_0 = 1 \times 10^{-2} \exp(-10860/T)$ $k_\infty = 6.6 \times 10^{16} \exp(-12240/T)$ $F_c = 0.23$	that of $\text{CCl}_2\text{FOONO}_2$ (c)
$\text{CF}_3\text{CCl}_2\text{OONO}_2 \xrightarrow{h\nu} \text{CF}_3\text{CCl}_2\text{O}_2 + \text{NO}_2$	that of $\text{CCl}_2\text{FOONO}_2$	(f)
$\text{CF}_3\text{CCl}_2\text{OOH} + \text{OH} \rightarrow \text{CF}_3\text{CCl}_2\text{O}_2 + \text{H}_2\text{O}$	$1.7 \times 10^{-12} \exp(220/T)$	70% of the total reaction (d)
$\text{CF}_3\text{CCl}_2\text{OOH} \xrightarrow{h\nu} \text{CF}_3\text{CCl}_2\text{O} + \text{OH}$	that of $\text{CH}_3\text{OOH}$	(e)
$\text{CF}_3\text{CCl}_2\text{O} \rightarrow \text{CF}_3\text{C(O)Cl} + \text{Cl}$	very fast	
$\text{CF}_3\text{C(O)Cl} \xrightarrow{h\nu, \text{O}_2} \text{CF}_3\text{O}_2 + \text{CO} + \text{Cl}$	cross sections from	(h)
$\text{CF}_3\text{O}_2$ chemistry; see HCFC-134a		
<i>HCFC-124 Chemistry</i>		
$\text{CF}_3\text{CHClF} + \text{OH} \rightarrow \text{CF}_3\text{CFCl} + \text{H}_2\text{O}$	$6.3 \times 10^{-13} \exp(-1250/T)$	(a)
$\text{CF}_3\text{CClF} + \text{O}_2 \rightarrow \text{CF}_3\text{CFClO}_2$	very fast	
$\text{CF}_3\text{CClFO}_2 + \text{NO} \rightarrow \text{CF}_3\text{CFClO} + \text{NO}_2$	that of $\text{CF}_3\text{CCl}_2\text{O}_2$	(o)
$\text{CF}_3\text{CClFO}_2 + \text{NO}_2 \rightarrow \text{CF}_3\text{CFClOONO}_2$	$k_0 = 1.4 \times 10^{-28}(T/300)^{-6.4}$ $k_\infty = 7.5 \times 10^{-12}, F_c = 0.28$	(c) that of $\text{CClF}_2\text{O}_2$
$\text{CF}_3\text{CClFO}_2 + \text{HO}_2 \rightarrow \text{CF}_3\text{CFClOOH} + \text{O}_2$	that of $\text{CF}_3\text{CCl}_2\text{O}_2$	(o)
$\text{CF}_3\text{CClFOONO}_2 \xrightarrow{M} \text{CF}_3\text{CFClO}_2 + \text{NO}_2$	$k_0 = 1.8 \times 10^{-3} \exp(-10500/T)$ $k_\infty = 1.6 \times 10^{16} \exp(-11990/T), F_c = 0.26$	(c) like $\text{CClF}_2\text{O}_2\text{NO}_2$
$\text{CF}_3\text{CClFOONO}_2 \xrightarrow{h\nu} \text{CF}_3\text{CClFO}_2 + \text{NO}_2$	that of $\text{CCl}_2\text{FOONO}_2$	(f)
$\text{CF}_3\text{CClFOOH} \xrightarrow{h\nu} \text{CF}_3\text{CClFO} + \text{OH}$	that of $\text{CH}_3\text{OOH}$	(e)
$\text{CF}_3\text{CClFOOH} + \text{OH} \rightarrow \text{CF}_3\text{CClFO}_2 + \text{H}_2\text{O}$	$1.7 \times 10^{-12} \exp(220/T)$	(d) suggested for ROOH
$\text{CF}_3\text{CClFO} \rightarrow \text{CF}_3\text{COF} + \text{Cl}$	very fast	
$\text{CF}_3\text{COF} \xrightarrow{h\nu, \text{O}_2} \text{CF}_3\text{O}_2 + \text{CO} + \text{F}$	cross sections from	(h)
$\text{CF}_3\text{O}_2$ chemistry; see HCFC-134a		
<i>HCFC-134a Chemistry</i>		
$\text{CF}_3\text{CHF}_2 + \text{OH} \rightarrow \text{CF}_3\text{CHF} + \text{H}_2\text{O}$	$1.7 \times 10^{-12} \exp(-1750/T)$	(a)
$\text{CF}_3\text{CHF}_2 + \text{O}_2 \rightarrow \text{CF}_3\text{CHFO}_2$	very fast	
$\text{CF}_3\text{CHFO}_2 + \text{NO} \rightarrow \text{CF}_3\text{CHFO} + \text{NO}_2$	$1.56 \times 10^{-11}$	(p)
$\text{CF}_3\text{CHFO}_2 + \text{NO}_2 \rightarrow \text{CF}_3\text{CHFOONO}_2$	$5.0 \times 10^{-12}$	(q)
$\text{CF}_3\text{CHFO}_2 + \text{HO}_2 \rightarrow \text{CF}_3\text{CHFOOH} + \text{O}_2$	$4.0 \times 10^{-12}$	(o)
$\text{CF}_3\text{CHFOONO}_2 \xrightarrow{M} \text{CF}_3\text{CHFO}_2 + \text{NO}_2$	that of $\text{CClF}_2\text{OONO}_2$	(c)
$\text{CF}_3\text{CHFOOH} + \text{OH} \rightarrow \text{CF}_3\text{CHFO}_2 + \text{H}_2\text{O}$	$1.7 \times 10^{-12} \exp(220/T)$	that of $\text{C}_2\text{H}_5\text{O}_2$ (d, b)
$\text{CF}_3\text{CHFOOH} \xrightarrow{h\nu} \text{CF}_3\text{CHFO} + \text{OH}$	that of $\text{CH}_3\text{OOH}$ is used	(e)
$\text{CF}_3\text{CHFO} \xrightarrow{M1, \text{O}_2} \text{CF}_3\text{C(O)F} + \text{HO}_2 (k_1)$	$k_1 + k_2 = 3.9 \times 10^{-15} \exp(-900/T)$	$0.1 \times k_{\text{CH}_3\text{O} + \text{O}_2}$ (a)
$\text{CF}_3\text{CHFO} \xrightarrow{M2} \text{CF}_3 + \text{HCOF} (k_2)$	$k_1/k_2 = 1.58 \times 10^{-25} \times \exp(3600/T) \times (760/P)$	note 1 (i)
$\text{CF}_3 + \text{O}_2 \rightarrow \text{CF}_3\text{O}_2$	very fast	
$\text{CF}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CF}_3\text{OOH} + \text{O}_2$	$< 2 \times 10^{-12}$	(o)
$\text{CF}_3\text{OOH} + \text{OH} \rightarrow \text{CF}_3\text{O}_2 + \text{H}_2\text{O}$	that of $\text{CH}_3\text{OOH}$	(d)
$\text{CF}_3\text{OOH} \xrightarrow{h\nu} \text{CF}_3\text{O} + \text{OH}$	that of $\text{CH}_3\text{OOH}$	(e)
$\text{CF}_3\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{CF}_3\text{O}$	$1.6 \times 10^{-11}(T/300)^{-1.2}$	(b)
$\text{CF}_3\text{O}_2 + \text{NO}_2 \rightarrow \text{CF}_3\text{OONO}_2$	$k_0 = 2.7 \times 10^{-29}(T/300)^{-4.7}$ $k_\infty = 8.9 \times 10^{-12}(T/300)^{-0.7}, F_c = \exp(-T/416)$	(b)
$\text{CF}_3\text{OONO}_2 \xrightarrow{M} \text{CF}_3\text{O}_2 + \text{NO}_2$	that of $\text{CClF}_2\text{OONO}_2$	note 4
$\text{CF}_3\text{OONO}_2 \xrightarrow{h\nu} \text{CF}_3\text{O}_2 + \text{NO}_2$	that of $\text{CClF}_2\text{OONO}_2$	(f)
$\text{CF}_3\text{O} \rightarrow \text{COF}_2 + \text{F}$	simplification assumed to be very fast	
$\text{FNO}_2 \rightarrow \text{F} + \text{NO}_2$	very fast	
$\text{CF}_3\text{COOH} + \text{OH} \rightarrow \text{CF}_3\text{O}_2 + \text{H}_2\text{O}$	$2.0 \times 10^{-13} \exp(-146/T)$	(r)
<i>HCFC-141b Chemistry</i>		
$\text{CCl}_2\text{FCH}_3 + \text{OH} \rightarrow \text{CCl}_2\text{FCH}_2 + \text{H}_2\text{O}$	$1.3 \times 10^{-12} \exp(-1600/T)$	(a)
$\text{CCl}_2\text{FCH}_2 + \text{O}_2 \rightarrow \text{CCl}_2\text{FCH}_2\text{O}_2$	very fast	

