

N 9 2 - 1 5 4 4 7

**RELATIVE EFFECTS ON GLOBAL WARMING OF HALOGENATED
METHANES AND ETHANES OF SOCIAL AND INDUSTRIAL INTEREST**

**Donald A. Fisher and Charles H. Hales
E.I. du Pont de Nemours & Company**

**Wei-Chyung Wang, Malcolm K. W. Ko and N. Dak Sze
Atmospheric and Environmental Research, Inc.**

PRECEDING PAGE BLANK NOT FILMED

ABSTRACT

The relative potential global warming effects for several halocarbons (CFCs -11, 12, 113, 114, and 115; HCFCs 22, 123, 124, 141b, and 142b; and HFCs 125, 134a, 143a, and 152a; carbon tetrachloride; and methyl chloroform) have been calculated by two atmospheric modeling groups. These calculations were based on atmospheric chemistry and radiative convective models to determine the chemical profiles and the radiative processes. The resulting relative greenhouse warming when normalized to the effect of CFC-11 agree reasonably well as long as we account for differences between modeled lifetimes. Differences among results are discussed. Sensitivity of relative warming values is determined with respect to trace gas levels assumed. Transient relative global warming effects are analyzed.

1. INTRODUCTION

A systematic environmental evaluation of replacements for fully halogenated chlorofluorocarbons (CFCs) includes the potential effects of each replacement chemical on global warming. While the major focus for rising environmental concerns centers on the potential effects of long-lived CFCs on stratospheric ozone, the role of these gases as contributors to an enhanced greenhouse or global warming also needs examination. This concern is based on the ability of these gases to absorb infrared radiation in the atmospheric 'window' between 8 and 12 μm .

First, a brief background to establish the role of these gases in the 'greenhouse warming' phenomena. The radiative and thermal balance of planet Earth is established primarily by balancing the incoming (UV and visible) solar energy to the Earth's surface and atmosphere with the outgoing (infrared) radiation from the Earth's surface and atmosphere eventually being lost to space. Infrared energy is partially blocked at many wavelengths by naturally occurring gases such as carbon dioxide, methane, and stratospheric water vapor. These gases absorb energy at fundamental frequencies characteristic of their structure. This energy contributes to local warming and is eventually re-radiated. Changing gas concentrations change the radiative balance of the infra-red cooling process. Hence, the concern that increasing CO_2 concentration will significantly impede infrared cooling of the Earth with a decrease in energy loss to space and a corresponding increase in the Earth's surface temperature.

The atmosphere 'window' between 8 and 12 μm is virtually transparent, i.e. since few gases are present that absorb energy at these wavelengths, outgoing infrared radiation passes through the atmosphere essentially unimpeded. However, both C-Cl and C-F bonds have natural vibrational, bending, and rotational excitation frequencies in this infrared frequency range such that CFCs absorb the infrared energy to become very effective greenhouse gases. Their effectiveness as greenhouse gases is accentuated by their long lifetimes. Since functional replacements may also absorb infrared energy in the window region, it is important to estimate their potential impact on global climate as part of this evaluation. As will be demonstrated below, the effectiveness of these gases is determined in large part by their lifetimes. Longer lived gases build up higher tropospheric concentrations. Of fundamental importance in determining the effectiveness as greenhouse gases are the infra-red band strengths, i.e. the wave length intervals and the amount of energy absorbed within these intervals by each molecule.

Besides the influence on the infrared radiative fluxes at the top of the atmosphere and at the surface, there is yet another aspect of the radiative perturbations from halogenated compounds — namely the addi-

GLOBAL WARMING

tional heating induced in the tropical upper troposphere and lower stratosphere which has the potential to increase temperatures in this region. Any change in the temperatures near the tropopause region is of considerable significance for the tropospheric-stratospheric exchange water vapor.

