JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 105, NO. D5, PAGES 6903–6914, MARCH 16, 2000

Consistent sets of atmospheric lifetimes and radiative forcings on climate for CFC replacements: HCFCs and HFCs

Vaishali Naik, Atul K. Jain, Kenneth O. Patten, and Donald J. Wuebbles
Department of Atmospheric Sciences, University of Illinois at Urbana-Champaign

Abstract. Recognition of deleterious effects of chlorine and bromine on ozone and climate over the last several decades has resulted in international accords to halt the production of chlorine-containing chlorofluorocarbons (CFCs) and bromine-containing halons. It is well recognized, however, that these chemicals have had important uses to society, particularly as refrigerants, as solvents, as plastic blowing agents, as fire retardants and as aerosol propellants. This has led to an extensive search for substitute chemicals with appropriate properties to be used in place of the CFCs and halons. The purpose of this study is to evaluate in a consistent manner the atmospheric lifetime and radiative forcing on climate for a number of replacement compounds. The unique aspect of this study is its attempt to resolve inconsistencies in previous evaluations of atmospheric lifetimes and radiative forcings for these compounds by adopting a uniform approach. Using the latest version of our two-dimensional chemical-radiative-transport model of the global atmosphere, we have determined the atmospheric lifetimes of 28 hydrohalocarbons (HCFCs and HFCs). Through the comparison of the model-calculated lifetimes with lifetimes derived using a simple scaling method, our study adds to earlier findings that consideration of stratospheric losses is important in determining the lifetimes of gases. Discrepancies were found in the reported lifetimes of several replacement compounds reported in the international assessment of stratospheric ozone published by the World Meteorological Organization [*Granier et al.*, 1999] and have been resolved. We have also derived the adjusted and instantaneous radiative forcings for CFC-11 and 20 other halocarbons using our radiative transfer model. The sensitivity of radiative forcings to the vertical distribution of these gases is investigated in this study and is shown to be significant. The difference in the global radiative forcing arising from the assumption of a constant vertical profile for these gases is found to range from 0 to 36%, with higher difference for short-lived gases. Global Warming Potentials (GWPs) for the compounds are determined using the lifetimes and radiative forcings evaluated in this study and are found to differ from values reported by *Granier et al.* [1999] owing to the differences in our calculated radiative forcings and lifetimes.

1. Introduction

Over the last decade, in response to the Montreal Protocol on Substances That Deplete the Ozone Layer, a number of replacement compounds for chlorofluorocarbons (CFCs) and halons have been proposed. Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) often are suitable replacements, and many of these compounds are now in use as replacements in various applications.

Most of the HCFCs and HFCs are short-lived in comparison to CFCs as these gases are destroyed primarily in the troposphere by hydroxyl (OH) radicals. HFCs have the added advantage that they do not affect ozone because they do not contain chlorine or bromine atoms primarily responsible for the catalytic destruction of ozone. However, HCFCs and HFCs are strong absorbers of terrestrial infrared radiation and as a result are greenhouse gases. The absorption of infrared radiation varies linearly with the concentration of these gases. HCFCs and HFCs absorb strongly in the window region (8–12 μm) of the infrared spectrum, where their changing atmospheric concentration can lead to changes in the radiative forcing on climate. The potential contribution of these replacements to the greenhouse effect is generally expressed in terms of radiative forcing per unit concentration change of the molecule in the atmosphere. The radiative forcing is itself determined by the strength and frequencies of infrared (IR) absorption represented by infrared absorption coefficients and the concentration of the gas. One of the primary policymaking approaches being used for evaluating the relative potential greenhouse effect of a gas is quantitatively described by Global Warming Potentials (GWPs) for the particular gas [*Shine et al.*, 1990; *Albritton et al.*, 1995]. In turn, the GWPs are based primarily on the lifetime and concentration of the gas in the atmosphere, and its radiative forcing.

Paper number 1999JD901128.
0148-0227/00/1999JD901128$09.00

Existing evaluations of the atmospheric lifetimes, radiative forcings, and Global Warming Potentials of HCFCs and HFCs come from diverse sources and have been done with a range of different types of modeling and measurement approaches [*Barry et al.*, 1997; *Christidis et al.*, 1997; *Clerbaux et al.*, 1993; *Daniel et al.*, 1995; *Fisher et al.*, 1990; *Freckleton et al.*, 1998;

Table 1. List of Gases Analyzed for Their Lifetimes and Radiative Forcings

Species	Formula	*A* Factor	E_a/R	$k = A \exp(-E_a/R \times 277)$
HCFC-22	$CHClF_2$	1.00E-12[a]	1600	3.10E-15
HCFC-123	CF_3CHCl_2	7.00E-13	900	2.72E-14
HCFC-124	CF_3CHClF	8.00E-13	1350	6.12E-15
HCFC-141b	CH_3CFCl_2	1.70E-12	1700	3.67E-15
HCFC-142b	CH_3CF_2Cl	1.30E-12	1800	1.96E-15
HCFC-225ca	$C_3HF_5Cl_2$	1.00E-12	1100	1.89E-14
HCFC-225cb	$C_3HF_5Cl_2$	5.50E-13	1250	6.03E-15
HFC-23	CHF_3	1.00E-12	2440	1.49E-16
HFC-32	CH_2F_2	1.90E-12	1550	7.06E-15
HFC-43-10mee[b]	$C_5H_2F_{10}$	5.20E-13	1500	2.31E-15
HFC-125	C_2HF_5	5.60E-13	1700	1.21E-15
HFC-134	CF_2HCF_2H	1.60E-12	1680	3.72E-15
HFC-134a	CH_2FCF_3	1.50E-12	1750	2.71E-15
HFC-143	CF_2HCH_2F	4.00E-12	1650	1.04E-14
HFC-143a	CH_3CF_3	1.80E-12	2170	7.13E-16
HFC-152a	CH_3CHF_2	2.40E-12	1260	2.54E-14
HFC-161	CH_3CH_2F	7.00E-12	1100	1.32E-13
HFC-227ea	CF_3CHFCF_3	5.00E-13	1700	1.08E-15
HFC-236fa	$CF_3CH_2CF_3$	1.30E-12	2480	1.68E-16
HFC-236ea[b]	$CF_3CHFCHF_2$	1.10E-12	1590	3.54E-15
HFC-245ca[b]	$CH_2FCF_2CHF_2$	2.40E-12	1660	5.99E-15
HFC-245fa	$CHF_2CH_2CF_3$	6.10E-13	1330	5.01E-15
HFC-245eb[b]	CF_3CHFCH_2F	3.20E-12	1600	9.92E-15
HFC-356mcf[b]	$CF_3CF_2CH_2CH_2F$	1.70E-12	1110	3.09E-14
HFC-356mff[b]	$CF_3CH_2CH_2CF_3$	3.00E-12	1800	4.52E-15
HFC-365mfc	$CF_3CH_2CF_2CH_3$	2.00E-12	1750	3.61E-15
HFC-458mfcf[b]	$C_5H_4F_8$	1.20E-12	1830	1.62E-15
Methyl chloroform[c]	CH_3CCl_3	1.80E-12	1550	6.69E-15

Columns 3 and 4 give the kinetic data for reaction with hydroxyl (OH) radical used in the UIUC 2-D chemical-radiative-transport model for lifetime calculation. The rate constant of reaction with OH at 277 K, which is used to evaluate the lifetimes by *Prather and Spivakovsky* [1990] approach, is given in the last column.

[a] Read 1.00E-12 as 1.00×10^{-12}.

[b] Absorption cross-section data not available for radiative forcing calculations.

[c] Not considered in radiative forcing calculations.

Gierczak et al., 1996; *Good et al*., 1998; *Hansen et al*., 1997; *Imasu et al*., 1995; *Ko et al*., 1999; *Myhre and Stordal*, 1997; *Pappasava et al*., 1997; *Pinnock et al*., 1995]. The international assessments such as those by the Intergovernmental Panel on Climate Change (IPCC) [*Shine et al*., 1990; *Isaksen et al*., 1992; *Albritton et al*., 1995; *Schimel et al*., 1996; hereinafter referred to as IPCC, 1990, 1992, 1995, 1996, respectively] and the World Meteorological Organization (WMO) [*Pyle et al*., 1992; *Ramaswamy et al*., 1992; *Shine et al*., 1995; *Solomon et al*., 1995; hereinafter referred to as WMO, 1992a, b, 1995a, b, respectively] have used diverse results for these quantities. This has posed several problems in analyzing and contrasting the results (WMO, 1995a, b). In particular, direct comparisons of radiative forcing values are difficult when different approaches are used in their evaluation.

There has been no attempt to get a consistent set of analyses of the atmospheric lifetimes, radiative forcings, and Global Warming Potentials of CFC replacements. In addition, several new replacements have been suggested since the last IPCC assessment (IPCC, 1996). Our primary goal in this study is to evaluate the atmospheric lifetimes, radiative forcings, and resultant GWPs of HCFCs and HFCs in a consistent manner. In this study, we use our numerical models of atmospheric chemistry and physics [*Good et al*., 1998; *Patten et al*., 1994; *Rahmes et al*., 1998; *Wuebbles et al*., 1995, 1991, 1997, 2000] to evaluate the atmospheric lifetimes of 28 hydrohalocarbons presented in Table 1. On the basis of these distributions we then use our radiative transfer model [*Briegleb*, 1992a, b] to evaluate the radiative forcings of 20 hydrohalocarbons. We were unable to get measured absorption cross sections of 7 gases out of the 27 replacement compounds studied here, hence the radiative forcing calculation was restricted to 20 replacement compounds and CFC-11. Wherever possible we have used the most recent measurements of absorption cross sections. The model calculations of atmospheric lifetimes and radiative forcings are then used to derive Global Warming Potentials (GWPs) for each of the 20 replacement compounds and CFC-11. The GWPs include the latest approach to treatment of the carbon cycle and radiative forcing for carbon dioxide (CO_2) as used by *Granier et al*. [1999] (hereinafter referred to as WMO (1999a)).