**Table 2.** (continued)

Reaction	Reaction Rate* <i>k</i>	Reference
<i>HCFC-141b Chemistry</i>		
CCl <sub>2</sub> FCH <sub>2</sub> O <sub>2</sub> + NO → CCl <sub>2</sub> FCH <sub>2</sub> O + NO <sub>2</sub>	1.18 × 10 <sup>-11</sup>	that of CClF <sub>2</sub> CH <sub>2</sub> O <sub>2</sub>
CCl <sub>2</sub> FCH <sub>2</sub> O <sub>2</sub> + NO <sub>2</sub> → CCl <sub>2</sub> FCH <sub>2</sub> OONO <sub>2</sub>	$k_0 = 1.9 \times 10^{-30}(T/298)^{-4}$	that of CH <sub>3</sub> O <sub>2</sub>
	$k_\infty = 1.2 \times 10^{-11}(T/298)^{-1}, F_c = 0.4$	(b, d)
CCl <sub>2</sub> FCH <sub>2</sub> O <sub>2</sub> + HO <sub>2</sub> → CCl <sub>2</sub> FCH <sub>2</sub> OOH + O <sub>2</sub>	9.23 × 10 <sup>-12</sup>	(o)
CCl <sub>2</sub> FCH <sub>2</sub> OOH + OH → CCl <sub>2</sub> FCH <sub>2</sub> O <sub>2</sub> + H <sub>2</sub> O	that of CH <sub>3</sub> OOH	(d)
CCl <sub>2</sub> FCH <sub>2</sub> OONO <sub>2</sub> $\xrightarrow{M}$ CCl <sub>2</sub> FCH <sub>2</sub> O <sub>2</sub> + NO <sub>2</sub>	2.0 × 10 <sup>16</sup> exp (-10969/ <i>T</i> )	(k), note 5
CCl <sub>2</sub> FCH <sub>2</sub> OONO <sub>2</sub> $\xrightarrow{h\nu}$ CCl <sub>2</sub> FCH <sub>2</sub> O <sub>2</sub> + NO <sub>2</sub>	that of CClF <sub>2</sub> OONO <sub>2</sub>	(f)
CCl <sub>2</sub> FCH <sub>2</sub> OOH $\xrightarrow{h\nu}$ CCl <sub>2</sub> FCH <sub>2</sub> O + OH	that of CH <sub>3</sub> OOH	(e)
CCl <sub>2</sub> FCH <sub>2</sub> O O <sub>2</sub> → CCl <sub>2</sub> FCHO + HO <sub>2</sub>	very fast	
CCl <sub>2</sub> FCHO $\xrightarrow{h\nu, 2O_2}$ CCl <sub>2</sub> FO <sub>2</sub> + CO + HO <sub>2</sub>	cross sections from	(k)
CCl <sub>2</sub> FCHO + OH → CCl <sub>2</sub> FC(O)O <sub>2</sub> + H <sub>2</sub> O	1.2 × 10 <sup>-12</sup>	(l)
CCl <sub>2</sub> FC(O)O <sub>2</sub> + NO <sub>2</sub> → CCl <sub>2</sub> FC(O)OONO <sub>2</sub>	$k_0 = 2.7 \times 10^{-28} \times (T/300)^{7.1}$	that of PAN formation is used
	$k_\infty = 12.1 \times 10^{12} \times (T/300)^{0.9}, F_c = 0.3$	
CCl <sub>2</sub> FC(O)O <sub>2</sub> + HO <sub>2</sub> → CCl <sub>2</sub> FC(O)OOH + O <sub>2</sub> ( <i>k<sub>a</sub></i> )	$k_a + k_b = 4.3 \times 10^{-13} \exp(1040/T)$	that of CH <sub>3</sub> C(O)O <sub>2</sub> (b)
CCl <sub>2</sub> FC(O)O <sub>2</sub> + HO <sub>2</sub> → CCl <sub>2</sub> FCOOH + O <sub>3</sub> ( <i>k<sub>b</sub></i> )	$k_a/k_b = 330 \exp(-1430/T)$	that of CH <sub>3</sub> C(O)O <sub>2</sub> (m)
CCl <sub>2</sub> FC(O)OONO <sub>2</sub> $\xrightarrow{M}$ CCl <sub>2</sub> FC(O)O <sub>2</sub> + NO <sub>2</sub>	6.0 × 10 <sup>16</sup> exp (-14193/ <i>T</i> )	(k), note 5
CCl <sub>2</sub> FC(O)OONO <sub>2</sub> $\xrightarrow{h\nu}$ CCl <sub>2</sub> FC(O)O <sub>2</sub> + NO <sub>2</sub>	that of PAN	(n)
CCl <sub>2</sub> FCOOH + OH → CCl <sub>2</sub> FCO <sub>2</sub> + H <sub>2</sub> O	1.3 × 10 <sup>-12</sup> exp (-170/ <i>T</i> )	that of CH <sub>3</sub> C(O)OH
CCl <sub>2</sub> FCO <sub>2</sub> → CCl <sub>2</sub> F + CO <sub>2</sub>	very fast	
CCl <sub>2</sub> FC(O)O <sub>2</sub> + NO → CCl <sub>2</sub> F + CO <sub>2</sub> + NO <sub>2</sub>	5.1 × 10 <sup>-12</sup> exp (220/ <i>T</i> )	(d)
CCl <sub>2</sub> F + O <sub>2</sub> → CCl <sub>2</sub> FO <sub>2</sub>	very fast	
CCl <sub>2</sub> FO <sub>2</sub> + NO <sub>2</sub> → CCl <sub>2</sub> FOONO <sub>2</sub>	$k_0 = 5.5 \times 10^{-29}(T/300)^{-5.5}$	(d)
	$k_\infty = 8.3 \times 10^{-12}(T/300)^{-0.66}, F_c = 0.42$	
CCl <sub>2</sub> FOONO <sub>2</sub> $\xrightarrow{M}$ CCl <sub>2</sub> FO <sub>2</sub> + NO <sub>2</sub>	$k_0 = 10.1 \times 10^{-3} \exp(-10861/T)$	(k)
	$k_\infty = 6.6 \times 10^{16} \exp(-12393/T), F_c = 0.28$	
CCl <sub>2</sub> FOONO <sub>2</sub> $\xrightarrow{h\nu}$ CCl <sub>2</sub> FO <sub>2</sub> + NO <sub>2</sub>	cross section from	(f)
CCl <sub>2</sub> FO <sub>2</sub> + HO <sub>2</sub> → CCl <sub>2</sub> FOOH + O <sub>2</sub>	6.5 × 10 <sup>-13</sup> exp (650/ <i>T</i> )	that of C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> (b)
CCl <sub>2</sub> FOOH + OH → CCl <sub>2</sub> FO <sub>2</sub> + H <sub>2</sub> O	1.7 × 10 <sup>-12</sup> exp (220/ <i>T</i> )	that of ROOH (d)
CCl <sub>2</sub> FOOH $\xrightarrow{h\nu}$ CCl <sub>2</sub> FO + OH	that of CH <sub>3</sub> OOH	(e)
CCl <sub>2</sub> FO <sub>2</sub> + NO → CCl <sub>2</sub> FO + NO <sub>2</sub>	3.1 × 10 <sup>-12</sup> exp (500/ <i>T</i> )	(a)
CCl <sub>2</sub> FO → COFCl + Cl	very fast	
COFCl $\xrightarrow{h\nu}$	very slow	
<i>HCFC-142b Chemistry</i>		
CClF <sub>2</sub> CH <sub>3</sub> + OH → CClF <sub>2</sub> CH <sub>2</sub> + H <sub>2</sub> O	1.4 × 10 <sup>-12</sup> exp (-1800/ <i>T</i> )	(a)
CClF <sub>2</sub> CH <sub>2</sub> + O <sub>2</sub> → CClF <sub>2</sub> CH <sub>2</sub> O <sub>2</sub>	very fast	
CClF <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> + NO <sub>2</sub> → CClF <sub>2</sub> CH <sub>2</sub> OONO <sub>2</sub>	that of CH <sub>3</sub> OONO <sub>2</sub>	(b)
CClF <sub>2</sub> CH <sub>2</sub> OONO <sub>2</sub> $\xrightarrow{M}$ CClF <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> + NO <sub>2</sub>	2.0 × 10 <sup>16</sup> exp (-10933/ <i>T</i> )	(k), note 5
CClF <sub>2</sub> CH <sub>2</sub> OONO <sub>2</sub> $\xrightarrow{h\nu}$ CClF <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> + NO <sub>2</sub>	that of CClF <sub>2</sub> OONO <sub>2</sub>	(f)
CClF <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> + HO <sub>2</sub> → CClF <sub>2</sub> CH <sub>2</sub> OOH + O <sub>2</sub>	6.8 × 10 <sup>-12</sup>	(o)
CClF <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> + NO → CClF <sub>2</sub> CH <sub>2</sub> O + NO <sub>2</sub>	1.18 × 10 <sup>-12</sup>	(p)
CClF <sub>2</sub> CH <sub>2</sub> OOH + OH → CClF <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> + H <sub>2</sub> O	1.7 × 10 <sup>-12</sup> exp (220/ <i>T</i> )	like CH <sub>3</sub> OOH (d)
CClF <sub>2</sub> CH <sub>2</sub> OOH $\xrightarrow{h\nu}$ CClF <sub>2</sub> CH <sub>2</sub> O + OH	that of CH <sub>3</sub> OOH	(e)
CClF <sub>2</sub> CH <sub>2</sub> O O <sub>2</sub> → CClF <sub>2</sub> CHO + HO <sub>2</sub>	very fast	
CClF <sub>2</sub> CHO + OH O <sub>2</sub> → CClF <sub>2</sub> C(O)O <sub>2</sub> + H <sub>2</sub> O	0.7 × 10 <sup>-12</sup>	(l)
CClF <sub>2</sub> CHO $\xrightarrow{h\nu, 2O_2}$ CClF <sub>2</sub> C(O) + CO + HO <sub>2</sub>	cross sections from	(k)
CClF <sub>2</sub> C(O)O <sub>2</sub> + NO <sub>2</sub> → CClF <sub>2</sub> C(O)O <sub>2</sub> NO <sub>2</sub>	that of PAN formation	(b)
CClF <sub>2</sub> C(O)O <sub>2</sub> NO <sub>2</sub> $\xrightarrow{M}$ CClF <sub>2</sub> C(O)O <sub>2</sub> + NO <sub>2</sub>	6 × 10 <sup>16</sup> exp (-14265/ <i>T</i> )	(k)
CClF <sub>2</sub> C(O)O <sub>2</sub> NO <sub>2</sub> $\xrightarrow{h\nu}$ CClF <sub>2</sub> C(O)O <sub>2</sub> + NO <sub>2</sub>	that of PAN	(n), note 6
CClF <sub>2</sub> C(O)O <sub>2</sub> + HO <sub>2</sub> → CClF <sub>2</sub> C(O)OOH + O <sub>2</sub> ( <i>k<sub>a</sub></i> )	$k_a + k_b = 4.3 \times 10^{-13} \exp(1040/T)$	that of CH <sub>3</sub> C(O)O <sub>2</sub> (b)
CClF <sub>2</sub> C(O)O <sub>2</sub> + HO <sub>2</sub> → CClF <sub>2</sub> COOH + O <sub>3</sub> ( <i>k<sub>b</sub></i> )	$k_a/k_b = 330 \exp(-1430/T)$	that of CH <sub>3</sub> C(O)O <sub>2</sub> (m)
CClF <sub>2</sub> COOH + OH → CClF <sub>2</sub> CO <sub>2</sub> + H <sub>2</sub> O	1.3 × 10 <sup>-12</sup> exp (170/ <i>T</i> )	that of CH <sub>3</sub> COOH
CClF <sub>2</sub> CO <sub>2</sub> → CClF <sub>2</sub> + CO <sub>2</sub>	very fast	
CClF <sub>2</sub> C(O)O <sub>2</sub> + NO → CClF <sub>2</sub> + CO <sub>2</sub> + NO <sub>2</sub>	that of CCl <sub>2</sub> FC(O)O <sub>2</sub>	(d)
CClF <sub>2</sub> + O <sub>2</sub> → CClF <sub>2</sub> O <sub>2</sub>	very fast	
CClF <sub>2</sub> O <sub>2</sub> degradation; see HCFC-22 chemistry		

(a) DeMore et al. [1992]; (b) Lightfoot et al. [1992]; (c) Atkinson et al. [1992]; (d) Atkinson [1989]; (e) DeMore et al. [1987]; (f) Morel et al. [1980]; (g) Moortgat et al. [1980]; (h) Meller et al. [1991]; (i) Kirchner et al. [1991]; (j) Wallington et al. [1992]; (k) Libuda et al. [1991], Zabel [1993], Zabel et al. [1994]; (l) Scollard et al. [1993]; (m) Horie and Moortgat [1992]; (n) Senum et al. [1984]; (o) Hayman et al. [1991, 1994, and personal communication]; (p) Peeters and Pultau [1994]; (q) Mogelberg et al. [1994a]; (r) Mogelberg et al. [1994b]; Carr et al. [1994]. Note 1: P, pressure in torr; rate reported by Tuazon and Atkinson [1993] is also used for comparison. Note 2: Temperature dependence taken equal to that of CH<sub>3</sub>CHO; the work by Tuazon and Atkinson [1994] and G. Hayman (personal communication, 1994) indicates that at 1 atm and room temperature the intermediate product CFCl<sub>2</sub>CO is forming CFCl<sub>2</sub> + CO and CFCl<sub>2</sub>O<sub>3</sub> with yields of 75 and 25%, respectively. For CClF<sub>2</sub>CO these ratios are 39 and 61%, respectively. Note 3: Computing the photolysis rates of CClF<sub>2</sub>OONO<sub>2</sub>, the available literature data on the cross section of CCl<sub>2</sub>FOONO<sub>2</sub> are used (f). However, only cross sections for wavelengths between 200 and 280 nm are available. An extrapolation of these data to longer wavelength, which is crucial for the tropospheric lifetime, is carried out following the suggestions in the AFEAS report 1989. Note 4: In agreement with preliminary measurements by F. Zabel et al. (personal communication, 1993). Note 5: Small pressure dependence; see Zabel et al. [1994]. Note 6: Measurements of the absorption cross sections by O. Rattigan and T. Cox indicate that this nitrate absorbs stronger than PAN. This has not yet been taken into account.

\*The following notation is used for three-body reactions:

$$k = \frac{k_0(T) M}{k_0(T) M + k_\infty(T)} \cdot F^{(1 + [\log k_0(T) M / k_\infty(T)]^2)^{-1}}$$



which depends on the solubility of the species according to the Henry's law constants (Table 1):

$$L_p = \varepsilon \frac{P}{L} \quad (2)$$

where  $L$  is the liquid water content (LWC) of the precipitating cloud. Liquid water contents of precipitating clouds vary between 0.5 and 2 g m<sup>-3</sup>. Unpublished sensitivity studies performed on the highly soluble compound HNO<sub>3</sub> show that varying LWC by a factor of 2 (between 0.5 and 2 g m<sup>-3</sup>) resulted in much smaller responses of the wet deposition. In this study we used a liquid water content of 1 g m<sup>-3</sup>.

Input data for this scheme originate from measured climatological precipitation fields at the Earth's surface [Jaeger, 1976]. The vertical distribution of precipitation is scaled to the release of latent heat with height [Newell et al., 1974].

## 2.5. Oceanic Removal

The uptake and hydrolysis in the ocean of HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b is parameterized as recommended by Butler et al. [1991] and as explained previously for CH<sub>3</sub>CCl<sub>3</sub>. Also, for the uptake of the more reactive species COF<sub>2</sub>, COFCl, HCOF, CF<sub>3</sub>COF, CF<sub>3</sub>COCl, ROOH (where R: alkyl or halogenated alkyl), CCl<sub>2</sub>FC(O)OOH, CClF<sub>2</sub>C(O)OOH, and CClF<sub>2</sub>OONO<sub>2</sub> the atmosphere-ocean resistance model [Kindler et al., 1992] was used (Figure 4). However, in this case, the resistances at the ocean-atmosphere interface in the atmospheric marine layer ( $r_a = 1.85$  s cm<sup>-1</sup>) and in the oceanic sublayer ( $r_s = 170$  s cm<sup>-1</sup>) are taken into account as well as the diffusion in the oceanic surface layer ( $D_1 = 40$  cm<sup>2</sup> s<sup>-1</sup>):

$$L_0 = \frac{\varepsilon H R T}{\Delta Z_1 \left( r_s + r_a \frac{H}{R} + \sqrt{D_1 k_H} \right)} \quad (3)$$

This approximation neglects deep ocean loss for the above compounds, which is reasonable when the hydrolysis rate  $k_H$  is rather fast compared to diffusion (i.e.,  $k_H \gg D_1/(\Delta Z_2)^2 \approx 6 \times 10^{-7}$  s<sup>-1</sup>).

## 2.6. Removal in Clouds

Removal in clouds due to hydrolysis is introduced for COF<sub>2</sub>, COFCl, HCOF, CF<sub>3</sub>COF, CF<sub>3</sub>COCl, CCl<sub>2</sub>FC(O)OOH, and CClF<sub>2</sub>C(O)OOH, whereas for the remaining species, removal by hydrolysis in clouds is expected to be slow [Wine and Chameides, 1989].

Uptake and hydrolysis in clouds is considered using the statistical model of Rodhe and Grandell [1972]. At a certain height, longitude and latitude, the lifetime  $t(s)$  due to loss in clouds is given by

$$t = t_{nc}(1 - f) + (fk_d)^{-1} \quad (4)$$

with  $t_{nc}$ , the time that the air spends out of clouds (s);  $f$ , cloud volume fraction; and  $k_d$ , the pseudo-first-order scavenging frequency in clouds (s<sup>-1</sup>).