Candidate alternatives are composed of either carbon, hydrogen and fluorine (hydrofluorocarbons or HFCs) or carbon, hydrogen, chlorine and fluorine (hydrochlorofluorocarbons or HCFCs). For simplicity, both classes of compounds are referred to as hydrohalocarbons. Because they contain hydrogen, the hydrohalocarbons are subject to destruction in the atmosphere through reaction with hydroxyl radicals. This destruction mechanism leads to much shorter atmospheric lifetimes for the hydrohalocarbon compounds (see [Fisher et al. (1989a)] for a discussion of the chemistry affecting the atmospheric lifetimes of these gases). By contrast, the only known destruction process of CFCs is through photolysis in the upper stratosphere. As will be shown below, the shorter atmospheric lifetime of HCFCs and HFCs is a primary factor in reducing their potential to affect global warming.

This paper examines the calculated greenhouse effects of several one and two carbon halocarbons. Estimates of these effects will be quantified in terms of a relative potential to enhance global warming (halocarbons global warming potential or HGWP). Sensitivity to assumed levels of trace gases will be examined. Transient relative warming effects will be analyzed.

Table 1 Compounds Examined in this Study

HALOCARBON	FORMULA	IUPAC NAME
CFC-11	CCl_3F	METHANE, TRICHLOROFLUORO-
CFC-12	CCl_2F_2	METHANE, DICHLORODIFLUORO-
CFC-113	$\text{CCl}_2\text{FCClF}_2$	ETHANE, 1,1,2-TRICHLORO-1,2,2-TRIFLUORO-
CFC-114	$\text{CCClF}_2\text{CClF}_2$	ETHANE, 1,2-DICHLORO-1,1,2,2-TETRAFLUORO-
CFC-115	CClF_2CF_3	ETHANE, CHLOROPENTAFLUORO-
HCFC-22	CHClF_2	METHANE, CHLORODIFLUORO-
HCFC-123	CF_3CHCl_2	ETHANE, 2,2-DICHLORO-1,1,1-TRIFLUORO-
HCFC-124	CF_3CHClF	ETHANE, 2-CHLORO-1,1,1,2-TETRAFLUORO-
HFC-125	CF_3CHF_2	ETHANE, PENTAFLUORO-
HFC-134a	$\text{CF}_3\text{CH}_2\text{F}$	ETHANE, 1,1,1,2-TETRAFLUORO-
HCFC-141b	CCl_2FCH_3	ETHANE, 1,1-DICHLORO-1-FLUORO-
HCFC-142b	CClF_2CH_3	ETHANE, 1-CHLORO-1,1-DIFLUORO-
HFC-143a	CF_3CH_3	ETHANE, 1,1,1-TRIFLUORO-
HFC-152a	CHF_2CH_3	ETHANE, 1,1-DIFLUORO-
CARBON- TETRACHLORIDE	CCl_4	METHANE, TETRACHLORO-
METHYL CHLOROFORM	CCl_3CH_3	ETHANE, 1,1,1-TRICHLORO-

Halocarbon Global Warming Potential is based on a concept similar to Ozone Depletion Potential and is used to describe the relative potential of each halocarbon as a greenhouse gas. No attempt is made to calculate HGWPs for non-halocarbon gases such as carbon dioxide and methane. Because of the current atmospheric concentrations and spectral locations of the infrared absorption bands of these other gases, calculated global warming is not a linear function with increases in their atmospheric concentrations. In contrast, a calculated warming is linearly proportional to concentrations of halocarbons. Thus, Greenhouse Warming Potentials for carbon dioxide and methane would not be meaningful.

Two atmospheric modeling groups, Atmospheric and Environmental Research, Inc. (AER), and Du Pont Central Research (Du Pont), have calculated HGWP values for sixteen gases. These groups used Radiative Convective models that are described in the literature (Wang and Molnar 1985, Owens et al. 1985). The halocarbons considered in this study are listed in Table 1 along with their chemical formula and IUPAC names and are the same as evaluated for effect on stratospheric ozone (Fisher, et al., 1989a).

This paper will discuss the definition of HGWP, as well as examine the basis for selecting its definition. The results calculated by the two models and an examination of the differences and uncertainties in model results is also presented.