2. Atmospheric Lifetimes

The atmospheric lifetime of a species is defined as the ratio of the total atmospheric burden to the integrated global loss rate. At present, atmospheric lifetimes of hydrohalocarbons are typically derived by two approaches in different assessments and analyses as well as in various literature studies. The primary method involves modeling the chemistry of the species along with relevant physical processes such as transport and radiative transfer in order to determine the distribution of the species. All of the important loss processes (both thermal and photolytic reactions) for each compound are included in the model to represent its global budget and total loss rate. Since tropospheric loss of HCFCs, and HFCs is dominated by reaction with OH radical, it is necessary to represent the OH concentration accurately in determining the atmospheric lifetime for these gases. However, there remain significant uncertainties in the model-calculated OH concentrations. Furthermore, the global distributions of OH cannot readily be measured directly, as OH has small atmospheric concentrations and is highly variable, responding instantly to changes in a variety of parameters including solar flux, temperature, and concentrations of O_3, H_2O, NO_x, CO, and CH_4. Uncertainties in the model-derived OH distribution are tested, at least in an averaged sense, by comparison with the measured amounts of gases removed primarily by tropospheric OH. At present, methyl chloroform is the primary gas used to estimate the globally averaged tropospheric OH. Well-defined losses apart from OH removal, a reasonably long lifetime, and extensive measurements and calibrations make CH_3CCl_3 an ideal reference compound. Various analyses [IPCC, 1995, 1996; *Prinn et al*., 1992, 1995; WMO, 1992a, 1995b] have used measurements of methyl chloroform and its trend over time in combination with evaluations of its emissions to determine an empirically based total atmospheric lifetime for CH_3CCl_3.

The second method for deriving lifetimes involves simple scaling introduced by *Prather and Spivakovsky* [1990] (hereinafter called P-S method). This method assumes that reaction with OH in the troposphere is the only factor contributing to the lifetime of a compound in the troposphere. Reactions with other radicals in the troposphere are ignored. The atmospheric lifetime of a reference compound due to reaction with OH is scaled by the ratio of the rate coefficients for reaction with OH to calculate the tropospheric lifetime. Methyl chloroform is used as a reference gas in this method too.

$$\tau_{OH-trop}(X) = \tau_{OH-trop}(CH_3CCl_3)\,\frac{k_{OH+CH_3CCl_3}(277\text{ K})}{k_{OH+X}(277\text{ K})}. \qquad (1)$$

The P-S method, while reasonably accurate for many replacement compounds, has not been fully evaluated over the wide range of lifetimes now being determined for recently considered replacement compounds (many of which have extremely short atmospheric lifetimes). This approach was developed for long-lived gases and may not be accurate for short-lived (lifetime of about a year) replacement compounds because of large spatial gradients in their atmospheric distributions. Also, this approach is only accurate for determining the total atmospheric lifetime if the lifetime due to stratospheric loss (or lifetime due to other losses) is known, can otherwise be accounted for, or is insignificant compared to tropospheric reaction with OH. In the present study, both of the approaches have been used to derive the lifetimes of replacements, and the results are compared.

Table 2. Historical Changes in the Total Lifetime of Methyl Chloroform and in the Atmospheric Lifetimes Due to Reaction With Tropospheric OH, Loss to the Oceans, and Loss in the Stratosphere

Reference	τ_{OH}	τ_{Ocean}	$\tau_{Stratosphere}$	τ_{Total}
WMO (1995b) and IPCC (1995)	6.6 [±25%]	85 [>50]	45 [40–50]	5.4 ± 0.6
Prinn et al. [1995]	···	···	···	4.8 ± 0.3
IPCC (1996)	5.9 ± 0.7	85	45	4.9 ± 0.4
Wuebbles et al. [2000]	5.7 ± 0.3[a]	85	45	4.8 ± 0.3

Units are in years.

[a] Derived from total lifetime of *Prinn et al*. [1995] by taking into account the oceanic and stratospheric lifetimes used by WMO (1995b) and IPCC (1995).

Since both of the methods rely heavily on the tropospheric lifetime of CH_3CCl_3, it is important to discuss the changes in understanding of the estimated lifetime of CH_3CCl_3 over the past decade. For the 1994 international ozone assessment (WMO, 1995b) the lifetime of methyl chloroform due to reaction with OH was taken to be 6.6 years, with an uncertainty of ±25%. This value was also used in the 1994 IPCC assessment on the radiative forcing of climate change (IPCC, 1995). This lifetime was derived based on a total lifetime of 5.4 years, taken as average of the two major measurement networks, Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment (ALE/GAGE) [*Prinn et al*., 1995] and National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA CMDL) [*Bloomfield et al*., 1994], respectively, with the primary difference in the derivation for these two networks coming from differences in their absolute calibration for the concentration of CH_3CCl_3. From this total lifetime together with an evaluated loss lifetime of CH_3CCl_3 due to the oceans of 85 years [*Butler et al*., 1991] and a model-estimated lifetime due to stratospheric loss processes (τ_{strat}) of 45 years (WMO, 1995b), a tropospheric lifetime (τ_{OH}) of 6.6 years can be inferred using

$$\frac{1}{\tau_{OH}} = \frac{1}{\tau_{total}} - \frac{1}{\tau_{ocean}} - \frac{1}{\tau_{strat}}. \qquad (2)$$

Later studies [IPCC, 1996; *Prinn et al*., 1995] have derived even shorter lifetimes for CH_3CCl_3 due to reaction with OH. Table 2 describes the changes in lifetime of CH_3CCl_3 from recent studies. The 1995 assessment of climate change by the IPCC (IPCC, 1996) assumed a total lifetime for CH_3CCl_3 of 4.9 ± 0.4 years. This total lifetime was based on the earlier NOAA/CMDL evaluation [*Bloomfield et al*., 1994] along with a new absolute calibration of the ALE/GAGE network by *Prinn et al*. [1995]. This resulted in an evaluated lifetime for tropospheric OH loss of 5.9 years when combined with the same lifetimes due to ocean and stratospheric losses as used by WMO (1995b) and IPCC (1996). However, analysis by *Prinn et al*. [1995] suggests that the absolute calibration should not be an issue in deriving the tropospheric lifetime.

Prinn et al. [1995] examined a number of different approaches to determine the tropospheric lifetime (due to tropospheric loss only, i.e., not considering the total atmospheric burden) of CH_3CCl_3 from the analysis of the ALE/GAGE data. Their best estimate of this lifetime, 4.6 ± 0.3 years, is much smaller than the earlier evaluations. Part of this is due to the revision of their absolute calibration of the measured CH_3CCl_3, but as discussed below, the value of 4.6 years can be justified without the change in calibration. By accounting for the ocean sink of CH_3CCl_3 at a lifetime of 85 years, Prinn et al. determine the CH_3CCl_3 lifetime due to reaction with tropospheric OH (again due to tropospheric losses only) to be 4.9 ± 0.3 years, as shown in Table 2. Prinn et al. then derive the “total atmospheric lifetime” to be 4.8 ± 0.3 years. This is evaluated by accounting for oceanic loss and stratospheric loss, which is dominated by photolysis. If the oceanic lifetime of 85 years [*Butler et al*., 1991] and the stratospheric lifetime of 45 years (WMO, 1995b) is subtracted from the total lifetime of 4.8 years, then the lifetime of CH_3CCl_3 due to reaction with tropospheric OH is 5.7 years. Prinn et al. contend that their trend-based lifetime of 4.6 years (accounting for the magnitude and phase lag in the observed trend in emissions) should be independent of absolute calibration errors. As discussed by *Wuebbles et al*. [2000], this would imply that the WMO approach of averaging the total lifetime from ALE/GAGE and NOAA CMDL analyses in order to account for calibration differences is not the best approach. This would also imply the current best value for the CH_3CCl_3 lifetime due to reaction with tropospheric OH is 5.7 years. We have used this as the best estimate of CH_3CCl_3 partial lifetime due to reaction with tropospheric OH to scale the lifetimes due to reaction with tropospheric OH of replacement compounds. *Kurylo et al*. [1999] (hereinafter referred to as WMO (1999b)) also chose to use this, based on *Wuebbles et al*. [2000].

There still remain uncertainties about scaling the partial lifetimes of short-lived compounds that react rapidly with OH, as they are not well mixed in the atmosphere. Such short-lived compounds are unlikely to have significant effects on climate, but for those containing chlorine and bromine, effects on ozone may be important, and their loss processes must be carefully considered.

2.1. Two-Dimensional Chemical-Radiative-Transport Model Description and Application

The University of Illinois at Urbana-Champaign (UIUC) two-dimensional chemical-radiative-transport model used for this study is a coupled numerical model that includes explicit description of both atmospheric dynamical processes and atmospheric chemistry [*Patten et al*., 1994; *Rahmes et al*., 1998; *Wuebbles et al*., 1995, 1991, 1997, 2000]. This model has been used extensively in the past international ozone assessments to determine the lifetimes of CFCs and other halocarbons and their effects on ozone (WMO, 1992a, 1995). The model attempts to represent the tropospheric and stratospheric processes appropriate to evaluating the distribution of gases important to the global-scale atmosphere. The current version of the zonally averaged model determines the atmospheric distributions of 66 chemically active atmospheric trace constituents. The model's grid is 5° in latitude from pole to pole and about 1.5 km in log pressure altitude from the surface to 84 km. The model incorporates the important species and relevant chemistry to evaluate the spatially and temporally varying concentrations in the distributions of the O_x, HO_x, NO_y, Cl_y, Br_y, and CH_xO_y constituents affecting the global atmosphere. Transport of species in the model is self-consistently calculated using the predicted model ozone and seasonally varying climatological temperatures. Effects of heterogeneous chemistry on sulfate aerosols and polar stratospheric clouds are included in the model.