The first term of this sum,  $t_{nc}(1 - f)$ , accounts for the statistical probability for an air parcel to become incorporated in clouds and the term  $(fk_d)^{-1}$  for the real removal rate in clouds. At high scavenging rates (i.e., when hydrolysis rates and Henry's law coefficients are high), the total loss ( $t^{-1}$ ) is dependent on the frequency of cloud occurrence alone. On the other hand, when hydrolysis rates ( $k_H$ ) and Henry's law coef-

ficients ( $H$ ) are low, the loss rate ( $t^{-1}$ ) is determined by the cloud volume fraction, the liquid water content of the cloud, and the  $H$  and  $k_H$  values. For most  $H$  and  $k_H$  values given in Table 1, the latter condition prevails. Thus (4) can be simplified to

$$t = (fk_d)^{-1} \quad (5)$$

where  $k_d$  is given by

$$k_d = k_H H T LWC F_{AD} \quad (6)$$

with  $R = 0.083$  (atm M<sup>-1</sup> K<sup>-1</sup>);  $T$  is the temperature (K); LWC is the dimensionless liquid water content (or volume fraction of the air occupied by liquid water, 1 gm<sup>-3</sup>  $\approx$  10<sup>-6</sup>) of the clouds; and  $F_{AD}$  is a factor correcting for the effects of aqueous phase diffusion.

According to Schwartz and Freiberg [1981] the steady state solution for diffusion in cloud droplets can be expressed by relating the average concentration in the droplet  $C_m$  to the concentration at the surface of the droplet  $C_d$  through the equation

$$F_{AD} = \frac{C_m}{C_d} \left( \frac{\coth q}{q} - \frac{1}{q^2} \right) \quad (7)$$

with  $q = r(k_H/D_a)^{1/2}$ ;  $r$  is the droplet radius (cm) and  $D_a$  is the aqueous phase diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>). For all compounds we used a relatively slow aqueous phase diffusion coefficient of 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>. This correction is of no significance (correction factor  $F_{AD}$  almost 1) for slow hydrolysis rates and small droplets but becomes significant for large droplets and fast hydrolysis rates. For instance, using the set of parameters in Table 1, for a 50- $\mu$ m radius cloud droplet nucleated on sea-salt aerosols in the marine environment, the correction factors for COFCl, CF<sub>3</sub>COCl, and CF<sub>3</sub>COF are calculated to be 0.25, 0.10, and 0.20, respectively. Adopting a typical droplet radius of 10  $\mu$ m, correction factors of 0.75, 0.50, and 0.65 were calculated for COFCl, CF<sub>3</sub>COCl, and CF<sub>3</sub>COF, respectively; the remaining species were not affected by aqueous phase diffusion limitation.

Note that in this parameterization the uptake limitation by gas phase diffusion and transfer through the gas-aqueous interface were neglected. Gas phase diffusion limitation is negligible for the range of Henry's law coefficients of the species studied. This would not be the case if the Henry's law coefficients were substantially larger than those used here. Transport through the gas-droplet interface is dependent on the value of the sticking coefficient  $\alpha$  (the probability that after collision a gas phase molecule will remain on the droplet surface). The measurements by George et al. [1992] and DeBruyn et al. [1992] give no indication that  $\alpha$  would be small, and thus we neglect gas-droplet interfacial transport limitations.

The cloud volume fraction in each grid box of the model and the liquid water content (LWC) vary seasonally and are derived from NCAR cloud statistics for different cloud types and assumptions on cloud height and liquid water described in detail by Dentener [1993]. The yearly average liquid water content integrated in the atmospheric column up to the 100-hPa level (g m<sup>-2</sup>) is shown in Figure 6. These values agree within a factor of 2 with liquid water paths derived from satellites. Recently, Haskins et al. [1995] compared the ISCCP satellite-observed cloudiness with the surface data of Warren et al. [1986] and Hahn et al. [1986]. Generally, cloudiness of the two data sets agrees within 20%, although regionally larger discrep-

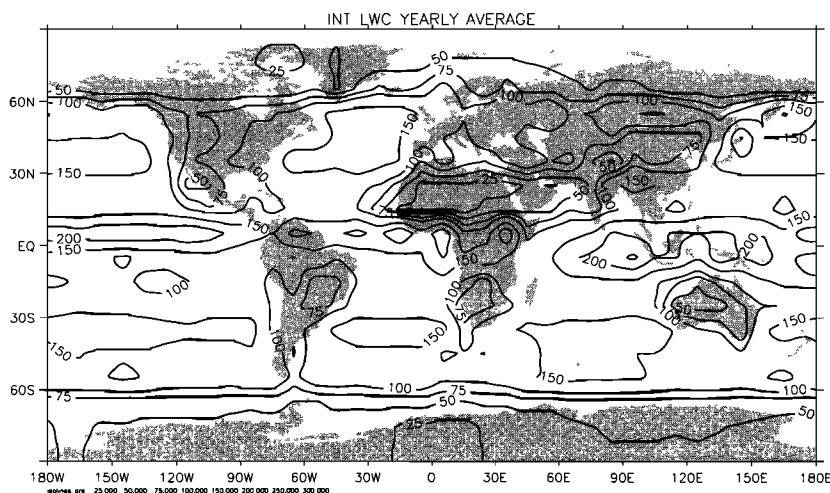


Figure 6. Column-integrated liquid water content distribution (yearly mean values) ( $\text{g m}^{-2}$ ).

ancies may exist. According to the statistics used in the present study, 5–7% of the tropospheric volume is occupied by clouds.

### 2.7. Stratospheric Lifetimes

Losses of HCFCs and HFC-134a to the stratosphere were parameterized using pseudo-first-order loss rates derived from the two-dimensional stratospheric model of the Max Planck Institute for Chemistry (C. Brühl, private communication, 1992). Monthly varying hemispheric average stratospheric loss rates of HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b, and HFC-134a, corresponding to lifetimes of 214, 62, 87, 90, 389, and 357 years, respectively, are applied at the 100-hPa model level. No stratospheric exchange of the oxidation products from these halogenated hydrocarbons could be taken into consideration in this study, although measurements by *Wilson et al.* [1988] in the NH suggested a flux of some halogenated carbonyl species (RCOX) from the stratosphere to the troposphere. However, on the whole, the stratospheric

sinks of the HCFCs and HFCs are much smaller than those in the troposphere, justifying our assumption.

### 2.8. Emissions

On the basis of production and sales data, release of HCFC-22 was introduced in the model for the period 1970–1990 [Midgley and Fisher, 1993]. This release is augmented by 5% to account for nonreported emissions (mainly by the CIS states and China), since the AFEAS data are assumed to cover in excess of 95% of the global HCFC-22 production [United Nations Environmental Program (UNEP), 1995]. The HCFC-22 emissions were spatially distributed using the regional distribution of CFC-12 emissions [McCulloch *et al.*, 1994], together with the population distribution of *Fung et al.* [1991]. All other HCFCs were geographically distributed like HCFC-22. For the period 1990–2020 the emission scenarios by *McCulloch* [1993] were used (see Figure 7). No calculations were made for the period after 2020, when under the revised

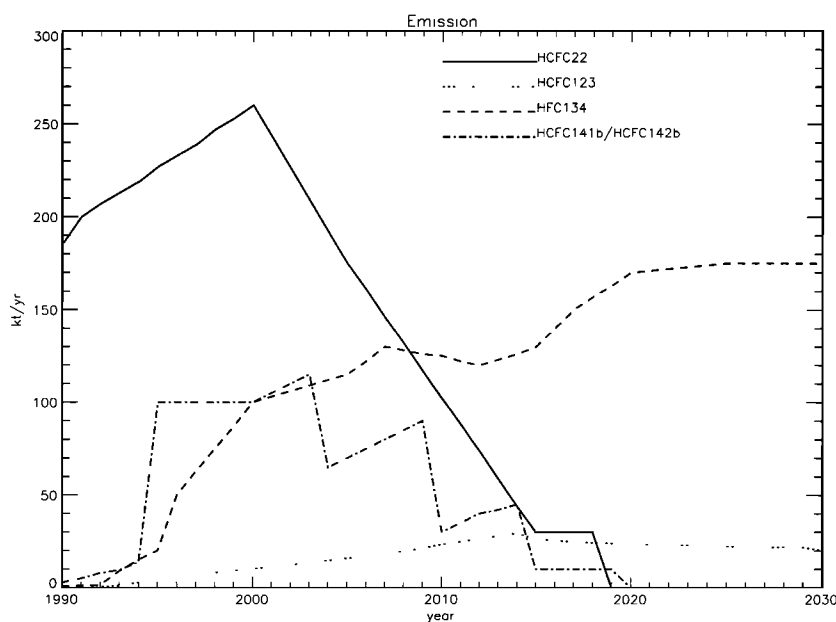


Figure 7. Emission scenario adopted for HCFCs and HFC-134a.

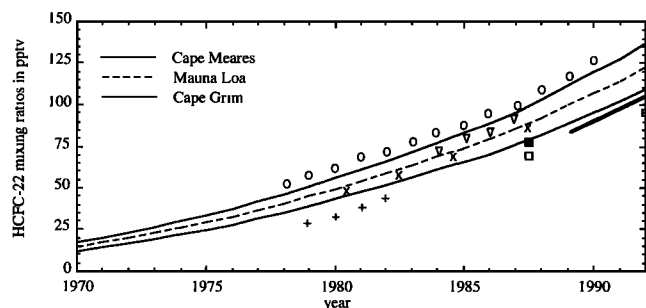
Montreal Protocol the consumption of HCFCs will be phased down at least by 99.5% in 2020 relative to a 1996 baseline of 3.1% of 1989 CFC use and 1989 HCFC use, in ODP tons. The same emission scenario which describes HCFC-123 is used for HCFC-124. Large uncertainties are associated with these emission scenarios (A. McCulloch, personal communication, 1994). Differences in emissions of HCFCs and HFC-134a will linearly translate in the calculated concentrations. Initial concentrations of HCFC-22 for the year 1970 (13 parts per trillion by volume (pptv) in the NH and of 10 pptv in the SH) are used in this study, based on an extrapolation of measured concentrations. Initial 1990 concentrations of the remaining HCFCs and HFC-134a are assumed to be zero.

### 3. Model Results and Discussion

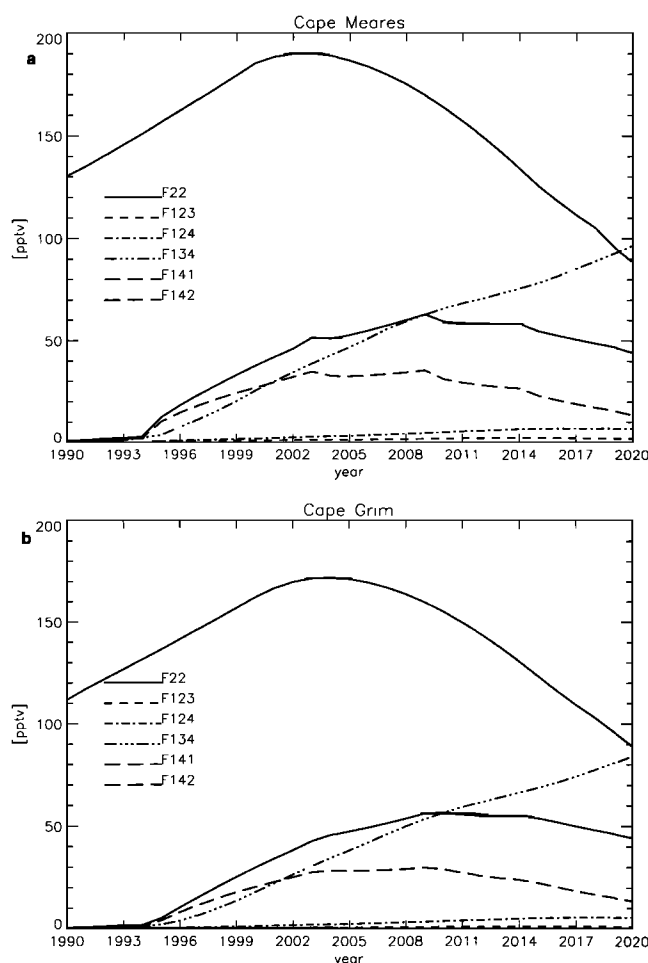
#### 3.1. Tropospheric Distributions

##### 3.1.1. HCFC-22 concentrations for the period 1970–1992.

An annual increase of 6–7% in the tropospheric content of HCFC-22 is calculated for the period 1980–1990, corresponding to a calculated increase of 5–9 pptv/yr for Cape Meares (NH) and 4–7 pptv/yr for Cape Grim (SH). Figure 8 shows the measured and calculated mixing ratios of HCFC-22 for the period 1970–1992. There is a large discrepancy between the observed HCFC-22 reported by the experimental groups, which can mainly be attributed to differences in calibration standards. The mixing ratios of HCFC-22 determined by *Khalil and Rasmussen* [1981, 1987] from ground-based chromatographic measurements in the NH are 10–40% higher than those determined from long-path absorption measurements within the troposphere and lower stratosphere [*Rinsland et al.*, 1989, 1990]. They are also higher than the grab sample measurements in the lower troposphere by *Pollock et al.* [1992] and recently reported measurements of NH and SH air for the period November 1991 to December 1992 [*Montzka et al.*, 1993]. These discrepancies in the experimental data prohibit better evaluation of the model results. Our model results are in the range of these two sets of experimental data. The calculated increase of HCFC-22 corresponds rather well to the



**Figure 8.** HCFC-22 mixing ratios for the period 1970–1992. Top line, calculated concentrations for Cape Meares; middle line, calculated concentrations for Mauna Loa; bottom line, calculated concentrations for Cape Grim; circles, measurements at Cape Meares, Oregon [*Khalil and Rasmussen*, 1987; *Borchers et al.*, 1994]; triangles, measurements at Cape Grim, Tasmania [*Khalil and Rasmussen*, 1987]; dashed line and solid square, NH measurements; open squares, SH measurements by *Montzka et al.* [1993]; crosses, spectroscopic measurements by *Rinsland et al.* [1990] at 31°–32°N; pluses, south pole measurements [*Khalil and Rasmussen*, 1987].