2. DEFINITION BASIS

Halocarbon Global Warming Potential (HGWP) is defined in a manner parallel to the definition of Ozone Depletion Potential. It is defined as the ratio of calculated warming for each unit mass of a gas emitted into the atmosphere relative to the calculated warming for a mass unit of reference gas CFC-11. This definition was chosen as a representative measure of the potential of a compound to effect global warming for several reasons:

- (1) It provides a measure of the cumulative effect on the radiative balance over its chemical lifetime for each unit released into the atmosphere (see below).
- (2) The HGWP yields a single value for each compound rather than a time varying multitude of values.
- (3) It provides a measure of the maximum calculated effect of a compound compared to the maximum calculated effect of CFC-11 on an equal mass basis.

The first of these reasons is perhaps the most important in that it estimates the cumulative chronic effect on global warming of each unit released. An illustrative test was performed which quantified the chronic effect from a single pulsed release of test gas into the atmosphere, analogous to a test on effect on stratospheric ozone (Fisher et al., 1989a). The test used the Du Pont model to calculate cumulative global warmings over a 500 year time period following impulse releases of HCFCs -123, -22, and CFC-11.

GLOBAL WARMING

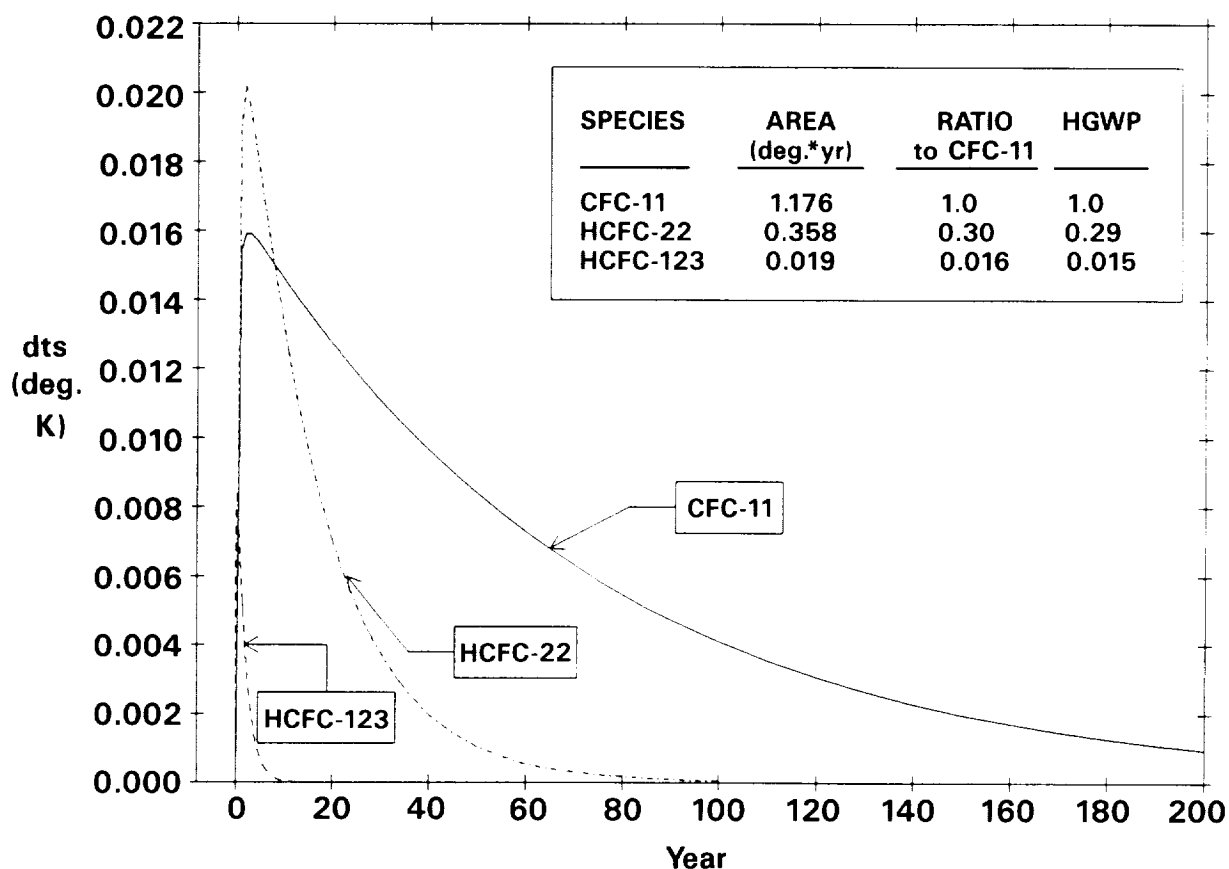


Figure 1. Calculated Change in Surface Temperature Following a Pulsed Emission of 5.0×10^9 kg of Specified Gas

The calculated cumulative warmings are shown in Figure 1. For each case, the effect peaks very rapidly following the release and tails off with an exponential decay function having a time constant equal to the atmospheric lifetime of the species. As seen in the insert table, the time-integrated warming following such an event echo the relative values of the HGWP calculated from steady state figures. Referring to Appendix A of Fisher et al. (1989a), this is not surprising if the response function, $g(t)$, is to represent greenhouse warming.

3. DEFINITIONS

In order to make the definition of HGWP consistent between models as well as a conservative estimate of relative effects, the following criteria have been selected:

1) Trace gas levels -- Changing the concentration of other trace gases will affect the calculated future equilibrium temperature rise from gases under evaluation here for two reasons. First if there is overlap of absorption spectra, certain bands have less effect. Secondly, chemistry and therefore lifetime can be