Fifty-two thermal reactions and seven photolytic reactions were added to the chemical mechanism that includes reactions of HCFCs and HFCs with OH, $O^1(D)$, and Cl in the atmosphere. Kinetic data for reaction of these gases with OH are shown in Table 1. Most thermal reaction rates are taken from the NASA panel recommendations provided by *DeMore et al*. [1997], with updates made as newer data are available. Absorption cross-section information for HCFCs has been assembled primarily following the recommendations of *DeMore et al*. [1997]. A background surface mixing ratio of 5 parts per trillion (ppt, 10^{-12} mol mol^{-1}) was assumed for the replacement compounds in the atmospheric lifetime derivations. The surface concentrations for CFC-11 and HCFC-22 are assigned to be 270.1 and 105.8 ppt, respectively. The model was run to a steady state concentration, and the total atmospheric lifetime in years of each compound was determined. This was done by taking the ratio of globally and annually averaged concentration of the species and the total loss rate in the atmosphere. Tropospheric and stratospheric lifetimes were determined by replacing the total loss rate with tropospheric and stratospheric loss rates, respectively. The total atmospheric lifetime can be represented as

$$\tau_{\text{total}} = \left(\frac{1}{\tau_{\text{trop}}} + \frac{1}{\tau_{\text{strat}}} \right)^{-1}. \tag{3}$$

2.2. Model-Derived Atmospheric Lifetimes for CFC-Replacement Compounds

Atmospheric lifetimes of CFC-replacement compounds were derived using both the model described above and the P-S approach. Table 3 gives the lifetimes derived using the model and the P-S approach for each gas. The parameter $\tau_{\text{OH,trop}}$ is the lifetime due to reaction with OH in the troposphere, $\tau_{\text{trop,scaled}}$ is the tropospheric lifetime (due to reaction with all radicals including OH) scaled with respect to the lifetime of methyl chloroform (5.7 years), τ_{strat} is the stratospheric lifetime, and τ_{total} is the total lifetime obtained by using (3). The total atmospheric lifetime of CH_3CCl_3 includes our model-derived stratospheric lifetime of 42.9 years and 85 years due to ocean loss taken from *Butler et al*. [1991]. The total model-derived lifetime of 4.74 for CH_3CCl_3 is slightly less than the value of 4.8 years [*Prinn et al*., 1995] as our model-derived stratospheric lifetime of 43 years is about 4% lower than that derived by *Ko et al*. [1994] (45 years). As described in the previous section, model-derived tropospheric lifetimes are scaled to account for the concentration of OH as our model overestimates the concentration of OH, thereby underestimating the lifetime due to reaction with OH. Stratospheric lifetimes are higher as most of the hydrohalocarbons considered here have very small sink in the stratosphere. This can be seen in Figure 1, which shows the model-derived vertical distributions of mixing ratios of gases considered in this study. It can be seen from the figure that gases which have longer stratospheric lifetimes have higher mixing ratios in the stratosphere irrespective of the total atmospheric lifetime; for example, HCFC-124 (τ_{strat} = 111 years) has higher mixing ratio in the stratosphere than HCFC-141b (τ_{strat} = 65 years) although the total atmospheric lifetime of HCFC-141b (9.06 years) is higher than that of HCFC-124 (6.23 years).

The percent difference between the model-derived tropospheric lifetimes and those calculated using P-S approach is presented in the last column of Table 3. As is evident from the table, the P-S method is good to within about 6–7% for tropospheric lifetimes for many HCFCs and HFCs. However, HFC-161 is an exception. The model-derived lifetime for this gas is about 11% lower than that calculated using P-S method. HFC-161 is a short-lived gas with an atmospheric lifetime of 95 days. As stated previously, P-S method may be inaccurate for short-lived species as they may not be well-mixed in the atmosphere. There are also questions about the validity of the two-dimensional model for such short-lived gases. Owing to their transient existence in the atmosphere, the lifetimes and distributions of short-lived species are likely to depend upon the location and time of emission.

For most gases examined, consideration of the stratospheric losses is important. This implies that simpler approaches to estimating atmospheric lifetimes based on tropospheric OH

Table 3. Atmospheric Lifetimes of CFC-Replacement Compounds Calculated Using the 2-D Chemical-Radiative-Transport Model and the *Prather and Spivakovsky* [1990] (P-S) Approach

Species	Model-Calculated Lifetimes					
	$\tau_{OH,trop}$	$\tau_{trop,scaled}$	τ_{strat}	τ_{total}	$\tau_{trop,P\text{-}S}$	$(\tau_{trop,P\text{-}S} - \tau_{trop,scaled})$, %
HCFC-22	9.11	13.1	186.0	12.2	12.3	−6.1
HCFC-123	0.99	1.42	35.6	1.36	1.40	−1.4
HCFC-124	4.61	6.60	111.0	6.23	6.20	−6.1
HCFC-141b	7.36	10.5	64.9	9.06	10.4	−1.0
HCFC-142b	14.2	20.3	160.0	18.0	19.5	−4.0
HCFC-225ca	1.44	2.06	43.7	1.97	2.02	−2.0
HCFC-225cb	4.67	6.69	101.0	6.28	6.32	−5.5
HFC-23	181.8	260.3	2347.0	234.3	255.0	−2.0
HFC-32	3.93	5.61	89.0	5.28	5.40	−3.7
HFC43-10-mee	12.2	17.5	157.0	15.7	16.5	−5.7
HFC-125	23.3	33.4	246.0	29.4	31.5	−5.7
HFC-134	7.59	10.9	216.0	10.4	10.3	−5.5
HFC-134a	10.4	14.9	232.0	14.0	14.1	−5.4
HFC-143	2.68	3.84	103.0	3.70	3.68	−4.2
HFC-143a	38.5	55.1	327.0	47.2	53.5	−3.0
HFC-152a	1.07	1.53	45.4	1.48	1.50	−2.0
HFC-161	0.19	0.26	15.1	0.26	0.29	11.5
HFC-227ea	26.4	37.8	633.0	35.7	35.3	−6.6
HFC-236fa	161.1	231.0	5676.0	222.0	226.6	−2.0
HFC-236ea	8.01	11.5	215.0	10.9	10.8	−6.1
HFC-245ca	4.68	6.71	151.0	6.42	6.36	−5.2
HFC-245fa	5.67	8.12	143	7.69	7.60	−6.4
HFC-245eb	2.81	4.02	105.0	3.87	3.84	−4.5
HFC-356mcf	0.88	1.26	41.0	1.22	1.23	−2.4
HFC-356mff	6.19	8.88	200.0	8.50	8.43	−5.1
HFC-365mfc	7.80	11.2	231.0	10.7	10.6	−5.4
HFC-458mfcf	17.4	25.0	471.0	23.7	23.5	−6.0
CH_3CCl_3	3.98	5.68	43.0	5.02 4.74[a]	5.70	0.4

Lifetimes are reported in years. The parameter $\tau_{OH,trop}$ is the model-derived lifetime due to reaction with tropospheric OH, $\tau_{trop,scaled}$ is the total lifetime due to tropospheric losses scaled with respect to methyl chloroform lifetime of 5.7 years, τ_{strat} is lifetime due to stratospheric losses, τ_{total} is the total atmospheric lifetime, and $\tau_{trop,P\text{-}S}$ is the lifetime derived by P-S approach. Percent difference between $\tau_{trop,P\text{-}S}$ and $\tau_{trop,scaled}$ is provided in the last column.

[a] Includes ocean sink of 85 years.

loss only are likely to have some degree of error depending on the relative loss rate in the stratosphere. Generally, loss in the stratosphere is an important contribution to the total lifetime. The model-derived lifetimes should generally be more realistic as they take into account the vertical distribution and loss rates of the gases. However, uncertainties in our model-derived lifetimes for replacement compounds arise from the uncertainties in the measured rate constants for various reactions considered.

Table 4 shows the comparison of our model-derived atmospheric lifetimes with those presented in the most recent ozone assessment (WMO, 1999a). We have also provided the published lifetimes from other literature sources for gases whose lifetimes were not given in this assessment. Lifetimes given by WMO (1999a) come from a variety of sources. Lifetimes for most gases are taken from IPCC (1996) and do not account for the slight revision in methyl chloroform lifetimes as discussed earlier. Lifetimes for HCFC-22, HCFC-141b, HCFC-142b, HFC-23, and HFC-134a have been updated from their IPCC (1996) values by WMO (1999b). The lifetimes for these gases have been evaluated using (3) in which τ_{trop} is calculated using the P-S method (methyl chloroform lifetime is 5.7 years), and τ_{strat} is calculated using the Atmospheric and Environmental Research Inc. (AER) two-dimensional (2-D) model [*Prather and Remsberg*, 1993]. Our model-calculated stratospheric lifetimes for these gases appear to be significantly lower than those calculated using the AER model and are balanced by higher model-derived tropospheric lifetimes resulting in smaller difference in our model-calculated total atmospheric lifetimes and those presented by WMO (1999a, b) for these gases.