**Figure 9.** Volume mixing ratios of HCFC-22, HFC-134a, HCFC-123, HCFC-124, HCFC-141b, and HCFC-142b at (a) Cape Meares, 45°N and (b) at Cape Grim, 42°S calculated for the period 1990–2020, based on the scenario shown in Figure 7 (pptv).

observed 7%/yr increase of HCFC-22 in the period 1980–1992 measured by *Zander et al.* [1994].

**3.1.2. Future HCFCs and HFC-134a atmospheric concentrations.** By using the scenario for the future emissions of substitutes (Figure 7) and assuming that these emissions will be geographically distributed like those of HCFC-22, we calculated the buildup of concentrations of the studied halogenated hydrocarbons. The calculated mixing ratios of the HCFCs and HFC-134a from 1990 to 2020 are presented in Figures 9a and 9b.

HCFC-22, HFC-134a, and HCFC-142b are the substitutes with the longest lifetimes in the atmosphere with turnover times due to oxidation in the troposphere by OH radicals of 13.7, 13.9, and 20.3 years, respectively (Table 3). HCFC-22 and HFC-134a are expected to become the predominant compounds among the substitutes reaching maximum volume mixing ratios of 190 pptv (HCFC-22 in the year 2003) and 100 pptv (HFC-134a in the year 2020) in the NH. In the following section, results for HCFC-22 and its oxidation products are presented for the year 2005 and for HFC-134a in 2020. HCFC-123, HCFC-124, HCFC-141b, and HCFC-142b mixing ratios are expected to remain lower than 60 pptv. Finally, in Figures 10a, 10b, 11a, and 11b we depict the June 1000 hPa and zonal mean mixing ratios of HCFC-22 and HFC-134a. At the surface

**Table 3.** Atmospheric Turnover Times for HCFCs, HFC-134a, and Some of Their Oxidation Products

Compound	Oxidation by OH in Troposphere, years	Oceanic Loss	In-Cloud Loss	Stratospheric Loss,* years
CH <sub>3</sub> CCl <sub>3</sub>	6.5	63 years		54
HCFC-22	13.7	986 years	...	214
HFC-134a	13.9	...	...	357
HCFC-123	1.3	306 years	...	62
HCFC-124	6.0	1802 years	...	87†
HCFC-141b	9.5	1856 years	...	90
HCFC-142b	20.3	1455 years	...	389
RCOX species				
COF <sub>2</sub>	...	3.9 months	3.9 days	...
COFCl	...	1.7 years	6.4 days	...
CF <sub>3</sub> COCl	...	2.9 years	5.9 days	...
CF <sub>3</sub> COF	...	2.0 years	6.1 days	...
HCOF	...	3.0 months	4.3 years‡	...

Three dots, not taken into consideration in this study.

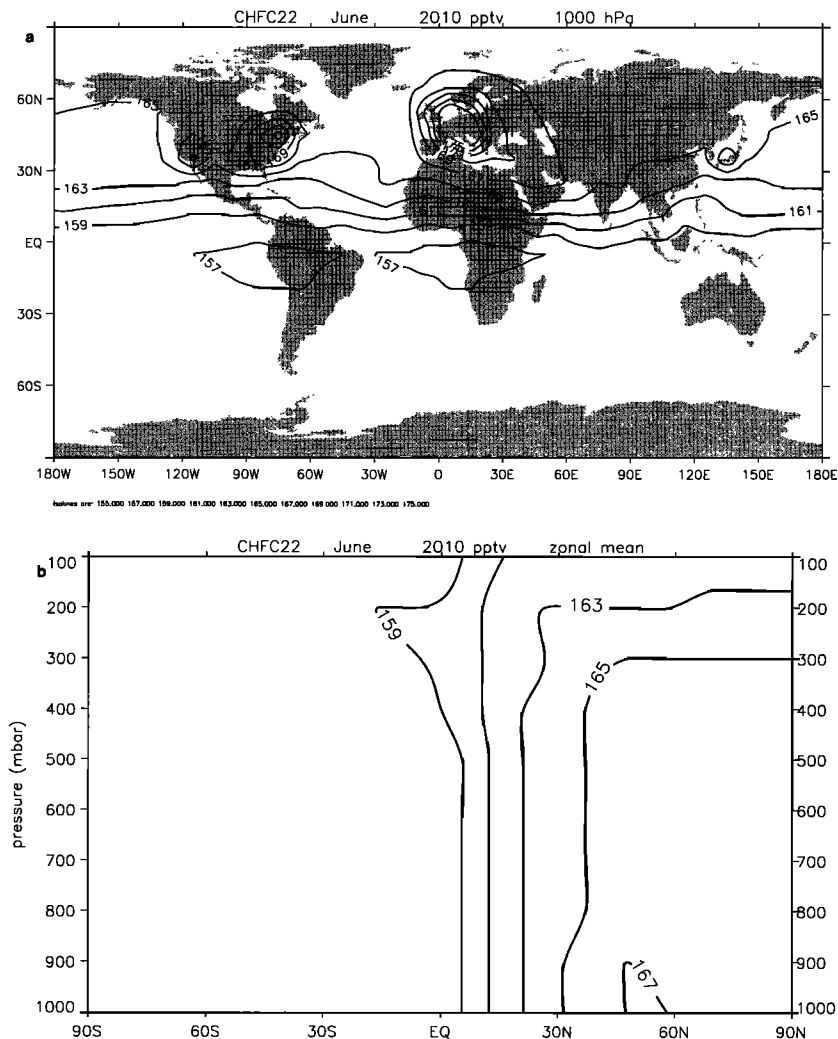
\*Input to the model based on results of a two-dimensional stratospheric model (C. Brühl, private communication, 1992).

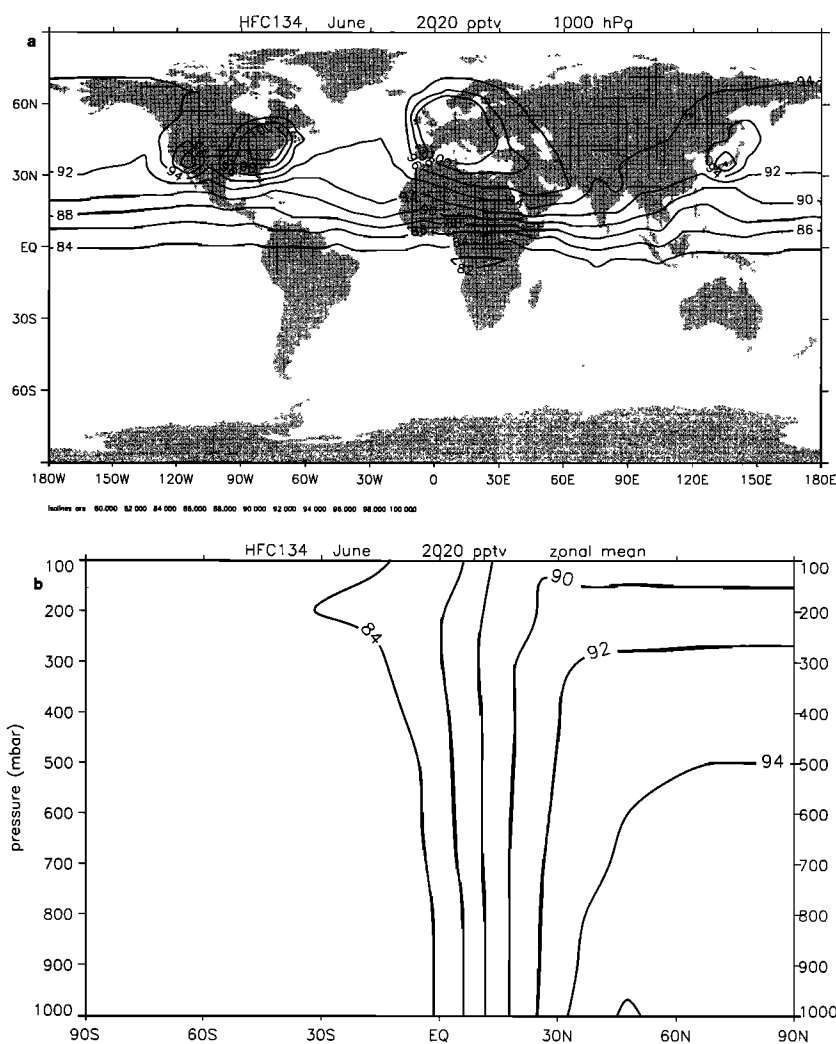
†Stratospheric loss rate assumed to be similar to that of HCFC-141b.

‡No experimental data on Henry's law coefficient ( $H$ ) and hydrolysis rates ( $k_H$ ) are available (see text).

the highest concentrations are found near the emission areas in the United States, Europe, and Japan. In the SH the concentration gradients are small, reflecting a long lifetime and relatively small SH emissions.

**3.1.3. Carbonyl compounds (COF<sub>2</sub>, COFCl, HCOF, CF<sub>3</sub>COF, CF<sub>3</sub>COCl) and TFA.** Heterogeneous processes are the main loss of the halogenated carbonyl compounds (RCOX) from the atmosphere. The experimental determina-

**Figure 10.** Volume mixing ratios of HCFC-22 in January 2010 at (a) 1000 hPa and (b) zonal mean (pptv).



**Figure 11.** Volume mixing ratios of HFC-134a in January 2020 at (a) 1000 hPa and (b) zonal mean (pptv).

tion of the Henry's law coefficients ( $H$ ) and unimolecular hydrolysis rates ( $k_H$ ), used in (3) and (6), are extremely difficult, resulting in order of magnitude differences in the results of the different experimental groups [George *et al.*, 1992, 1993, 1994; DeBruyn *et al.*, 1992, 1995]. We used the results of George *et al.* [1992, 1993, 1994] and varied their hydrolysis rates by a factor of 10, encompassing the range of results obtained by the experimentalists. Furthermore, as shown in Table 1, we do not consider a  $pH$  dependency of the hydrolysis rates, which has been reported by George *et al.* [1993] and DeBruyn *et al.* [1992]. At high  $pH$  (basic solutions) the uptake rates of the studied

RCOX species were observed to be enhanced, possibly due to  $\text{OH}^-$  catalysis of RCOX hydrolysis. In the present study, reported values valid for a  $pH$  of 6 are used. In large parts of the world,  $pH$  values in cloudwater are about 5 [Dentener, 1993], justifying this assumption. The lifetimes of the carbonyl species are calculated to range from a few days ( $\text{COF}_2$ ) to about 2 years (HCOF); see Tables 3 and 4. The concentration distribution of the RCOX species reflects the net effect of oxidation of the HCFCs and HFC-134a by  $\text{OH}$ , oceanic removal, and hydrolysis in clouds.

Because the formation of the gas phase degradation prod-

**Table 4.** RCOX Lifetimes Resulting From the Removal at the Oceanic Surface, Rainout, and Loss in Clouds

RCOX	In-Cloud Loss			Oceanic Removal			Rainout, years		
	A	B	C	A	B	C	A	B	C
$\text{COF}_2$	3.9 days	7.1 days	3.1 days	3.9 months	2.3 months	5.4 months	72	38	86
$\text{CF}_3\text{COCl}$	5.9 days	6.9 days	5.4 days	2.9 years	1.9 years	4.4 years	900	550	970
$\text{CF}_3\text{COF}$	6.1 days	7.6 days	5.9 days	2.0 years	1.9 years	3.3 years	675	450	819
HCOF	4.3 years	39 years	3.2 months	3.0 months	3.2 years	1.8 months	180	154	105
$\text{COFCl}$	6.4 days	7.6 days	4.8 days	1.7 years	0.9 years	2.1 years	265	156	277

A, using the Henry law coefficients and hydrolysis rates as reported in Table 1; B, using 10 times slower hydrolysis rates; C, using 10 times faster hydrolysis rates than in Table 1.