affected by perturbation of these chemicals. Current levels of CO₂, CH₄, N₂O, O₃ and stratospheric H₂O were used in model calculations. Sensitivity of this assumption will be tested in a following section.

2) Gas perturbation levels -- Atmospheric concentrations of the test gases were chosen to yield model responses large enough to avoid the "noise levels" of the numerical models and still be in a linear response region.

3) Reference gas -- CFC-11 has been chosen as the reference compound for HGWP calculations in order to have a reference material consistent for both HGWP and ODP.

4) Specific Surface Temperature Change -- We define the calculated surface temperature increase for a one part per billion surface increase of any gas to be specific surface temperature change, or symbolically dT_s.

The HGWP definition resembles the ODP definition. Thus for any gas, the general definition is:

$$\text{HGWP} = \frac{\text{Calculated IR forcing due to Compound X} / \text{Emission rate (steady state) of Compound X}}{\text{Calculated IR forcing due to CFC-11} / \text{Emission rate (steady state) of CFC-11}}$$

Note: IR forcing is the net change in IR flux at the tropopause.

Since radiative convective models calculate a surface temperature change approximately proportional to the IR forcing level (to be examined below) and since lifetimes are proportional to the ratio of atmospheric abundance to (molecular weight * emission rate), an equivalent form of this definition is:

$$\text{HGWP} = \frac{[\text{dT}_s(x) * \text{Lifetime}(x) / \text{Molecular weight}(x)]}{[\text{dT}_s(\text{CFC11}) * \text{Lifetime}(\text{CFC11}) / \text{Molecular weight}(\text{CFC11})]}$$

Note also, many of the gases have the potential of affecting heating rates indirectly as well since they can chemically influence the distribution of ozone which would affect both the solar and the long wave heating rates. An examination of model results indicates that this is a second order effect, at least two orders of magnitude below the IR effect and well below the sensitivity of these calculations (Wang et al. private communication, 1989).

4. MODEL CALCULATIONS

The primary input to these radiative calculations are the altitudinal steady-state concentration profiles using appropriate chemistry models.