Atmospheric lifetimes of HFC-143a and HFC-236fa have been evaluated using the P-S approach by WMO (1999a). Our model-calculated lifetime for HFC-143a is appreciably lower than the WMO (1999a) reported value, with the difference resulting from the slow, but not trivial loss in the stratosphere (see Table 3). The contribution of stratospheric lifetime to the total lifetime of HFC-236fa is not significant, as it is considerably long-lived in the stratosphere; hence the difference in our model-calculated lifetime and that reported by WMO (1999a) is not significant. Atmospheric lifetime for HFC-236ea reported by WMO (1999a) has been taken from *Gierczak et al.* [1996]. *Gierczak et al.* [1996] used the rate constant for OH + HFC-236fa recommended by *DeMore et al.* [1994] while we used a revised rate constant [*DeMore et al.*, 1997] which is lower than the previously reported value. Hence the difference in our calculated lifetime and that reported WMO (1999a) is significant.

Atmospheric lifetimes for HFC-161 and HFC-365mfc reported by WMO (1999a) have been taken from *Christidis et al.* [1997] and *Barry et al.* [1997], respectively. Both studies have

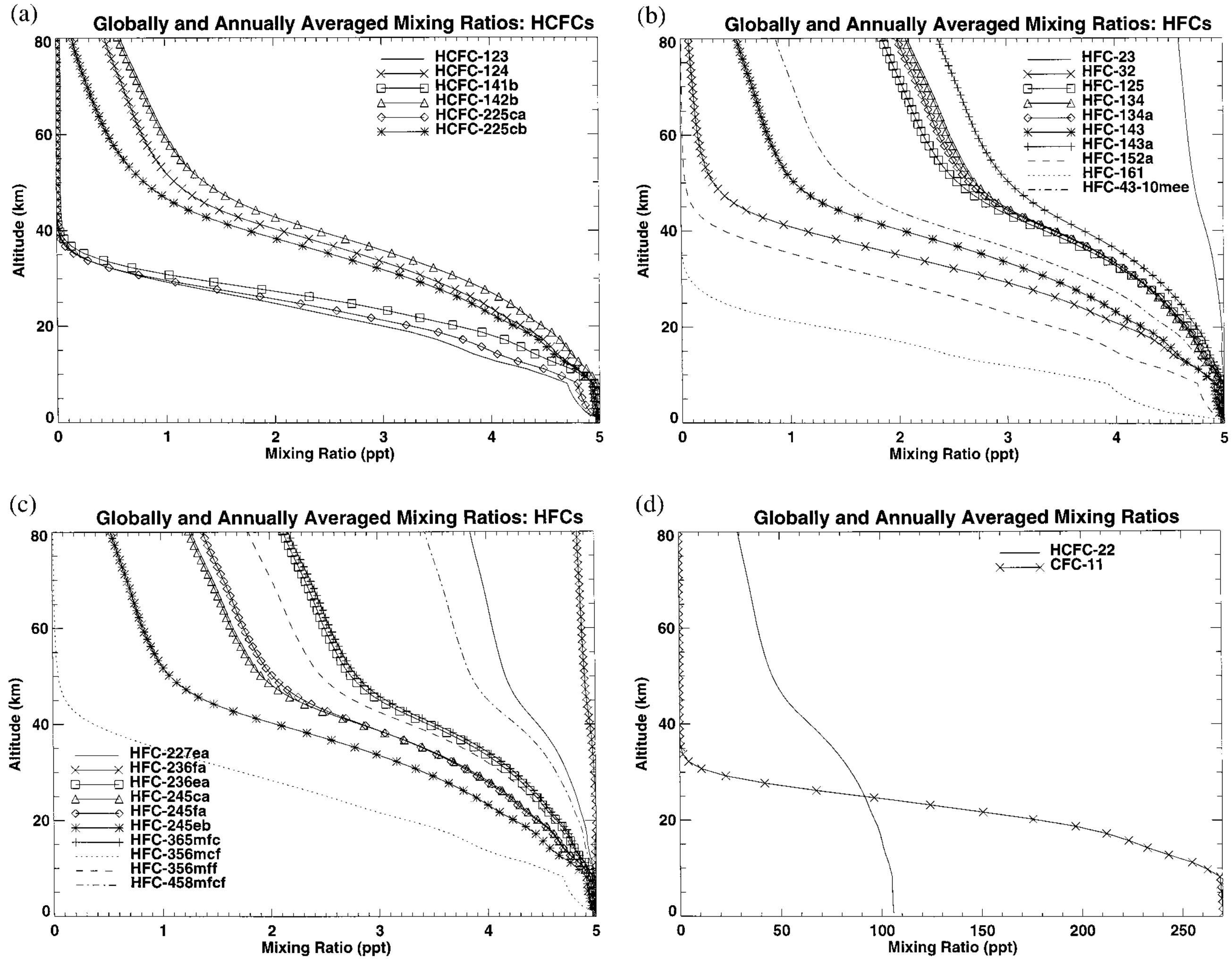

Figure 1. Globally and annually averaged mixing ratios for CFC-11, HCFCs, and HFCs derived from UIUC 2-D chemical-radiative-transport model. The CFC-11 and HCFC-22 mixing ratios are calculated for the fixed surface mixing ratios of 270 and 106 ppt, respectively. The HCFC and HFC mixing ratios are calculated for the fixed surface mixing ratio of 5 ppt.

not taken into account the revised methyl chloroform lifetime of 5.7 years, hence our model-derived lifetimes differ slightly from the WMO (1999a) values. Atmospheric lifetime for HFC-245fa has been evaluated by *Ko et al.* [1999]. Our model-calculated lifetime for the gas is in good agreement with their calculation. For the remaining gases, WMO (1999a) adopted IPCC (1996) values. These lifetimes do not take into account the revised methyl chloroform lifetime. Although not very significant, there is a slight difference in our model-calculated lifetimes and those reported by IPCC (1996).

A revision in atmospheric lifetimes for replacement compounds will also result in the modification of their Ozone Depletion Potentials (ODPs), specifically for HCFCs. The concept of ODPs [*Wuebbles*, 1981, 1983; WMO, 1995] provides a relative cumulative measure of the expected effects on ozone of the emission of a gas relative to CFC-11. These are calculated by a number of methods described by WMO (1995). Recently, *Madronich et al.* [1999] updated the ODPs for a number of HCFCs from their WMO (1995) values, in order to reflect the revision in the lifetimes these gases. Following a similar argument, ODPs for HCFCs need to be scaled with respect to the lifetimes derived in our study. ODPs for HFCs is close to zero. As is seen from Table 4, our model-derived lifetimes of HCFCs do not differ significantly from those of WMO (1999a), therefore the ODPs will not differ considerably from the values reported by *Madronich et al.* [1999].

3. Radiative Forcing

The definition of radiative forcing adopted by IPCC (1990) was based on earlier work by *Hansen et al.* [1981] and *Ramanathan et al.* [1985]. It is defined as the change in forcing at the tropopause after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with the surface and tropospheric temperature and atmospheric moisture fields held fixed at their surface values. It is generally expressed in terms of the change in radiative forcing (W m^{-2} ppb^{-1}) when the surface mixing ratio of the gas is 1 part per billion (ppb, 10^{-9} mol mol^{-1}). If no change in stratospheric temperature is accounted for, the greenhouse gas radiative forcing is referred to as instantaneous radiative forcing.

A variety of different radiative transfer models are available to compute the radiative forcing, ranging from wide band model to line-by-line models. Many details of the radiation schemes such as the treatment of clouds, tropopause height, vertical profiles and regional and seasonal distribution of gases, spectral overlap of gases, spectroscopic data, treatment of water vapor infrared continuum, and inclusion of stratospheric adjustment affect the radiative forcing calculation and are not dealt with in the same way by all schemes. In the work of IPCC (1996) the radiative forcing of a number of halocarbons was based on unpublished material for which details were not available. These were based on calculations from a wide variety of models that lacked consistency in terms of the parameters mentioned above. The radiative forcing values were reported relative to the absolute radiative forcing due to CFC-11, in order to achieve some uniformity. Since then, several studies [*Barry et al.*, 1997; *Christidis et al.*, 1997; *Freckleton et al.*, 1998; *Gierczak et al.*, 1996; *Good et al.*, 1998; *Imasu et al.*, 1995; *Myhre and Stordal*, 1997; *Pinnock et al.*, 1995] have been conducted to evaluate the radiative forcings of various hydrohalocarbons, several of which were not studied previously. However, different modeling techniques and parameters have been adopted for these studies, hence there is a lack of uniformity. The radiative forcings from these studies have been included by WMO (1999a) in an effort to update previous assessments. In order to avoid confusion resulting from updated CFC-11 forcing, absolute radiative forcings are reported by WMO (1999a). For the purpose of consistency, the literature values for some gases are scaled on the basis of whether clouds are included, whether stratospheric adjustment is performed, what atmosphere is used, and what vertical profile for the gas is assumed. As stated by WMO (1999a), these scalings may only be regarded as approximate and are not always possible. Hence radiative forcings reported by WMO (1999a) still lack uniformity.

The absolute radiative forcing for a gas depends on a number of quantities of which the vertical distribution of gases of interest is of particular relevance in this study. Various studies have emphasized the need to use a realistic vertical profile to calculate the radiative forcing. For example, *Pinnock et al.* [1995] and *Christidis et al.* [1997] examined the effects of changes in the vertical distribution on radiative forcing for a number of hydrohalocarbons. However, neither considered a realistic distribution of the gases studied. *Pinnock et al.* [1995] compared the radiative forcing when the hydrohalocarbons are inserted with constant mixing ratios in both the troposphere and stratosphere with the radiative forcing when the gases are inserted into the troposphere only. *Christidis et al.* [1997] evaluated the effect of changes in vertical profile by keeping the tropospheric concentration equal to 0.1 ppb and decreasing the stratospheric concentration to 0.01 ppb. Both of the studies concluded a reduction in the radiative forcing by 10–15% when the stratospheric concentrations were decreased. *Freckleton et al.* [1998] investigated the impact of vertical inhomogeneity in the distributions of HCFCs and HFCs by considering five species with lifetimes ranging from 2 to 26 years. They found that the error in the global mean forcing from assuming the gas to be well-mixed ranged from 5% (for gases with lifetimes greater than 15 years) to 30% (for gases with a 2-year lifetime).