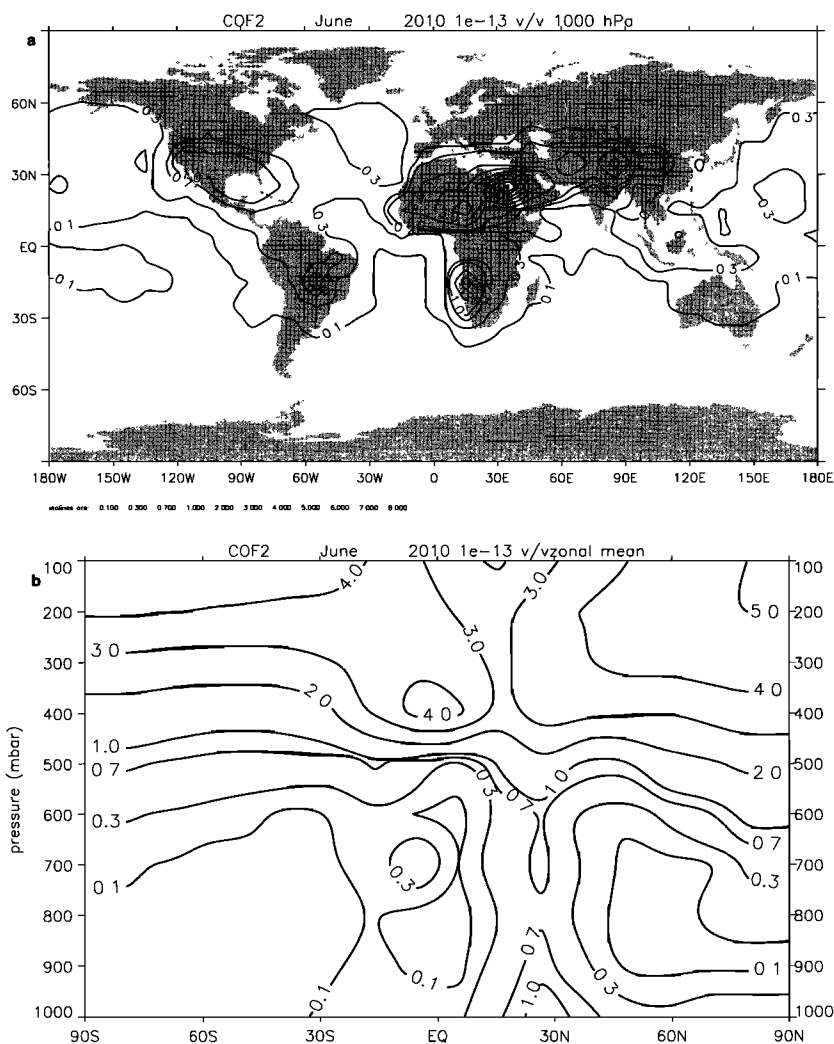


Figure 12. Volume mixing ratios of COF<sub>2</sub> in June 2010 at (a) 1000 hPa and (b) zonal mean ( $10^{-13}$  v/v).

ucts of HCFCs and HFC-134a is closely connected to the presence of the OH radical, the tropics and subtropics are also the areas with the highest abundances of these carbonyl compounds. In Figures 12a, 13a, 14a, and 15a the mixing ratios of COF<sub>2</sub>, CF<sub>3</sub>COF, CF<sub>3</sub>COCl at 1000 hPa and HCOF at 600 hPa calculated for June (in 2010 for COF<sub>2</sub> and 2020 for CF<sub>3</sub>COF and HCOF) are shown. For the tropics our model yields maximum surface mixing ratios in the low pptv range for COF<sub>2</sub> and HCOF and sub-ppt levels for COFCl, CF<sub>3</sub>COF, and CF<sub>3</sub>COCl. The highest concentrations are calculated above 7 km in cloudless regions. Figures 12b, 13b, 14b, and 15b show the zonal mean mixing ratios of COF<sub>2</sub>, CF<sub>3</sub>COF, CF<sub>3</sub>COCl, and HCOF.

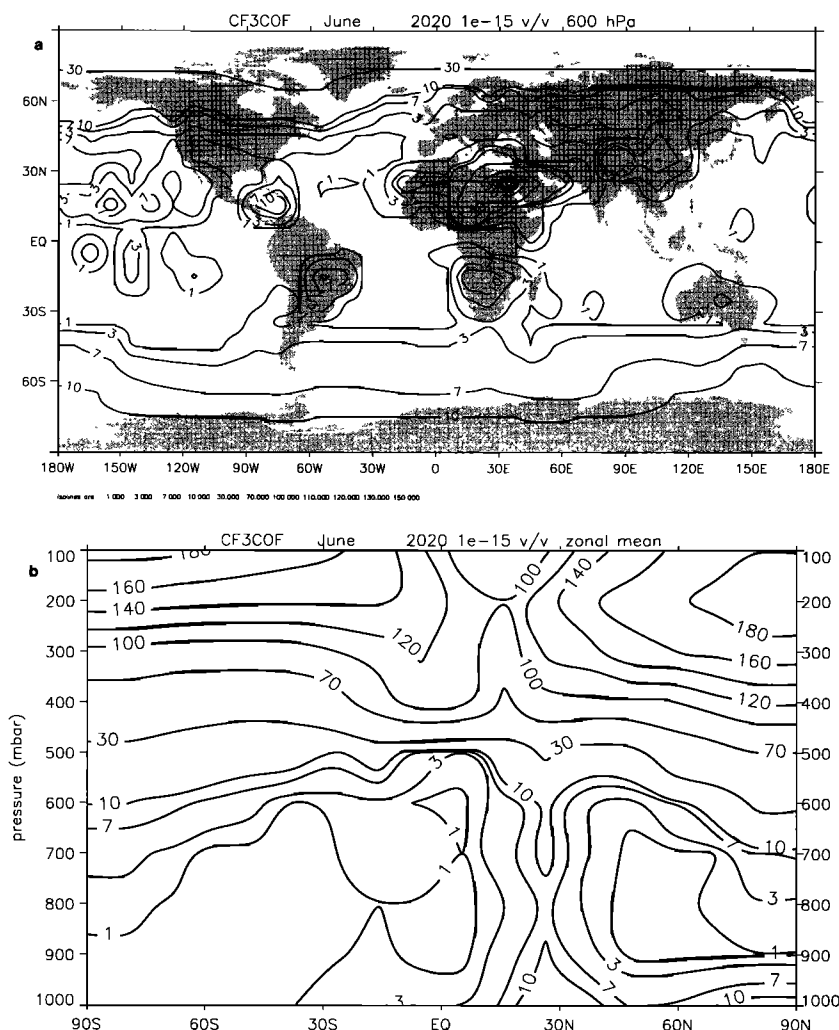
The tropics are also the main regions of deep convective clouds, associated with typical timescales of the order of an hour for the transport from the boundary layer to the high troposphere. Within this period, even for the fastest reacting RCOX species (Table 3), only a small fraction can hydrolyze in the cumulonimbus (Cb) clouds. Thus a fraction of these oxidation products could even be transported into the stratosphere. However, concentrations of the oxidation products are considerably lower than those of the parent compounds (Table 5), rendering transport of these species into the stratosphere insignificant.

Since most of the RCOX species are slowly photolyzed, the

oxidation of CFCs and HCFCs in the stratosphere may even be an additional source for these species in the troposphere [Kindler *et al.*, 1995; Wilson *et al.*, 1988]. This is not taken into consideration in the present study.

For the branching ratio between CF<sub>3</sub>COF and HCOF formation from HFC-134a oxidation we use the temperature and pressure dependence presented by Wallington *et al.* [1992]. A 30–35% higher branching ratio for the production of CF<sub>3</sub>COF from HCFC-134a oxidation, as recently determined by Tuazon and Atkinson [1993], has also been used to evaluate uncertainties in the CF<sub>3</sub>COF and HCOF yields. We calculate that 64–71% of the annually oxidized amount of HFC-134a in the model domain (between the surface and 100 hPa), is converted to HCOF, whereas 29–36% gives CF<sub>3</sub>COF. In the present study, CF<sub>3</sub>COF, also produced from HCFC-124 oxidation, reaches maximum values above 7 km of about 0.1 pptv.

The calculated concentrations of HCOF strongly depend on the assumptions made for  $H$  and  $k_H$ . Unfortunately, no experimental data are available for this carbonyl compound. In this study we used the hydrolysis rate for CH<sub>3</sub>COF [Bunton and Fendler, 1966] and a Henry's law coefficient of 3 like for CF<sub>3</sub>COF, which is 1000 times smaller than the Henry's law coefficient for CH<sub>2</sub>O [Ledbury and Blair, 1925]. Our results, which rely totally on assumptions given in Tables 1 and 2,



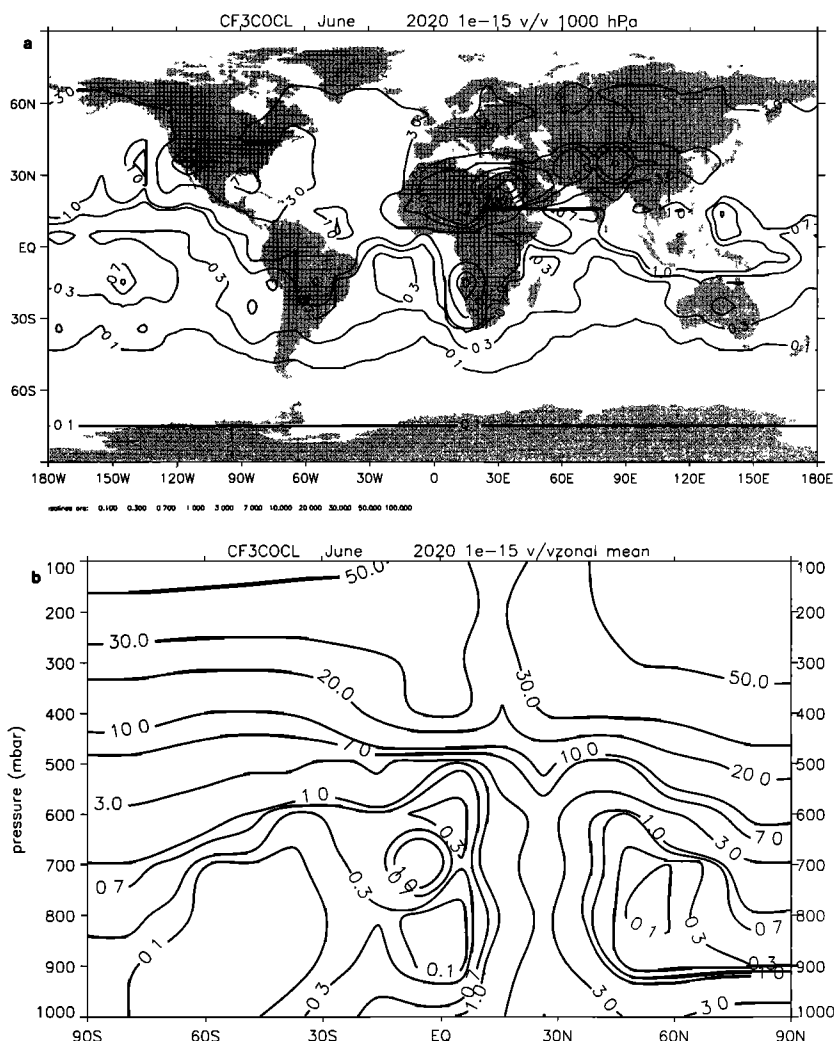
**Figure 13.** Volume mixing ratios of  $\text{CF}_3\text{COF}$  calculated for June 2020 (a) at 1000 hPa (b) zonal mean ( $10^{-15}$  v/v).

indicate that HCOF could build up in the troposphere and low stratosphere. Clearly, measurements of the HCOF hydrolysis rate and Henry's law coefficient are needed to properly assess its importance in the atmosphere.

After hydrolysis in clouds from  $\text{CF}_3\text{COF}$  (and from  $\text{CF}_3\text{COCl}$  derived from HCFC-123 oxidation), trifluoroacetic acid (TFA) ( $\text{CF}_3\text{C}(\text{O})\text{OH}$ ) is produced, which is of some environmental concern due to its stability in the environment. It is uncertain, whether TFA will be released into the atmosphere after cloud evaporation (only 10% of all clouds form precipitation), or remain in the aerosol phase. Measurements by *Edney et al.* [1992] indicate some evaporation of TFA from surface films.

Because TFA is a strong acid ( $pK_a = 0.25$ ), it is, in this work, assumed to be removed by wet and dry deposition with rates identical to those of  $\text{HNO}_3$  [Dentener, 1993]. At present, there are only two known pathways which can degrade TFA in the environment. In the atmosphere, oxidation of gas phase TFA by OH can lead to some TFA destruction [Mogelberg et al., 1994b; Carr et al., 1994]; and *Visscher et al.* [1994] found that in certain soils, TFA can rapidly degrade. In this work we calculate, based on the assumption that all TFA is present in the gas phase, that at most, 5% of the TFA can be destroyed by the OH reaction.

In Figures 16 and 17 we show the total (wet and dry) deposition in the year 2020 and the accumulated deposition in the period 1990–2020, respectively. We calculate that wet deposition contributes by at least 75% to the total deposition. Areas of maximum deposition are found in the tropics, associated with high rainfall amounts. Maximum deposition fluxes of  $2 \mu\text{mol}/\text{m}^2/\text{yr}$  in 2020 (rainwater concentration about  $1 \text{ nmol}/\text{L}$ ) are an order of magnitude larger in the tropics than at midlatitudes. Accumulated deposition ranges from 1 to  $70 \mu\text{mol}/\text{m}^2/\text{yr}$ . Our calculated maximum TFA rainwater concentration of  $1 \text{ nmol}/\text{L}$  is of the same order of magnitude as the calculations by *Rodriguez et al.* [1994], although the assumptions on the emissions of HCFC-123, HCFC-124, and HFC-134a and the removal of TFA are quite different from ours. Similarly to our results, their study indicates areas of maximum deposition in the tropics. We calculate latitudinal variations in deposition of TFA of a factor of 40, whereas longitudinal variations are much smaller (up to a factor of 3). As indicated in Table 4, hydrolysis of  $\text{CF}_3\text{COF}$  in clouds should be slower by about 2 orders of magnitude to significantly influence TFA deposition patterns. Likewise, a change of value of the removal rate by precipitation  $L_p$  (equation (2)) will not strongly influence the total deposition pattern, although the gas phase TFA



**Figure 14.** Volume mixing ratios of  $\text{CF}_3\text{COCl}$  calculated for June 2020 (a) at 1000 hPa and (b) zonal mean ( $10^{-15}$  v/v).

concentrations (which are well below pptv levels) may be slightly influenced.