Once the concentration profile is determined, the effect of each gas is calculated using a Radiative Convective model. These models utilize infrared absorption spectra to quantify a gas's ability to absorb IR

GLOBAL WARMING

Table 2 Total Band Strengths of Halocarbons

Species	Rogers & Stephens (1988)	Varanasi & Chudamani (1988)	Kagann et al. (1983)	Gehring (1987)	Magid + (1988)
CFC-11		2389	2566		2389*
CFC-12		3267	3364	3310	3240*
CFC-113	4822	3507		3126	3401*
CFC-114	5935	3937			4141*
CFC-115					4678*
HCFC-22				2399	2554*
HCFC-123				2552	2859*
HCFC-124				4043*	
HFC-125				3908*	
HFC-134a				3169	3272*
HCFC-141b				1732	1912*
HCFC-142b				2474	2577*
HFC-143a				3401*	
HFC-152a					1648*
CCl ₄				1195*	
CH ₃ CCl ₃				1184	1209*

* Infrared data used in model calculations

+ The IR data from Magid (1988) were given with spectral resolutions of 0.5 to 0.25 cm⁻¹. The integrated band strengths are given here so that they can be compared to other data.

energy and thereby impact the earth's heat balance. Equilibrium temperature profiles are calculated such that the solar heating is balanced by the infrared cooling at all altitudes through the atmosphere. The calculation accounts for the amount of energy absorbed by each IR gas (the band strength) at specified wavelengths (the band location) including spectral overlap with other IR gases. Quantitative infrared data for this input are available from literature sources for the CFCs (Kagann et al. 1983; Varanasi and Chudamani, 1988; and Rogers and Stephens, 1988) and measurements for the HCFCs and the HFCs were obtained from industry laboratories (Magid 1988, and Gehring 1987).

Total band strengths available for these calculations as shown in Table 2 are within about 10% with the exception of Rogers and Stephens (1988). The band strengths used for the model calculations are marked with an asterisk. Since there appear to be systematic differences between laboratories for band strength measurements, the values from a common data base [Magid (1988)] were used since it covered most of the compounds of interest in this study. For compounds not available from this source, data from Gehring (1987) was used.