Table 4. Model-Derived Lifetimes Compared With Lifetimes Reported by WMO (1999a)

Species	$\tau_{\text{total (WMO '99)}}$	$\tau_{\text{total (this study)}}$	($\tau_{\text{total (this study)}} - \tau_{\text{total (WMO '99)}}$), %
HCFC-22	11.8	12.2	3.31
HCFC-123	1.40	1.36	−2.86
HCFC-124	6.10	6.23	2.13
HCFC-141b	9.20	9.06	−1.41
HCFC-142b	18.5	18.0	−2.49
HCFC-225ca	2.10	1.97	−6.19
HCFC-225cb	6.20	6.28	1.29
HFC-23	243	234.3	−3.58
HFC-32	5.60	5.28	−5.71
HFC-43-10mee	17.1	15.7	−8.01
HFC-125	32.6	29.4	−9.88
HFC-134	10.6	10.4	−2.26
HFC-134a	13.6	14.0	2.87
HFC-143	3.80	3.70	−2.63
HFC-143a	53.5	47.2	−11.8
HFC-152a	1.50	1.48	−1.33
HFC-161	0.25	0.26	−4.00
HFC-227ea	36.5	35.7	−2.27
HFC-236fa	226	222.0	−1.80
HFC-236ea	8.10	10.9	35.00
HFC-245ca	6.60	6.42	−2.73
HFC-245fa	7.60[a]	7.69	−1.18
HFC-245eb	3.90[b]	3.87	−0.77
HFC-356mcf	1.20[b]	1.22	1.67
HFC-356mff	8.50[b]	8.50	0.00
HFC-365mfc	10.2	10.7	4.51
HFC-458mfcf	23.0[b]	23.7	3.00
CH_3CCl_3	4.80	4.74	−1.25

[a] *Ko et al.* [1999].

[b] *Nelson et al.* [1995].

Sensitivity studies are performed in this study to examine the effects of change in the global distribution of HCFCs and HFCs on their derived radiative forcings. We have tried to consider all of the replacement compounds in a consistent manner and perform radiative forcing calculations for each of these gases. We have evaluated the radiative forcings for all the compounds using one model. Cloudy-sky adjusted forcings are evaluated since these are regarded as most appropriate [see, e.g., IPCC, 1995; *Hansen et al.*, 1997]. We have also evaluated cloudy-sky instantaneous radiative forcings in order to provide direct comparisons with other studies.

3.1. Infrared Absorption Cross-Section Data

The infrared absorption cross sections for most replacement compounds analyzed for their radiative properties in this study were provided by M. Hurley. Details of the experimental setup used for measuring these absorption spectra are given by *Pinnock et al.* [1995] and *Christidis et al.* [1997], and comparisons have been made therein with other published works [e.g., *Capellani and Restelli*, 1992; *Clerbaux et al.*, 1993; *Fisher et al.*, 1990; *Li and Varanasi*, 1994]. Uncertainties in their measurements arose from the following: sample concentration (±2%), path length (±1.5%), spectrum noise ($\pm 10^{-20}$ cm^2 molecule^{-1} in each 0.5 cm^{-1} band), residual baseline offset after subtraction of the background (±0.5%), and spectrometer accuracy (±1%). From the individual uncertainties the total (random) uncertainties in the integrated cross sections were estimated to be about ±4%. This estimate was comparable to the uncertainties in the measurements of *Clerbaux et al.* [1993]. *Christidis et al.* [1997] compared CFC-11 absorption spectra (referred to as the Ford spectra), used for this study, with the spectra measured by *Li and Varanasi* [1994] and *Fisher et al.* [1990] (referred to as the Magid spectra). They found that the strength of the Ford spectra is 7% lower than the Li and Varanasi spectra and 4% lower than the Magid spectra. There was no significant difference in the radiative forcing due to CFC-11 using the Ford spectra and the Magid and the Li and Varanasi spectra. *Christidis et al*. [1997] analyzed the sensitivity of radiative forcing to the dependence of the spectra on temperature and pressure and concluded that the spectral dependence on pressure and temperature contributes to an uncertainty of less than 1% in the estimated forcing.

The absorption cross sections for HFC-245fa were provided by H. Magid (personal communication, 1997). Details of the experimental setup used to measure these spectra are given by *Ko et al*. [1999]. The spectra were measured at a spectral resolution of 0.5 cm^{-1}. The absorption cross sections for HFC-365mfc were provided by C. Clerbaux, based on *Barry et al*. [1997]. The spectra were measured at 287 ± 0.5 K and 0.03 cm^{-1} spectral resolution. The total uncertainty associated with the integrated cross sections was estimated to be lower than 4%. It was obtained by adding the uncertainties due to the following sources of error: pressure and temperature measurements, purity determination, path length, and standard deviation in the least squares fit.

No other measurements of the absorption cross sections for HFC-245fa and HFC-365mfc appear to be available in the literature. A single source of data was used for all of the other compounds to remove errors arising from the variety of instruments used and method of measurements. These data have been used in calculations of radiative forcing conducted by other groups [*Pinnock et al*., 1995; *Christidis et al*., 1997; *Freckleton et al*., 1998]. The use of a common source of data also allows us to directly compare our results with these published works.

3.2. Radiative Transfer Model Description and Application

Absolute radiative forcings due to HCFCs and HFCs were calculated using our column radiative transfer model. This model uses the National Center for Atmospheric Research (NCAR) Community Climate Model version 2 (CCM2) shortwave radiation code and longwave band model [*Briegleb*, 1992a, b]. It accounts for the radiative effects of H_2O, CO_2, O_3, along with the effects of other gases (CH_4, N_2O, CFCs, HCFCs, HFCs) and aerosols. This model has been used in studies of the effects of trace gases and aerosols, tropospheric and stratospheric simulations, as well as in studies comparing simulated longwave radiances in restricted bands (such as the 10 μm water vapor window) with observations [*Briegleb*, 1992a, b; *Kiehl and Briegleb*, 1993]. The changes in the total radiative flux caused by increase in trace gases predicted by the model agree well with detailed line-by-line calculations. This model was also used to estimate the radiative forcings of some fluoroethers [*Good et al*., 1998]. Our version of this radiative transfer model has been modified to better account for radiative convective processes.

The model is further modified in this study to include stratospheric adjustment. Both instantaneous and adjusted radiative forcing calculations were performed. Stratospheric adjustment is executed using an iterative method that involves adjusting the stratospheric temperature until the infrared cooling rate is equal to the solar heating rate. This restores radiative balance in the stratosphere, which was perturbed by the addition of a halocarbon. In most cases, allowing the stratosphere to reestablish a radiative equilibrium after inserting a small amount of halocarbon in the atmosphere results in an increase in the radiative forcing. The longwave radiation scheme used in this model is based on the Malkmus random band model of *Briegleb* [1992b]. The original model is a wide band model that calculates absorptivities and emissivities in the 0–3000 cm^{-1} range with spectral width of 100 cm^{-1}. The spectral width is modified to 10 cm^{-1} to compute narrow band absorptivities and emissivities in the wavelength range 400–2000 cm^{-1} since absorption bands for halocarbons below 400 cm^{-1} and above 2000 cm^{-1} have a negligible effect on the radiative forcing. Transmittance for each halocarbon in the 100 cm^{-1} band is evaluated as an average of transmittance evaluated in the 10 cm^{-1} band. This transmittance is then used to evaluate the absorptivities and emissivities. The absorption spectra are averaged into 160 by 10 cm^{-1} bands used in the model. This version of the model has three layers of clouds and no aerosols. Cloud cover and properties have been taken from *Christidis et al*. [1997]. A global and annual mean atmosphere (GAM) is used for radiative forcing calculations, which has also been taken from the same source. This atmosphere contains vertical profiles of pressure, temperature, H_2O, and O_3 at 16 levels. CO_2, CH_4, and N_2O mixing ratios are assumed to be constant throughout the atmosphere and equal to 364, 1.75, and 0.28 ppmv, respectively. The spectroscopic data for the five gases, H_2O, O_3, CO_2, CH_4, and N_2O are from the HITRAN-86 database [*Rothman et al*., 1987]. As discussed by *Freckleton et al*. [1998], specification of tropopause height is crucial to the determination of radiative forcing. They showed that the choice of tropopause definition (i.e., lapse rate criteria, temperature minimum, top of convective level) could influence radiative forcing results by up to 9%. For the calculation presented here, we defined the tropopause height according to location of a minimum in GAM temperature profile.

In order to study the sensitivity of radiative forcing to the change in greenhouse gas concentration, two cases are considered: (1) constant change in vertical mixing ratio from 0 to 1 ppb throughout the atmosphere, and (2) change in vertical mixing ratio from 0 to a globally and annually averaged 2-D model-estimated vertical distribution (Figure 1). Many past studies have assumed constant vertical mixing ratios for radiative forcing calculations; hence we use this to compare our radiative forcing values with previously reported values. Adjusted and instantaneous cloudy-sky radiative forcings for the species are calculated with respect to the surface concentration. Generally, radiative forcings are expressed in W m^{-2} ppb^{-1}; hence our results are rescaled to reflect the impact of a 1 ppb change in mixing ratio.