**3.1.4. Other products resulting from HCFC-141b and HCFC-142b oxidation.** The oxidation of  $\text{CH}_3\text{CCl}_2\text{F}$  and  $\text{CH}_3\text{CClF}_2$  in the troposphere produces  $\text{CCl}_2\text{FCHO}$  and  $\text{CClF}_2\text{CHO}$  which in turn are either photolyzed or react with OH radicals.

Oxidation by the OH radical leads to the formation of the RCO radical ( $\text{RCHO} + \text{OH} \rightarrow \text{RCO} + \text{H}_2\text{O}$ ; R, halogenated alkyl) which could subsequently produce PAN-like compounds ( $\text{CCl}_2\text{FC(O)O}_2\text{NO}_2$  and  $\text{CClF}_2\text{C(O)O}_2\text{NO}_2$ ). These organic nitrates are of some concern because they could build up in the middle and high troposphere and contribute to the transport of reactive halogens to the stratosphere [Zabel *et al.*, 1994].

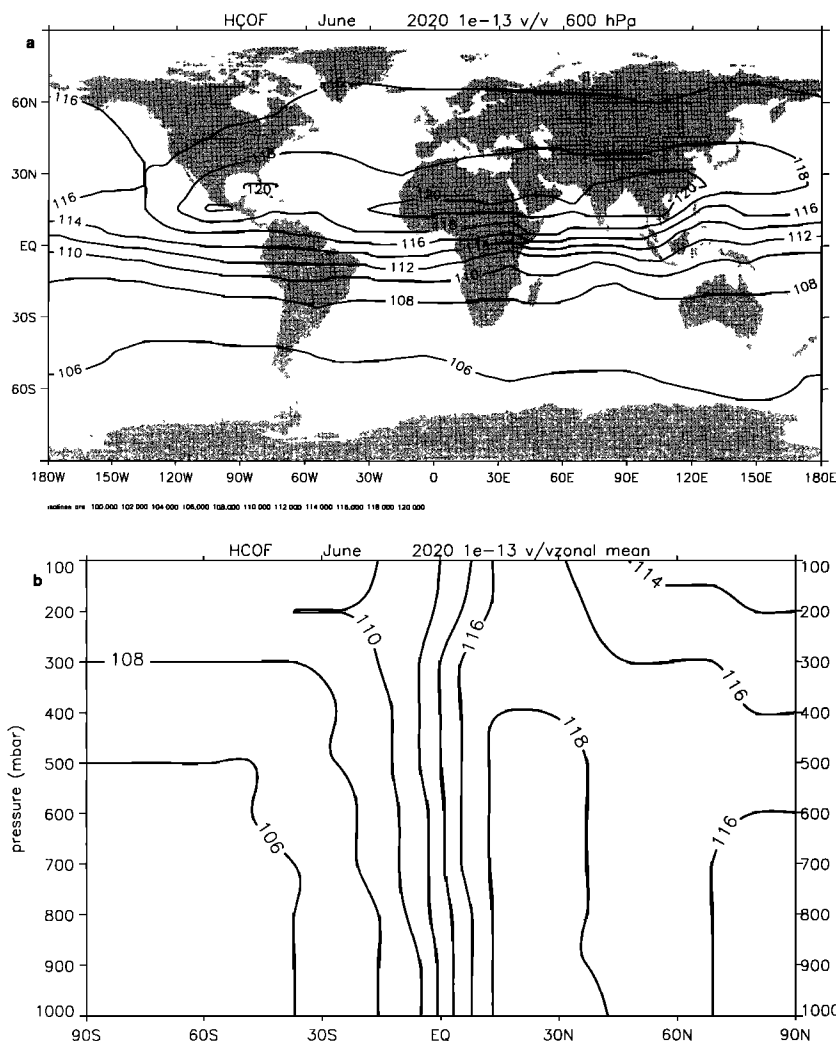
The photolysis of aldehydes produces halogenated peroxy radicals ( $\text{CFCl}_2\text{O}_2$  and  $\text{CF}_2\text{ClO}_2$ ) and does not yield PAN-like species ( $\text{RCHO} + h\nu + 2\text{O}_2 \rightarrow \text{RO}_2 + \text{CO} + \text{HO}_2$ ). Absence of experimental data on the quantum yield of these photolytic reactions prohibits determination of the importance of the photolysis of these halogenated aldehydes relative to the reaction with OH. In the present study we assume a quantum yield equal to unity which could lead to an underestimate in the concentrations of the PAN-like compounds. The chemistry of

these PAN-like species is simulated by using the reaction and photodissociation rates of PAN. Based on these assumptions, the concentrations of  $\text{CCl}_2\text{FC(O)O}_2\text{NO}_2$  and  $\text{CClF}_2\text{C(O)O}_2\text{NO}_2$  calculated here are well below the pptv level. These results could change moderately when reaction and photolysis rates for the specific reactions will become available.

### 3.2. Tropospheric Lifetimes and Environmental Consequences

Oxidation by OH radicals is responsible for the main loss of HCFCs and HFC-134a from the troposphere. The calculated tropospheric lifetimes (Table 3) resulting from oxidation by OH radicals are defined as the ratio of the annual mean tropospheric burden to the annual tropospheric loss by gas phase reaction with OH. With the exception of HCOF, for the RCOX species, hydrolysis in cloud droplets represents the major loss process. Lifetimes resulting from the loss in clouds vary from several days to years depending on the adopted Henry's law coefficients and the hydrolysis rates. As mentioned above, large uncertainties persist on the experimental determination of these coefficients with results from different experimental groups varying by an order of magnitude. In particular for HCOF, no experimental data are available at all. Therefore





**Figure 15.** Volume mixing ratios of HCOF at (a) at 600 hPa and (b) zonal mean (pvt).

to test the sensitivity of the hydrolysis rates, we also report in Table 4 the lifetimes of RCOX species calculated for 10 times higher and 10 times lower values of the hydrolysis rates than those reported in Table 1, which encompasses the uncertainties in the measurements (note that a variation of the Henry's law coefficients would yield very similar results; see (1) and (6)).

Table 4 shows that for all the carbonyl species considered, hydrolysis in clouds is the dominant removal pathway. Inter-

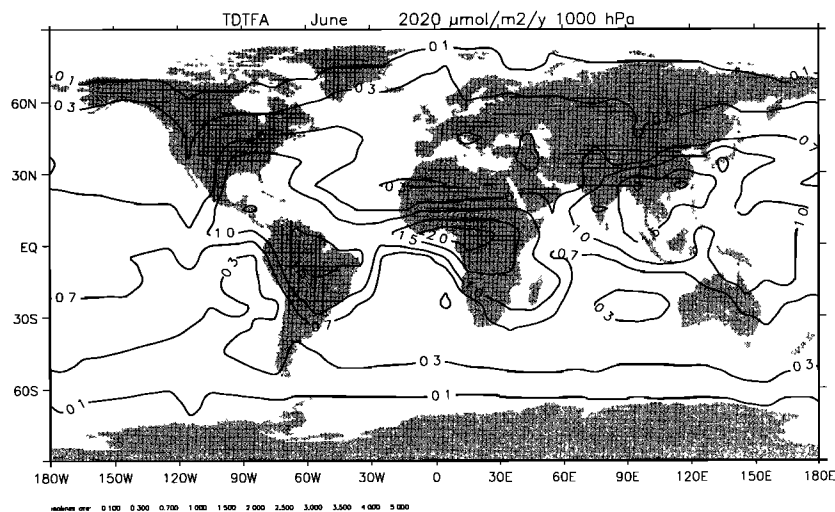
estingly, except for HCOF, the lifetimes due to hydrolysis in clouds are not very sensitive to the adopted hydrolysis coefficients. Instead, the lifetimes of these species seem to depend more on meteorological processes like rapid transport into the upper troposphere by deep convection, subsequent downward transport in the high-pressure regions of the Hadley circulation, and finally, incorporation in clouds. When removal by clouds becomes slower, oceanic removal gains importance be-

**Table 5.** Tropospheric Abundances of the HCFCs and Selected Oxidation Products (mol) in Year 2015

Parent Compound	Carbonyl Compound	Nitrates
HCFC-22, $1.9 \times 10^{10}$	COF <sub>2</sub> <sup>*,†</sup> , $1.7 \times 10^7$	CClF <sub>2</sub> OONO <sub>2</sub> <sup>†</sup> , $3 \times 10^4$
HCFC-123, $2.3 \times 10^8$	CF <sub>3</sub> COCl, $2.7 \times 10^6$	CF <sub>3</sub> CCl <sub>2</sub> OONO <sub>2</sub> , $2 \times 10^3$
HCFC-124, $9.4 \times 10^8$	CF <sub>3</sub> COF <sup>*</sup> , $6.8 \times 10^6$	CF <sub>3</sub> CFClOONO <sub>2</sub> , $4 \times 10^3$
HFC-134a, $1.2 \times 10^{10}$	HCOF, $4.0 \times 10^8$	CF <sub>3</sub> CFHOONO <sub>2</sub> , $2 \times 10^6$
		CF <sub>3</sub> OONO <sub>2</sub> , small
HCFC-141b, $3.3 \times 10^9$	COFCl, $1.5 \times 10^6$	CFCl <sub>2</sub> CH <sub>2</sub> OONO <sub>2</sub> , $6 \times 10^3$
		CFCl <sub>2</sub> C(O)ONO <sub>2</sub> , $4 \times 10^6$
		CCl <sub>2</sub> FOONO <sub>2</sub> , small
HCFC-142b, $8.5 \times 10^9$	...	CClF <sub>2</sub> CH <sub>2</sub> OONO <sub>2</sub> , $2 \times 10^3$
		CClF <sub>2</sub> C(O)ONO <sub>2</sub> , $4 \times 10^6$

\*Also from HFC-134a.

†Also from HCFC-142b.



**Figure 16.** Total annual (wet plus dry) deposition of  $\text{CF}_3\text{C}(\text{O})\text{OH}$  in 2020 ( $\mu\text{mol m}^{-2} \text{yr}^{-1}$ ). Wet deposition represents the major fraction of the total deposition.

cause RCOX species are then long enough lived to be transported to the oceanic boundary layer, resulting in shorter oceanic lifetimes (Table 4). With the exception of HCOF the hydrolysis rates of the carbonyl species should be at least 2 orders of magnitude lower to have a significant impact on the lifetime of these trace gases. Using the estimated hydrolysis rates for HCOF, loss in the oceans determines the turnover time for HCOF. In Table 5 we show that in the year 2015, very small amounts of the oxidation products are residing in the atmosphere, with the molar ratio of the oxidation products and the parent compounds generally less than 1%.

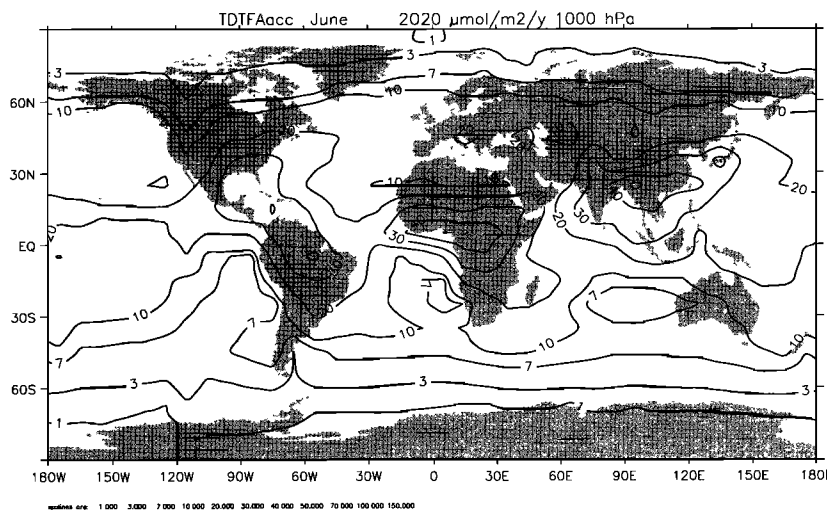
Maximum concentrations of TFA in rainwater are calculated to be 1 nmol/L in the tropics in the year 2020. Assuming the hypothetical case that no biological destruction in soils would occur and that all TFA would reevaporate after deposition, an upper limit of 35 nmol TFA/L in rainwater is calculated. It is unlikely that these concentrations will have an effect on human or animal health [Kaminsky, 1989]. Phytotoxicity

threshold of mono- and trichloroacetic acid are 60–200  $\mu\text{mol/L}$ , respectively [Frank, 1994]. Assuming analogous values for TFA, it is unlikely that TFA from HCFCs will have effects on plants either.

On the basis of the model-derived lifetimes of HCFCs and HFC-134a (Table 3) and CFC-11 (53 years) we can calculate the chlorine loading potential (CLP) of the species under consideration, which represents the upper limit of the steady state effect of HCFCs and HFC-134a on ozone depletion relative to that of emitted CFC-11. CLP is defined by the ratio of chlorine transported across the tropopause to the stratosphere per unit of mass of HCFC emitted relative to the chlorine transported per unit of mass of CFC-11 [e.g., Pyle *et al.*, 1992]:

$$\text{CLP} = \frac{\tau_x}{\tau_{\text{cfc-11}}} \frac{M_{\text{cfc-11}}}{M_x} \frac{n_x}{3} \quad (8)$$

where  $t$  is the overall lifetime,  $M$  the molar mass, and  $n$  the number of chlorine atoms per molecule. The calculated CLP



**Figure 17.** Total accumulated (wet plus dry) deposition of  $\text{CF}_3\text{C}(\text{O})\text{OH}$  from 1990 to 2020 ( $\mu\text{mol m}^{-2} \text{yr}^{-1}$ ). Wet deposition represents the major fraction of the total deposition.