3.3. Model-Derived Radiative Forcings for CFC-Replacement Compounds

Absolute adjusted and instantaneous radiative forcings for CFC-11 and 20 other hydrohalocarbons are presented in Table 5. Absolute instantaneous and adjusted forcings for the two cases described in section 3.2 are given in the table. A few important observations can be made from the table. As expected, stratospheric adjustment results in an increase in the radiative forcing by a few percent (1–6%) for all hydrohalocarbons, except for HFC-161. Absorption by a halocarbon (in the window region of the infrared spectrum) in the stratosphere increases the heating rate of the stratosphere resulting in warming if the temperature is allowed to adjust, while absorption in the troposphere decreases the heating rate of the stratosphere resulting in cooling when the temperature is allowed to adjust. For most halocarbons the net effect is warming in the stratosphere resulting in an increase in the adjusted radiative forcing. For HFC-161 there is no difference in the

Table 5. Absolute Instantaneous and Adjusted Radiative Forcings for CFC-11 and Replacement Compounds

	Instantaneous		Adjusted				
Species	Constant Profile	Model-Derived Profile	Constant Profile	Model-Derived Profile	Difference, %	WMO (1999)	(WMO (1999) − Adjusted for Model-Derived Profile), %
CFC-11	0.261	0.237	0.271	0.242	−11	0.25	−3
HCFC-22	0.194	0.189	0.202	0.196	−3	0.22	−11
HCFC-123	0.192	0.164	0.201	0.168	−16	0.20	−16
HCFC-124	0.202	0.192	0.211	0.199	−6	0.22	−10
HCFC-141b	0.127	0.116	0.131	0.118	−10	0.14	−16
HCFC-142b	0.174	0.169	0.183	0.176	−4	0.20	−12
HCFC-225ca	0.234	0.204	0.244	0.208	−15	0.27	−23
HCFC-225cb	0.266	0.251	0.276	0.259	−6	0.32	−19
HFC-23	0.260	0.259	0.271	0.271	0	0.20	−36
HFC-32	0.148	0.140	0.152	0.141	−7	0.13	9
HFC-125	0.223	0.218	0.234	0.229	−2	0.23	−0.6
HFC-134	0.179	0.175	0.186	0.181	−3	0.18	0.1
HFC-134a	0.218	0.213	0.228	0.222	−3	0.19	17
HFC-143	0.116	0.110	0.119	0.112	−6	0.13	−14
HFC-143a	0.136	0.134	0.143	0.141	−1	0.16	−12
HFC-152a	0.120	0.106	0.126	0.109	−13	0.13	−16
HFC-161	0.037	0.024	0.037	0.024	−36	0.03	−22
HFC-227ea	0.275	0.273	0.291	0.288	−0.8	0.30	−4
HFC-236fa	0.221	0.221	0.233	0.233	0.0	0.28	−17
HFC-245fa	0.281	0.270	0.291	0.279	−4	. . .	
HFC-365mfc	0.207	0.202	0.219	0.212	−3	0.21	1

The forcing is calculated due to change in the mixing ratio from 0 to 1 ppb and 0 to a model-estimated vertical distribution. Forcings are expressed in units of W m^{-2} ppb^{-1}. The percent difference in adjusted radiative forcing when the change in mixing ratio from 0 to model-estimated profile is considered relative to the change in mixing ratio from 0 to 1 ppbv is shown in the table. The percent difference between WMO (1999a) reported radiative forcing and the adjusted forcing for change in vertical profile from 0 to a model-estimated vertical distribution is shown in the last column.

adjusted and instantaneous forcings. This is attributed to two strong absorption bands of HFC-161, one of which overlaps with a strong O_3 band, and the other lies in the region where increase in stratospheric opacity results in cooling [*Christidis et al.*, 1997] which cancels the warming effect.

For both the adjusted and instantaneous cases the forcing decreases when a decreasing vertical profile is used. The difference in adjusted radiative forcing when a change in vertical mixing ratio from 0 to model-estimated profile is considered relative to the change in mixing ration from 0 to 1 ppb is shown in Table 5. As seen in Table 5, the percent reduction in radiative forcing is not the same for all the gases. The percent reduction is particularly significant for short-lived gases, for example, HFC-161, HFC-152a, and HCFC-225ca, while it is negligible for long-lived gases such as HFC-23, HFC-227ea, and HFC-236ea. The shorter timescales of vertical mixing in the troposphere ensure homogeneous mixing of gases with lifetimes longer than a few years, while slow vertical mixing combined with even slower chemical loss rates result in a steep gradient in the vertical mixing ratios in the stratosphere. The downwelling radiation into the troposphere decreases due to reduced amounts of the gas in the stratosphere, resulting in a lower radiative forcing. Stratospheric adjustment further reduces the radiative forcing as cooling dominates over warming in the stratosphere due to reduced upwelling radiation in the stratosphere. This effect is reflected in our results and is found to be significant for short-lived gases. Hence it is important to consider the lifetimes of these gases in radiative forcing calculations as they determine the vertical abundance.

The radiative forcing has also been shown to be dependent on the seasonal and regional variation in the distribution of gases of interest by *Myhre and Stordal* [1997]. Hence the radiative forcing for these gases will depend considerably on the chosen distributions. However, the radiative forcing values evaluated for the realistic profile in this study (Table 5) are representative of the real forcing to a larger extent than that evaluated for a constant vertical profile. Uncertainties in our calculated radiative forcing values may arise from uncertainties in the 2-D model-derived vertical profiles (use of a global mean) and measured absorption cross sections of halocarbons.

Since radiative forcing for CFC-replacement compounds were reported relative to that of CFC-11 in previous assessments, we also derived the radiative forcing for this gas. Our best estimate of CFC-11 adjusted radiative forcing is 0.271 W m^{-2} ppb^{-1} with a constant profile and 0.242 W m^{-2} ppb^{-1} with a realistic profile. These values can be considered to be accurate to within 15%, given all sources of errors. A significant discrepancy between the radiative forcing for CFC-11 used since IPCC (1990) (based on *Hansen et al.* [1988]) and a more recent calculation [*Pinnock et al.*, 1995] was reported by IPCC (1996). Since then, several other studies [*Hansen et al.*, 1997; *Christidis et al.*, 1997; *Myhre and Stordal*, 1997; *Good et al.*, 1998] have confirmed that the IPCC (1990) value of 0.22 W m^{-2} ppb^{-1} for CFC-11 forcing is too low. *Hansen et al.* [1997] used a GCM with an updated absorption cross section for CFC-11 (based on *Christidis et al.* [1997]) to arrive at their best estimate of 0.25 W m^{-2} ppb^{-1}; *Myhre and Stordal* [1997] also derived a value of 0.25 W m^{-2} ppb^{-1} using a vertical profile from a chemical model. This value has been reported by WMO (1999a) as their best estimate. Our value is about 23% higher than that reported by IPCC (1996). However, our values agree well with the range of values encompassed by WMO (1999a), with their best estimated value being 0.25 W m^{-2} ppb^{-1}. The forcing for constant profile compares well with the *Pinnock et* *al*. [1995] value of 0.264 W m^{-2} ppb^{-1} and the *Christidis et al*. [1997] value of 0.285 W m^{-2} ppb^{-1}.

The percent difference between derived adjusted forcing values for the realistic profile and WMO (1999a) reported values is also given in Table 5. For most gases, derived radiative forcings are within 15% of values given by WMO (1999a). However, values for a few gases (HCFC-225ca, HCFC-225cb, HFC-23, HFC-161, and HFC-236fa) show notable deviations. WMO (1999a) radiative forcing values for these compounds are unchanged from IPCC (1996) values except the forcings have been increased by a factor of 1.14 to account for the change in the recommended forcing for CFC-11. Radiative forcings for a few gases (HFC-134, HFC-161, HFC-227ca) in the work of WMO (1999a) have been reproduced from *Christidis et al*. [1997] after a simple scaling based on *Freckelton et al*. [1998] to account for the decrease in stratospheric concentration. Our values are based on a consistent set of actual radiative transfer calculations. Moreover, radiative forcing values of IPCC (1996) were taken from varied sources both published and unpublished. There may be differences in the models and atmospheres used in these studies. We feel it is not justified to simply scale IPCC values relative to the recent changes made in CFC-11 forcing, owing to the difference in conditions and assumptions used to evaluate the forcings.

4. Global Warming Potentials

Global Warming Potential (GWP) is an important radiative forcing index that is used to estimate the relative impact of emission of a fixed amount of one greenhouse gas compared to another for the globally averaged radiative forcing over a specified timescale. The concept of Global Warming Potential was originally developed for IPCC (1990) as a tool for policy consideration. GWPs provide a better measure of the relative greenhouse impacts than radiative forcing alone as they include the lifetime of gases that helps in differentiating the forcing from long- and short-lived gases. GWPs have also been used to motivate the choice of replacements for the CFCs and play a role in the Kyoto Protocol (WMO, 1999a). Direct GWPs (considering only the absorptive and emissive properties) have been evaluated for a number of replacement compounds and have been reported by the IPCC and WMO assessments. GWPs are expressed as the time-integrated radiative forcing from the instantaneous release of a kilogram of a gas expressed relative to that of a kilogram of the reference gas, CO_2 (IPCC, 1990).

$$\mathrm{GWP}_X(t') = \frac{\displaystyle\int_0^{t'} F_X \exp\left(-t/\tau_X\right)\, dt}{\displaystyle\int_0^{t'} F_{\mathrm{CO_2}} R(t)\, dt}$$

where F_X is the radiative forcing per unit mass of species of X, τ_X is the atmospheric lifetimes of species X, $F_{\mathrm{CO_2}}$ is the radiative forcing due to CO_2, and $R(t)$ represents the response function which describes the decay of an instantaneous pulse of CO_2. The numerator and the denominator represent the absolute global warming potential (AGWP) of species X and CO_2, respectively. Recently, in the work of WMO (1999a) the formula for radiative forcing due to a pulse of CO_2 was revised from the one used in previous assessments, as the previous formula did not reproduce the results of *Hansen et al*. [1988] properly. This resulted in about 12% decrease in the forcing compared to the IPCC (1996) value. This decrease manifests itself in lower values of CO_2 AGWPs. This decrease in CO_2 AGWPs would lead to slightly larger GWPs for other gases.