**Table 6.** Chlorine Loading Potentials (CLP) of Selected HCFCs and HFC-134a Based on Tropospheric Turnover Times (years) With Respect to Oxidation by OH and Stratospheric Loss Lifetimes (Years) Calculated in This Study

Compound	Oxidation by OH	Stratospheric Loss	Total Lifetime	CLP
HCFC-22	13.7	214	12.9	0.132
HFC-134a	13.9	357	13.4	...
HCFC-123	1.2	62	1.2	0.014
HCFC-124	6.0	87	5.6	0.036
HCFC-141b	9.5	90	8.6	0.126
HCFC-142b	20.3	389	19.3	0.166

values are reported in Table 6, ranging from 0.014 to 0.166. According to our calculations, HCFC-22 and HCFC-142b could be the most aggressive HCFCs among the replacements toward stratospheric ozone. The other studied species are expected to be 3 to 10 times less effective in transporting chlorine from the troposphere to the stratosphere. Note that the CLP of HCFC-134a is, by definition, zero.

#### 4. Conclusions

We studied the degradation chemistry and removal of the alternative chlorofluoro- and fluorohydrocarbons, HCFC-22, HCFC-123, HCFC-124, HFC-134a, HCFC-141b, and HCFC-142b. We showed that application of the oceanic and stratospheric loss parameterizations and precalculated OH fields yields good agreement of calculated CFC-11 and methyl chloroform concentrations with measurements. Calculated and measured mixing ratios HCFC-22 for the period 1980–1992 agree within the uncertainty of the measurements.

Lifetimes of the parent HCFCs and HFC-134a range from 1.3 to 20 years with oxidation by the OH radical being the dominant removal reaction. Only minor amounts of the replacements are calculated to be transported to the stratosphere; hydrolysis in the oceans is of minor significance for these compounds.

Using emission scenarios based on future demand and supply [McCulloch, 1993], we calculate that HCFC-22 will reach a maximum concentration of 190 pptv around the year 2005, the concentrations of all other HCFCs remain below 100 pptv. As mentioned above, large uncertainties are associated with the use of these emission scenarios. The chlorine loading potential of the HCFCs ranges from 0.014 for HCFC-123 to 0.166 for HCFC-142b. Volume mixing ratios of the halogenated carbonyl compounds (i.e., COF<sub>2</sub>, COFCl, CF<sub>3</sub>COF, CF<sub>3</sub>COCl) will reach at most a few pptv, and the abundances of the degradation products are, in general, less than 1% those of the parent compounds. A possible exception is HCOF, for which at present the hydrolysis rate and Henry's law coefficient are unknown. Hydrolysis in clouds, and to a lesser extent in seawater, efficiently remove these species from the atmosphere. Organic nitrates derived from HCFCs will not reach substantial concentrations and will not significantly deliver chlorine to the stratosphere. The deposition fluxes of the very stable trifluoroacetic acid (TFA), derived from HFC-134a, and HCFCs-123 and 124, will in the year 2020 reach maximum levels of 2  $\mu\text{mol}/\text{m}^2/\text{yr}$  (about 1 nmol/L rainwater). Maximum deposition will take place in tropical regions, associated with high oxida-

tion rates of the parent compounds, high cloudiness, and rainfall. It is unlikely that these minor concentrations will be phytotoxic or affect human health.

We estimate that at most, 5% of the TFA can be degraded by the reaction with OH radicals. It is recommended that research on biodegradation in soils will concentrate on wet tropical soils, as these will be receiving maximum TFA deposition fluxes.

**Acknowledgments.** We thank the Alternative Fluorocarbons Environmental Acceptability Study for financial support and for providing information prior to publication (SPA-AFEAS, contract CTR91-25/P90-047). Special thanks to C. Brühl for communicating to us his two-dimensional stratospheric model results and to J. Franklin and A. McCulloch for constructive discussions. We also thank R. Atkinson, R. Prinn, D. Hartley, F. Zabel, O. J. Nielsen, R. Borchers, J. W. Elkins, G. Hayman, and C. George for providing us information prior to publication and P. H. Zimmermann for programming assistance. M.K. expresses gratitude to the CNRS and the CEA for their support.

#### References

- Atkinson, R., Tropospheric reactions of haloalkyl radicals formed from hydroxyl radical reaction with a series of alternative fluorocarbons, in *Scientific Assessment of Stratospheric Ozone: 1989, WMO Rep. 20*, pp. 165–208, World Meteorol. Organ., Geneva, 1989.
- Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson Jr., J. A. Kerr, and J. Troe, Kinetic and photochemical data for atmospheric chemistry, *J. Phys. Chem. Ref. Data*, **21**, 1127–1143, 1992.
- Borchers, R., R. Gunawardena, and R. A. Rasmussen, Long term trend of selected halogenated hydrocarbons, in *Ozone in the Troposphere and Stratosphere*, edited by R. D. Hudson, pp. 259–262, *Nasa Conf. Publ. 3266*, 1994.
- Bunton, C. A., and J. H. Fendler, The hydrolysis of acetyl fluoride, *J. Organ. Chem.*, **31**, 2307–2312, 1966.
- Butler, J., J. Elkins, T. Thompson, B. Hall, T. Swanson, and V. Koropalov, Oceanic consumption of CH<sub>3</sub>CCl<sub>3</sub>; Implications for tropospheric OH, *J. Geophys. Res.*, **96**, 22,347–22,355, 1991.
- Carr, S., J. J. Treacy, H. W. Sidebottom, R. K. Connell, C. E. Canosmas, R. P. Wayne, and J. Franklin, Kinetics and mechanisms for the reaction of hydroxyl radicals with trifluoroacetic acid under atmospheric conditions, *Chem. Phys. Lett.*, **227**, 39–41, 1994.
- Crutzen, P. J., and P. H. Zimmermann, The changing chemistry of the troposphere, *Tellus*, **43AB**, 136–151, 1991.
- DeBruyn, W., J. A. Shorter, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, The heterogeneous chemistry of carbonyl and haloacetyl halides, in *Proceedings of Workshop on Atmospheric Wet and Dry Deposition of Carbonyl and Haloacetyl Halides*, Altern. Fluorocarbons Environ. Acceptability Study (AFEAS), Brussels, Sept. 22, 1992.
- DeBruyn, W., J. A. Shorter, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, Uptake of haloacetyl and carbonyl halides by water surfaces, *Environ. Sci. Technol.*, **29**, 1179–1185, 1995.
- DeMore, W. B., M. J. Molina, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, Chemical kinetics and photochemical data for use in stratospheric modeling, in *Evaluation 8, JPL Publ. 87-41*, Jet Propul. Lab., Pasadena, Calif., 196, 1987.
- DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, R. A. Ravishankara, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, in *Evaluation 10, JPL Publ. 92-20*, Jet Propul. Lab., Pasadena, Calif., 1992.
- Dentener, F. J., Heterogeneous chemistry in the troposphere, PhD thesis, Univ. of Utrecht, Netherlands, 1993.
- Dentener, F. J., and P. J. Crutzen, Reaction of N<sub>2</sub>O<sub>5</sub> on tropospheric aerosols: Impact on the global distributions of NO<sub>x</sub>, O<sub>3</sub>, and OH, *J. Geophys. Res.*, **98**, 7149–7163, 1993.
- Edney, E. O., D. J. Driscoll, E. W. Corse, and F. T. Blanchard, Atmospheric fate of trifluoroacetate during evaporation of complex aqueous solutions, in *Proceedings of Workshop on Atmospheric Wet and Dry Deposition of Carbonyl and Haloacetyl Halides*, AFEAS, Brussels, 1992.

- Feichter, J., and P. J. Crutzen, Parameterisation of deep cumulus convection in a global tracer transport model and its evaluation with  $^{222}\text{Rn}$ , *Tellus*, **42B**, 100–117, 1990.
- Frank, H., Airborne haloacetic acids, environmental occurrence and ecotoxicological relevance, paper presented at Workshop on Decomposition of TFA in the Environment, AFEAS, 8–9 February, Washington, D. C., 1994.
- Franklin, J., The atmospheric degradation and impact of 1,1,1,2-tetrafluoroethane, (hydrofluorocarbon 134a), *Chemosphere*, **27**, 1565–1601, 1993.
- Fung, I., J. John, J. Lerner, E. Matthews, M. Prather, C. P. Steele, and P. J. Fraser, Three-dimensional model synthesis of the global methane cycle, *J. Geophys. Res.*, **96**, 13,003–13,065, 1991.
- Gallardo, L., and H. Rodhe, Evaluation of a oxidized three-dimensional model of tropospheric nitrogen, Int. Meteorol. Inst., Stockholm, 1995.
- George, C., J. L. Ponche, and P. Mirabel, Experimental determination of mass accommodation coefficients, in *Proceedings of Workshop on the Atmospheric Wet and Dry Deposition of Carbonyl and Haloacetyl Halides*, pp. 18–24, AFEAS, Brussels, Sept. 22, 1992.
- George, C., J. L. Ponche, and P. Mirabel, Experimental determination of uptake coefficients for acid halides, in *Proceedings of Workshop on STEP-HALOCSIDE, AFEAS*, Dublin, March 23–25, 1993.
- George, C., J. Lagrange, P. Lagrange, P. Mirabel, C. Pallares, and J. L. Ponche, Heterogeneous chemistry of trichloroacetylchloride in the atmosphere, *J. Geophys. Res.*, **99**, 1255–1262, 1994.
- Hahn, C. J., S. G. Warren, J. London, R. M. Chervin, and R. Jenne, Atlas of simultaneous occurrence of different cloud types over land, *NCAR Tech. Note TN-273+STR*, Natl. Cent. for Atmos. Res., Boulder, Colo., 1986.
- Hartley, D., and R. Prinn, Feasibility of determining surface emissions of trace gases using an inverse method in a three-dimensional chemical transport model, *J. Geophys. Res.*, **98**, 5183–5198, 1993.
- Haskins, R. D., T. P. Barnett, M. M. Tyree, and E. Roeckner, Comparison of cloud fields from an atmospheric general circulation model, in situ and satellite measurements, *J. Geophys. Res.*, **100**, 1367–1378, 1995.
- Hayman, G. D., M. E. Jenkin, T. P. Murrels, and S. J. Shalliker, Kinetics and mechanistic studies associated with the atmospheric degradation of HCFC-123, in *Proceedings of Workshop on STEP-HALOCSIDE, AFEAS*, Dublin, 14–16 May, 1991.
- Hayman, G. D., M. E. Jenkin, T. P. Murrels, and C. E. Johnson, Tropospheric degradation chemistry of HCFC-123 ( $\text{CF}_3\text{CHCl}_2$ ): A proposed replacement chlorofluorocarbon, *Atmos. Environ.*, **28**, 421–437, 1994.
- Horie, O., and G. K. Moortgat, Reactions of  $\text{CH}_3\text{CO}_2$  radicals with  $\text{CH}_3\text{O}_2$  and  $\text{HO}_2$  between 263 and 333 K, *J. Chem. Soc. Faraday Trans.*, **88**, 3305–3312, 1992.
- Jaeger, L., Monatskarte des Niederschlags für die ganze Erde, *Ber. Dtsch. Wetterdienstes*, **139**, 1976.
- Junge, C. E., and P. E. Gustafson, On the distribution of seasalt over the United States and its removal by precipitation, *Tellus*, **9**, 164–173, 1957.
- Kaminsky, L. S., Toxicology of atmospheric degradation products of selected hydrofluorocarbons, in *Scientific Assessment of Stratospheric Ozone: 1989, WMO Rep. 20*, pp. 455–459, World Meteorol. Organ., Geneva, 1989.
- Kanakidou, M., and P. J. Crutzen, Scale problems in tropospheric chemistry modeling: Comparison of results obtained with a three-dimensional model, adopting longitudinally uniform and varying emissions of  $\text{NO}_x$  and NMHC, *Chemosphere*, **26**, 787–802, 1993.
- Kasibhatla, P. S., H. Levy II, and W. J. Moxim, Global  $\text{NO}_x$ ,  $\text{HNO}_3$ , PAN, and  $\text{NO}_y$  distributions from fossil-fuel combustion emissions: A model study, *J. Geophys. Res.*, **98**, 7165–7180, 1993.
- Khalil, M. A. K., and R. A. Rasmussen, Increase of  $\text{CHClF}_2$  in the earth's atmosphere, *Nature*, **292**, 823–824, 1981.
- Khalil, M. A. K., and R. A. Rasmussen, Chlorocarbons in the southern hemisphere: Concentrations and temporal trends, in *Baseline Atmospheric Programme (Australia) 1985*, edited by B. W. Morgan and P. J. Fraser, pp. 26–29, Bur. of Meteorol./CSIRO, Queensl., Australia, 1987.
- Kindler, T. P., W. L. Chameides, P. H. Wine, D. Cunnold, and F. Alyea, The fate and lifetime of tropospheric phosgene, in *Proceedings of Workshop on Atmospheric Wet and Dry Deposition of Carbonyl and Haloacetyl Halides*, pp. 33–43, AFEAS, Sept. 22, 1992.
- Kindler, T. P., W. L. Chameides, P. H. Wine, D. M. Cunnold, F. Alyea, and J. A. Franklin, The fate of atmospheric phosgene and the stratospheric chlorine loadings of its parent compounds:  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_4$ ,  $\text{C}_2\text{HCl}_3$ ,  $\text{CH}_3\text{CCl}_3$ , and  $\text{CHCl}_3$ , *J. Geophys. Res.*, **100**, 1235–1252, 1995.
- Kirchner, F., F. Zabel, and K. H. Becker, Thermal stability of  $\text{CCl}_2\text{CH}_2\text{O}_2\text{NO}_2$  and  $\text{CCl}_2\text{FCH}_2\text{O}_2\text{NO}_2$ , in *Proceedings of Workshop on Kinetic and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, pp. 73–78, STEP-HALOCSIDE, AFEAS, Dublin, May 14–26, 1991.
- Ledbury, W., and E. W. Blair, The partial formaldehyde vapor pressure of aqueous solutions of formaldehyde, *J. Chem. Soc.*, **127**, 2832–2839, 1925.
- Libuda, H. G., F. Zabel, and K. H. Becker, UV spectra of some organic chlorine and bromine compounds, in *Proceedings of Workshop on Kinetic and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, pp. 126–13, STEP-HALOCSIDE/AFEAS, Dublin, May 14–26, 1991.
- Lightfoot, P. D., R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Organic peroxy radicals: Kinetics, spectroscopy and tropospheric chemistry, *Atmos. Environ.*, **26A**, 1805–1964, 1992.
- McCulloch, A., Source of hydrochlorofluorocarbons and fluorocarbons and their potential emissions during the next twenty five years, in *Proceedings of the International Symposium on Non- $\text{CO}_2$  Greenhouse Gases*, edited by J. van Ham, L. J. H. M. Janssen, and R. J. Swart, pp. 167–174, Maastricht, Netherlands, December 14, 1993.
- McCulloch, A., P. M. Midgley, and D. A. Fisher, Distribution of emissions of chlorofluorocarbons (CFCs) 11, 12, 113, 114 and 115 among reporting and nonreporting countries in 1986, *Atmos. Environ.*, **28**, 1994.
- McLinden, M. O., Physical properties of alternatives to the fully halogenated chlorofluorocarbons, *Scientific Assessment of Stratospheric Ozone: 1989, WMO Rep. 20*, pp. 11–41, World Meteorol. Organ., Geneva, 1989.
- Meller, R., D. Boglu, and G. K. Moortgat, UV spectra of several halogenated carbonyl compounds and FTIR studies on the degradation of  $\text{CF}_3\text{COCl}$ , HCFC-123 and HFC-134a, in *Proceedings of Workshop on Kinetic and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere*, pp. 110–116, STEP-HALOCSIDE, AFEAS, Dublin, May 14–26, 1991.
- Midgley, P. M., The production and release to the atmosphere of 1,1,1-trichloroethane (methyl chloroform), *Atmos. Environ.*, **23**, 2663–2665, 1989.
- Midgley, P. M., and D. A. Fisher, The production and release to the atmosphere of chlorodifluoromethane (HCFC 22), *Atmos. Environ.*, **27A**, 2215–2223, 1993.
- Mogelberg, T. E., O. J. Nielsen, J. Sehested, T. J. Wallington, M. D. Hurley, and W. F. Schneider, Atmospheric chemistry of HFC-134a, Kinetic and mechanistic study of  $\text{CF}_3\text{CFHO}_2 + \text{NO}_2$  reaction, *Chem. Phys. Lett.*, **225**, 375–380, 1994a.
- Mogelberg, T. E., O. J. Nielsen, J. Sehested, T. J. Wallington, and M. D. Hurley, Atmospheric chemistry of the reaction with OH radicals, *Chem. Phys. Lett.*, **226**, 171–177, 1994b.
- Montzka, S. A., R. C. Myers, J. H. Butler, J. W. Elkins, and S. O. Cummings, *Geophys. Res. Lett.*, **20**, 20,703–20,706, 1993.
- Moortgat, G. K., W. Klippel, K. H. Möbius, W. Seiler, and P. Warneck, Laboratory measurements of photolytic parameters for formaldehyde, *Rep. FAA-EE-80-47*, U.S. Dep. of Transp., Washington, D. C., 1980.
- Morel, O., R. Simonaitis, and J. Heicklen, Ultraviolet absorption of  $\text{HO}_2\text{NO}_2$ ,  $\text{CCl}_3\text{O}_3\text{NO}_2$ ,  $\text{CCl}_2\text{FO}_2\text{NO}_2$ , and  $\text{CH}_3\text{O}_2\text{NO}_2$ , *Chem. Phys. Lett.*, **73**, 38–42, 1980.
- Newell, R. E., J. W. Kidson, D. G. Vincent, and G. L. Boer, *The General Circulation of the Tropical Atmosphere and Interactions With Extratropical Latitudes*, vol. 2, MIT Press, Cambridge, Mass., 1974.
- Oort, A. H., Global atmospheric circulation statistics, *NOAA Prof. Pap. 14*, U.S. Govt. Print. Off., Washington, D. C., 1983.
- Peeters, J., and V. Pultau, Reactions of hydrofluorocarbon and hydrochlorofluorocarbon-derived peroxy radicals with nitric oxide, Results for HFC-134a, HCFC-143a, HCFC-142b, HCFC-123 and HCFC-124, in *Physicochemical Behaviour of Atmospheric Pollutants, VI*, edited by G. Angeletti and G. Restelli, *Rep. EUR, 15609/1 EN*, Eur. Comm., Brussels, 1994.
- Penner, J. E., C. S. Atherton, J. Dignon, S. J. Ghan, J. J. Walton, and S. Hammed, Tropospheric nitrogen: A three-dimensional study of