IPCC (1996) reported the GWPs for a number of replacement compounds evaluated relative to CO_2. The latest assessment, WMO (1999a), reported the GWPs for the previously evaluated species and expanded the list to add some newer compounds. These values are greater than the IPCC (1996) values due to the above mentioned decrease in CO_2 forcing. We evaluated the GWPs for the replacements using our model-derived atmospheric lifetimes and radiative forcings relative to the revised CO_2 AGWPs. Direct GWPs for three time horizons (20, 100, and 500 years) using the radiative forcing for realistic vertical profiles are tabulated in Table 6. Generally, GWPs calculated over 100 year time horizon are used to provide a balanced representation of the various timescales for climatic responses. A comparison of our calculated 100 year GWPs with WMO (1999a) is presented in the same table. As seen in the table, our derived GWPs for most of the compounds differ appreciably from WMO (1999a) reported values. Differences in lifetimes and radiative forcings are reflected in the calculated GWPs. This is particularly observed for gases whose radiative forcings differ significantly from WMO (1999a) reported values; for example, derived GWPs of HCFC-225ca, HCFC-225cb, HFC23, HFC-152a, and HFC-161 differ by more than 20% from WMO (1999a) values.

5. Conclusions

Many assessments have reported the atmospheric lifetimes and radiative forcings for several CFC replacements; however, they lack uniformity in terms of model used and various other conditions applied. We recognized the need for consistent analyses of these parameters, wherein every detail is taken into account to perform a comprehensive study. In the present study, we have evaluated the atmospheric lifetimes, radiative forcings, and Global Warming Potentials for possible CFC replacement compounds in an attempt to perform self-consistent analyses.

Previous assessments have mostly reported atmospheric lifetimes derived using simple scaling methods. However, we have performed model calculations to derive the atmospheric lifetimes of a number of proposed CFC replacements. The simple scaling method provides a rough estimate of the lifetime, while modeling takes into account all the chemical and physical processes that a gas is subjected to in the atmosphere. Model-derived atmospheric lifetimes are within 10% of those evaluated by simple scaling method proposed by *Prather and Spivakovsky* [1990]. However, model-derived lifetimes are more realistic due to the inclusion of loss processes other than loss due to reaction with OH in the atmosphere. Discrepancies in the reported values of total atmospheric lifetimes were resolved by comparing recently revised values of WMO (1999a, b) and our model-derived lifetimes.

Radiative forcings for a large number of replacement compounds have been evaluated by various studies; however, direct comparison is rendered difficult due to the use of different models, cloud conditions, background atmospheres, absorption cross sections, and vertical profiles of gases and the type of forcing (adjusted or instantaneous) reported. In many cases some of these parameters are not reported in the literature. In

Table 6. Derived Direct Global Warming Potentials Based on Evaluated Atmospheric Lifetimes and Radiative Forcings for a Model-Estimated Profile for 20, 100, and 500 Year Time Horizons

			100			
Species	Lifetime, years	20	WMO (1999)	This Study	Difference, %	500
CFC-11	50.00	6,034	4,600	4,749	3	1,707
HCFC-22	12.19	4,662	1,900	1,722	−9	535
HCFC-123	1.36	303	120	90	−25	28
HCFC-124	6.23	1,823	620	565	−9	176
HCFC-141b	9.06	1,701	700	569	−19	177
HCFC-142b	18.04	4,396	2,300	1,957	−15	610
HCFC-225ca	1.97	414	180	123	−32	38
HCFC-225cb	6.28	1,597	620	495	−20	154
HFC-23	234.30	15,476	14,800	19,691	33	15,547
HFC-32	5.28	2,920	880	889	1	276
HFC-125	29.38	5,738	3,800	3,370	−11	1,083
HFC-134	10.36	3,288	1,200	1,145	−5	356
HFC-134a	13.99	4,845	1,600	1,896	19	589
HFC-143	3.70	1,017	370	304	−18	94
HFC-143a	47.18	5,695	5,400	4,352	−19	1,537
HFC-152a	1.48	499	190	149	−22	46
HFC-161	0.26	22	10	6	−40	2
HFC-227ea	35.67	5,395	3,800	3,543	−7	1,172
HFC-236fa	221.93	6,125	9,400	7,726	−17	5,930
HFC-245fa	7.69	3,094		995		309
HFC-365mfc	10.66	2,709	910	953	5	296

The percent difference in GWPs for 100 year time horizon evaluated in this study and those GWPs reported by WMO (1999a) is also shown.

order to overcome such inconsistencies we evaluated the radiative forcings for 20 hydrohalocarbons. Both instantaneous and adjusted cloudy-sky radiative forcings were calculated using a radiative transfer model. The sensitivity of the forcing to the halocarbon vertical mixing ratio profile was investigated. The effects of change in vertical profile on the radiative forcings were found to be considerable for short-lived gases. We recognize that the consideration of latitudinal and seasonal variation in the distributions of replacement compounds will provide a more accurate estimate of the radiative forcing applicable to realistic conditions.

Finally, model-derived atmospheric lifetimes and radiative forcings were used to evaluate the Global Warming Potentials for the replacement compounds considered in this study. Evaluated GWPs for most gases differ significantly from WMO (1999a) reported values because of significant differences in our evaluated radiative forcings and lifetimes.

Acknowledgments. This work was supported by grants from AFEAS, NASA, and EPA. The work of A. K. Jain was supported in part by the U.S. National Science Foundation (NSF DMS 9711624) and the U.S. Department of Energy (DOE DEFG 02-96ER62284). We would like to thank M. Hurley, Ford Motor Company, H. Magid, Allied Signal Inc., and C. Clerbaux, Service d'Aeronomie du CNRS for providing infrared absorption cross-section data.

References

Albritton, D. L., et al., Trace gas radiative forcing indices, in *Climate Change 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios*, edited by J. T. Houghton et al., chap. 5, pp. 204–231, Cambridge Univ. Press, New York, 1995.

Barry, J., G. Locke, D. Scollard, H. Sidebottome, J. Treacy, C. Clerbaux, R. Colin, and J. Franklin, Pentafluorocarbon (HFC-365mfc): Atmospheric degradation and contribution to radiative forcing, *Int. J. Chem. Kinet.*, *29*, 607–617, 1997.

Bloomfield, P., M. Heimann, M. Prather, and R. Prinn, Inferred lifetimes, *NASA Ref. Publ.*, *1339*, 1994.

Briegleb, B., Delta-Eddington approximation for solar radiation in the NCAR Community Climate Model, *J. Geophys. Res.*, *97*, 7603–7612, 1992a.

Briegleb, B., Longwave model for thermal radiation in climate studies, *J. Geophys. Res.*, *97*, 11,475–11,485, 1992b.

Butler, J. H., J. W. Elkins, T. M. Thompson, B. D. Hall, T. H. Swanson, and V. Koropalov, Oceanic consumption of CH_3CCl_3: Implications for tropospheric OH, *J. Geophys. Res.*, *96*, 22,347–22,355, 1991.

Capellani, F., and G. Restelli, Infrared band strengths and the temperature-dependence of the hydrohalocarbons HFC-134a, HFC152a, HCFC-22, HCFC-123, and HCFC-142b, *Spectrochim. Acta*, *Part A*, *48*, 1127–1131, 1992.

Christidis, N., M. D. Hurley, S. Pinnock, K. P. Shine, and T. J. Wallington, Radiative forcing of climate change by CFC-11 and possible CFC replacements, *J. Geophys. Res.*, *102*, 19,597–19,609, 1997.

Clerbaux, C., R. Colin, P. C. Simmon, and C. Granier, Infrared cross sections and global warming potentials due of 10 alternative hydrohalocarbons, *J. Geophys. Res.*, *98*, 10,491–10,497, 1993.

Daniel, J. S., S. Solomon, and D. Albritton, On the evaluation of halocarbon radiative forcing and global warming potentials, *J. Geophys. Res.*, *100*, 1271–1285, 1995.

DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ.*, *94-26*, 1994.

DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ.*, *97-4*, 1997.

Fisher, D. A., C. H. Hales, W.-C. Wang, M. K. W. Ko, and N. D. Sze, Model calculations of the relative effects of CFCs and their replacements on global warming, *Nature*, *244*, 513–516, 1990.

Freckleton, R. S., E. J. Highwood, K. P. Shine, O. Wild, K. S. Law, and M. G. Sanderson, Greenhouse gas radiative forcing: Effects of averaging and inhomogeneities in trace gas distribution, *Q. J. R. Meteorol. Soc.*, *124*, 2099–2127, 1998.

Gierczak, T., R. K. Talukdar, J. B. Burkholder, R. W. Portmann, J. S. Daniel, S. Solomon, and A. R. Ravishankara, Atmospheric fate and greenhouse warming potentials of HFC-236fa and HFC-236 ea, *J. Geophys. Res.*, *101*, 12,905–12,911, 1996.