- sources, distributions, and deposition, *J. Geophys. Res.*, **96**, 959–990, 1991.
- Pollock, W. H., L. E. Heidt, R. A. Lueb, J. F. Vedder, M. J. Mills, and S. Solomon, On the age of stratospheric air and ozone depletion potentials in polar regions, *J. Geophys. Res.*, **97**, 12,993–12,999, 1992.
- Prinn, R., et al., Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (methyl chloroform) data for 1978–1990, *J. Geophys. Res.*, **97**, 2445–2461, 1992.
- Prinn, R. G., R. F. Weiss, B. R. Miller, F. N. Alyea, D. M. Cunnold, D. E. Hartley, P. B. Fraser, and P. G. Simmonds, Global weighted-average concentration and trend of OH based on 15 years of ALE/GAGE  $\text{CH}_3\text{CCl}_3$  data, paper presented at Joint Meeting on global atmospheric chemistry, Int. Assoc. of Meteorol. and Atmos. Phys., Fuji-Yoshida, Japan, September 5–9, 1994.
- Pyle, J. A., S. Solomon, D. Wuebbles, S. Zvenigorodsky, Ozone depletion and chlorine loading potentials, in *Scientific Assessment of Stratospheric Ozone: 1991*, WMO Rep. 25, chap. 6, World Meteorol. Organ., Geneva, 1992.
- Rinsland, C., D. Johnson, A. Goldman, and J. Levine, Evidence for a decline in the atmospheric accumulation rate of  $\text{CHClF}_2$  (CFC-22), *Nature*, **337**, 535–537, 1989.
- Rinsland, C., A. Goldman, F. Murcray, R. Blatherwick, J. Kusters, D. Murcray, N. Sze, and S. Massie, Long-term trends in the concentrations of  $\text{SF}_6$ ,  $\text{CHClF}_2$ , and  $\text{COF}_2$ , in the lower stratosphere from analysis of high-resolution infrared solar occultation spectra, *J. Geophys. Res.*, **95**, 16,477–16,490, 1990.
- Rodhe, H., and J. Grandell, On the removal time of aerosol particles from the atmosphere by precipitation scavenging, *Tellus*, **24**, 442–454, 1972.
- Rodriguez, J. M., M. K. W. Ko, C. W. Heisey, T. K. Tromp, and N. D. Sze, Modeling dosage projections for trifluoroacetic acid, in *Proceeding of Workshop on Decomposition of TFA in the Environment*, AFEAS, Washington, Feb. 8–9, 1994.
- Saathoff, H., and R. Zellner, LIF detection of  $\text{CF}_3\text{O}$  radical and kinetics of its reactions with  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ , *Chem. Phys. Lett.*, **206**, 349–354, 1993.
- Schwartz, S. E., and J. E. Freiberg, Mass-transport limitations to the rate of reaction of gases in liquid droplets, application to oxidation of  $\text{SO}_2$  in aqueous solutions, *Atmos. Environ.*, **15**, 1129–1144, 1981.
- Scollard, D. J., J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. LeBras, H. MacLeod, and S. Téton, Rate constants for the reactions of hydroxyl radicals and chlorine atoms with halogenated aldehydes, *J. Phys. Chem.*, **97**, 4683–4688, 1993.
- Senum, G. I., Y. N. Lee, and J. S. Gaffney, Ultraviolet absorption spectrum of peroxyacetyl nitrate and peroxypropionyl nitrate, *J. Phys. Chem.*, **88**, 1269–1270, 1984.
- Spivakovsky, C. M., R. Yevich, J. A. Logan, S. C. Wofsy, M. B. McElroy, and M. J. Prather, Tropospheric OH in a three-dimensional chemical tracer model: An assessment based on observations of  $\text{CH}_3\text{CCl}_3$ , *J. Geophys. Res.*, **95**, 18,441–18,471, 1990.
- Talukdar, R. K., A. Mellouki, A. Schmoltner, T. Watson, S. Montzka, and A. R. Ravishankara, Kinetics of the OH reaction with methyl chloroform, *Science*, **257**, 227–230, 1992.
- Tuazon, E. C., and R. Atkinson, Tropospheric degradation products of  $\text{CH}_2\text{FCF}_3$  (HFC-134a), *J. Atmos. Chem.*, **16**, 301–312, 1993.
- Tuazon, E. C., and R. Atkinson, Tropospheric reaction products and mechanisms of the hydrochlorofluorocarbons (HCFCs) 141b, 142b, 225ca, 225cb, *Environ. Sci. Technol.*, **28**, 2306–2313, 1994.
- United Nations Environmental Program (UNEP), *Montreal Protocol on Substances that Deplete the Ozone Layer*, 1994 report of the refrigeration, air conditioning and heat pumps, Tech. Options Comm., Assess., Nairobi, 1995.
- Visscher, P. T., C. W. Culbertson, and R. S. Oremland, Degradation of trifluoroacetate in oxic and anoxic sediments, *Nature*, **369**, 729–731, 1994.
- Wallington, T. J., M. D. Hurley, J. C. Ball, and E. W. Kaiser, Atmospheric chemistry of hydrofluorocarbon 134a: Fate of the alkoxyradical  $\text{CF}_3\text{CFHO}$ , *Environ. Sci. Technol.*, **26**, 1318–1324, 1992.
- Warren, S. G., C. J. Hahn, J. London, R. M. Chervin, and R. Jenne, Global distribution of total cloud cover and cloud type amounts over land, *NCAR Tech. Note TN-273+STR*, Natl. Cent. for Atmos. Res., Boulder, Colo., 1986.
- Wilson, S. R., P. J. Crutzen, G. Schuster, D. W. T. Griffith, and G. Helas, Phosgene measurements in the upper troposphere and lower stratosphere, *Nature*, **334**, 689–691, 1988.
- Wine, P. H., and W. L. Chameides, Possible atmospheric lifetimes and chemical reaction mechanisms for selected HCFC's, HCF's,  $\text{CH}_3\text{CCl}_3$ , and their degradation products against dissolution and/or degradation in seawater and cloudwater, in *Scientific Assessment of Stratospheric Ozone: 1989*, WMO Rep. 20, 273–298, World Meteorol. Organ., Geneva, 1989.
- Zabel, F., *Habilitationsschrift "Thermische Stabilität von Peroxynitrat"*, Bergische Univ., 185 pp., Wuppertal, Germany, 1993.
- Zabel, F., F. Kirchner, and K. H. Becker, Thermal decomposition of  $\text{CF}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ ,  $\text{CClF}_2\text{CH}_2\text{O}_2\text{NO}_2$ ,  $\text{CCl}_2\text{FCH}_2\text{O}_2\text{NO}_2$  and  $\text{CCl}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ , *Int. J. Chem. Kin.*, **26**, 827–845, 1994.
- Zander, R., E. Mahieu, P. Dumoulin, C. P. Rinsland, D. K. Weisenstein, M. K. W. Ko, N. D. Sze, and M. R. Gunson, Secular evolution of the vertical column abundances of  $\text{CHClF}_2$  (HCFC-22) in the earth's atmosphere inferred from ground-based IR solar observations at the Jungfraujoch and at Kitt Peak, and comparison with model calculations, *J. Atmos. Chem.*, **18**, 129–148, 1994.
- Zimmermann, P. H., J. Feichter, H. K. Rath, P. J. Crutzen, and W. Weiss, A global three-dimensional source-receptor model investigation using  $^{85}\text{krypton}$ , *Atmos. Environ.*, **23**, 25–35, 1989.
- P. J. Crutzen, Max Planck Institute for Chemistry, Atmospheric Chemistry Division, P. O. Box 3060 D-55020, Mainz, Germany.  
F. J. Dentener, Department of Air Quality, Biotechnion, Bomenweg 2, P. O. Box 8129, NL 6700 EV Wageningen, Netherlands.  
M. Kanakidou (corresponding author), Centre des Faibles Radioactivités, Laboratoire Mixte CNRS/CEA, Orme des Merisiers, Bât 709/LMCE, CE Saclay, F-91191, Gif-sur-Yvette, Cedex, France.

(Received November 14, 1994; revised June 12, 1995; accepted June 17, 1995.)