Good, D. A., J. S. Francisco, A. K. Jain, and D. J. Wuebbles, Lifetimes and global warming potentials for dimethyl ethers and for fluorinated ethers: CH_3OCF_3 (E143a), CHF_2OCHF_2 (E134), CHF_2OCF_3 (E125), *J. Geophys. Res.*, *103*, 28,181–28,186, 1998.

Granier, C., et al., Climate effects of ozone and halocarbon changes, in *Scientific Assessment of Ozone Depletion: 1998*, chap. 10, *Rep. 44*, pp. 383–416, Global Ozone Res. and Monit. Proj., World Meteorol. Org., Geneva, Switzerland, 1999.

Hansen, J. E., D. Johnson, A. Lacis, S. Lebedeff, P. Lee, D. Rind, and G. Russell, Climate impacts of increasing carbon dioxide, *Science*, *213*, 957–966, 1981.

Hansen, J. E., I. Fung, A. Lacis, D. Rind, S. Lebedeff, R. Ruedy, G. Russell, and P. Stone, Global climate changes as forecast by Goddard Institute for Space Studies three-dimensional model, *J. Geophys. Res.*, *93*, 9341–9364, 1988.

Hansen, J. E., M. Sato, and R. Ruedy, Radiative forcing and climate responses, *J. Geophys. Res.*, *102*, 6831–6864, 1997.

Imasu, R., A. Suga, and T. Matsuno, Radiative effects and halocarbon global warming potentials of replacement compounds for chlorofluorocarbons, *J. Meteorol. Soc.*, *Jpn.*, *73*, 1123–1136, 1995.

Isaksen, I. S. A., et al., Radiative forcing of climate, in *Climate Change, 1992: The Supplementary Report to the IPCC Scientific Assessment*, edited by J. T. Houghton, B. A. Callader, and S. K. Varney, chap. 2, pp. 47–67, Cambridge Univ. Press, New York, 1992.

Kiehl, J. T., and B. Briegleb, The relative role of sulfate aerosols and greenhouse gases in climate forcing, *Science*, *260*, 311–314, 1993.

Ko, M. K. W., C. H. Jackman, B. A. Boville, C. Brüehl, P. Connell, A. Golombek, J. Levy, J. M. Rodgriguez, T. Sasaki, and K. K. Tung, Model calculations of atmospheric lifetime, *NASA Ref. Publ.*, *1339*, 1994.

Ko, M., R.-L. Shia, N.-D. Sze, H. Magid, and R. G. Bray, Atmospheric lifetime and global warming potential of HFC-245fa, *J. Geophys. Res.*, *104*, 8173–8181, 1999.

Kurylo, M. J., et al., Short-lived ozone-related compounds, in *Scientific Assessment of Ozone Depletion: 1998*, chap. 2, *Rep. 44*, pp. 44–88, Global Ozone Res. and Monit. Proj., World Meteorol. Org., Geneva, Switzerland, 1999.

Li, Z., and P. Varanasi, Measurement of the absorption cross-sections of CFC-11 at conditions representing various model atmospheres, *J. Quant. Spectrosc. Radiat. Transfer*, *52*, 137–144, 1994.

Madronich, S., et al., Halocarbon scenarios for the future ozone layer and related consequences, in *Scientific Assessment of Ozone Depletion: 1998*, chap. 11, *Rep. 44*, pp. 417–453, Global Ozone Res. and Monitor. Proj., World Meteorol. Org., Geneva, Switzerland, 1999.

Myhre, G., and F. Stordal, Role of spatial and temporal variations in the computation of radiative forcing and GWP, *J. Geophys. Res.*, *102*, 11,181–11,200, 1997.

Nelson, D. D., M. S. Zahniser, and C. E. Kolb, OH reaction kinetics and atmospheric lifetimes estimates for several hydrofluorocarbons, *J. Phys. Chem.*, *99*, 16,301–16,306, 1995.

Pappasava, S., S. Tai, K. H. Illinger, and J. E. Kenny, Infrared radiative forcing of CFC substitutes and their atmospheric reaction products, *J. Geophys. Res.*, *102*, 13,643–13,650, 1997.

Patten, K. O., P. S. Connell, D. E. Kinnison, D. J. Wuebbles, L. Froidevaux, and T. G. Slanger, Effect of vibrationally excited oxygen on ozone production in the stratosphere, *J. Geophys. Res.*, *99*, 1211–1224, 1994.

Pinnock, S., M. D. Hurley, K. P. Shine, T. J. Wallington, and T. J. Smyth, Radiative forcing of climate by hydrochlorofluorocarbons and hydrofluorocarbons, *J. Geophys. Res.*, *100*, 23,227–23,238, 1995.

Prather, M. J., and E. Remsberg (Eds.), The atmospheric effects of stratospheric aircraft: Report of the 1992 Models and Measurements Workshop, *NASA Ref. Publ.*, *1292*, 1993.

Prather, M. J., and C. M. Spivakovsky, Tropospheric OH and the lifetimes of hydrochlorofluorocarbons, *J. Geophys. Res.*, *95*, 18,723–18,729, 1990.

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*, 2445–2462, 1992.

Prinn, R., R. F. Weiss, B. R. Miller, J. Huang, F. Alyea, D. M. Cunnold, P. J. Fraser, D. Hartley, and P. Simmonds, Atmospheric trends and lifetime of trichloroethane and global average of hydroxyl radical concentrations based on 1978–1994 ALE/GAGE measurements, *Science*, *269*, 187–192, 1995.

Pyle, J. A., S. Solomon, D. Wuebbles, S. Zvenigorodsky, P. Connell, D. Fisher, M. K. W. Ko, F. Stordal, and D. Weisenstein, Ozone depletion potentials and chlorine loading potentials, in *Scientific Assessment of Ozone Depletion: 1991*, chap. 6, *Rep. 25*, pp. 136–155, Global Ozone Res. and Monitor. Proj., World Meteorol. Org., Geneva, Switzerland, 1992.

Rahmes, T. F., A. H. Omar, and D. J. Wuebbles, Atmospheric distributions of soot particles by current and future aircraft fleets and resulting radiative forcing on climate, *J. Geophys. Res.*, *103*, 31,657–31,667, 1998.

Ramanathan, V., R. J. Cicerone, H. B. Singh, and J. T. Kiehl, Trace gas trends and their potential role in climate change, *J. Geophys. Res.*, *90*, 5547–5566, 1985.

Ramaswamy, V., et al., Radiative forcing of climate, in *Scientific Assessment of Ozone Depletion: 1991*, chap. 7, *Rep. 25*, pp. 156–184, Global Ozone Res. and Monit. Proj., World Meteorol. Org., Geneva, Switzerland, 1992.

Rothman, L. S., et al., The HITRAN database: 1986 edition, *Appl. Opt.*, *26*, 4058–4097, 1987.

Schimel, D., et al., Radiative forcing of climate change, in *Climate Change 1995: The Science of Climate Change*, edited by J. T. Houghton et al., chap. 2, pp. 65–131, Cambridge Univ. Press, New York, 1996.

Shine, K. P., et al., Radiative forcing of climate, in *Climate Change: The IPCC Scientific Assessment*, edited by J. T. Houghton, G. J. Jenkins, and J. J. Ephraums, chap. 2, pp. 41–68, Cambridge Univ. Press, New York, 1990.

Shine, K. P., et al., Radiative forcing and temperature trends, in *Scientific Assessment of Ozone Depletion: 1994*, chap. 8, *Rep. 37*, pp. 319–348, Global Ozone Res. and Monit. Proj., World Meteorol. Org., Geneva, Switzerland, 1995.

Solomon, S., et al., Ozone depletion potentials, global warming potentials, and future chlorine/bromine loading, in *Scientific Assessment of Ozone Depletion: 1994*, chap. 13, *Rep. 37*, pp. 469–508, Global Ozone Res. and Monit. Proj., World Meteorol. Org., Geneva, Switzerland, 1995.

Wuebbles, D. J., The relative efficiency of number of halocarbons for destroying ozone, *Rep. UCID 18924*, Lawrence Livermore Natl. Lab., Livermore, Calif., 1981.

Wuebbles, D. J., Chlorocarbon emission scenarios: Potential impact on stratospheric ozone, *J. Geophys. Res.*, *88*, 1433–1443, 1983.

Wuebbles, D. J., D. E. Kinnison, K. E. Grant, and J. Lean, The effect of solar flux variations and trace gas emissions on recent trends in stratospheric ozone and temperature, *J. Geomagn. Geoelectr.*, *43*, 709–718, 1991.

Wuebbles, D. J., P. S. Connell, and K. O. Patten, Evaluating the potential effects of halon replacements on the global environment, in *Halon Replacements: Technology and Science*, edited by A. W. Miziolek, pp. 59–71, Am. Chem. Soc., Washington, D. C., 1995.

Wuebbles, D. J., A. K. Jain, K. O. Patten, and P. S. Connell, Evaluation of ozone depletion potentials for chlorobromomethane (CH_2ClBr) and 1-bromo propane (C_3H_7Br), *Atmos. Environ.*, *32*, 107–114, 1997.

Wuebbles, D. J., A. K. Jain, R. Kotamarthi, V. Naik, and K. O. Patten, Replacements for CFCs and halons and their effects on stratospheric ozone, in *Recent Advances in Stratospheric Processes*, edited by T. Nathan and E. Cordero, Res. Signpost, Kerala, India, in press, 2000.

A. Jain, V. Naik, K. O. Patten, and D. J. Wuebbles, Department of Atmospheric Sciences, University of Illinois at Urbana-Champaign, Urbana, IL 61801. (wuebbles@atmos.uiuc.edu)

(Received September 2, 1999; revised November 9, 1999;
accepted November 11, 1999.)