Table 3 Absorbance Bands Used in Study
(1/atm*cm*cm) @STP

BIN MIN	BIN MAX	CFC- 11	CFC- 12	CFC- 113	CFC- 114	CFC- 115	HCFC- 22	HCFC- 123	HCFC- 124	HCFC- 125	HFC- 134a	HCFC- 141b	HCFC- 142b	HCFC- 143a	HFC- 152a	CC14	CH3- CC13
0.000	220.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
220.00	440.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
440.00	500.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	24.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
500.00	555.00	0.0	0.0	0.0	0.0	0.0	0.0	49.6	30.6	30.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
555.00	616.256	0.0	0.0	0.0	23.9	0.0	0.0	21.3	61.0	61.0	0.0	82.2	0.0	65.1	0.0	0.0	0.0
616.256	618.030	0.0	0.0	0.0	3.8	0.0	0.0	0.0	0.4	0.4	0.0	0.0	0.0	3.4	0.0	0.8	0.0
618.030	647.085	0.0	0.0	14.7	17.1	20.9	0.0	0.0	6.2	10.8	0.0	0.0	0.0	18.6	0.0	9.3	0.0
647.085	648.825	0.0	0.0	1.2	0.0	8.1	0.0	0.0	0.0	0.3	2.0	0.0	0.0	0.0	0.0	0.3	0.0
648.825	667.370	0.0	19.8	19.1	0.0	21.8	0.0	27.6	11.2	2.5	64.9	0.0	17.2	0.0	0.0	0.0	0.0
667.370	669.250	0.0	3.0	0.0	3.0	1.3	0.0	6.9	0.6	0.0	9.2	0.0	6.6	0.0	0.0	0.0	0.0
669.250	718.550	0.0	23.3	0.0	14.2	0.0	0.0	77.5	137.4	24.5	52.2	0.0	160.6	0.0	0.0	0.0	172.1
718.550	720.800	0.0	0.0	0.0	0.0	0.0	0.0	43.8	0.0	11.4	0.0	0.0	0.0	0.0	0.0	0.0	73.2
720.800	775.000	0.0	0.0	0.0	0.0	107.4	0.0	0.0	0.0	79.0	0.0	542.1	0.0	0.0	0.0	260.0	488.5
775.000	862.000	21.8	962.0	722.4	578.6	0.0	566.3	449.6	200.5	46.8	69.6	33.3	0.0	16.5	17.1	910.0	24.8
862.000	924.000	32.0	924.0	706.1	394.0	0.0	0.0	83.8	294.9	120.3	14.4	97.7	406.2	13.2	65.6	11.5	0.0
924.000	928.000	7.4	144.5	32.3	66.7	0.0	0.0	0.0	0.0	0.7	0.0	45.2	2.9	1.4	16.0	1.1	0.0
928.000	934.000	15.0	228.0	30.7	64.2	0.0	0.0	0.0	0.0	1.1	0.0	54.3	0.0	2.4	28.2	1.7	0.0
934.000	1004.000	34.6	67.2	36.9	57.4	923.3	0.0	0.0	0.0	0.0	220.8	70.3	203.0	423.4	178.7	0.0	0.0
1004.000	1036.000	0.0	0.0	71.2	19.3	51.7	0.0	0.0	0.0	0.0	11.8	9.0	5.7	10.4	7.6	0.0	9.4
1036.000	1042.000	1.9	0.0	90.7	53.2	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	0.0	1.2	0.0	2.9
1042.000	1048.000	2.8	0.0	105.6	129.9	0.0	0.0	0.0	0.0	0.0	3.8	0.0	0.0	0.0	1.3	0.0	0.0
1048.000	1060.000	17.3	0.0	156.9	352.1	0.0	0.0	0.0	0.0	0.0	14.4	3.3	0.0	0.0	3.6	0.0	6.6
1060.000	1065.000	27.5	2.3	21.0	57.2	0.0	0.0	0.0	1.5	0.0	9.2	2.1	0.0	0.0	0.0	0.0	9.1
1065.000	1071.000	71.1	5.3	8.5	11.4	0.0	1.4	0.0	2.2	1.9	13.7	3.6	0.0	0.0	0.0	0.0	18.8
1071.000	1190.000	504.6	1763.0	1023.0	1539.0	1178.0	1661.0	926.1	1393.0	1106.0	1118.0	890.3	916.8	96.3	1026.0	0.0	371.3
1190.000	1225.000	0.0	0.0	329.0	551.5	202.5	11.3	514.0	791.5	1653.0	533.9	6.2	636.0	473.9	6.6	0.0	0.0
1225.000	1250.000	0.0	0.0	13.3	13.5	1702.0	0.0	101.4	257.0	370.2	30.0	0.0	128.6	1317.0	5.7	0.0	0.0
1250.000	1301.000	0.0	0.0	0.0	172.4	204.6	45.9	619.8	423.6	236.3	693.8	0.0	0.0	551.6	12.3	0.0	0.0
1301.000	1307.000	0.0	0.0	0.0	0.0	5.6	32.8	9.7	126.8	155.8	170.9	0.0	0.0	14.9	0.0	0.0	0.0
1307.000	1397.000	0.0	0.0	19.1	18.7	251.0	236.6	0.0	283.2	0.0	194.7	60.2	94.1	68.6	148.6	0.0	32.0
1397.000	1420.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	24.6	0.0	32.4	12.9	0.0	154.9	128.9	0.0	0.0
1420.000	1535.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	169.9	0.0	0.0	0.0
1535.000	1590.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1590.000	1640.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1640.000	1717.500	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1717.500	1845.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1845.000	1972.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1972.000	2100.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2100.000	2450.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

GLOBAL WARMING

Both these data sets were measured at room temperature. Since temperature dependent data sets are not yet available, band strengths used in the study were assumed constant through the atmosphere. This assumption will need to be checked once temperature dependent measurements become available.

Individual band strengths and band locations are important in these calculations. Table 3 details the locations and strengths for the absorption spectra used in this work broken down into the bin structure of the Du Pont radiative-convective model. The greatest amount of absorption for many species occurs at wave lengths between 1070 and 1400 cm^{-1} . Absorption by methane and N_2O in the background atmosphere occurs in this region of the spectrum. Some species (e.g. CFC-113 and CFC-114) show significant absorption in the 934 to 1070 cm^{-1} region and therefore overlaps the IR absorption bands of ozone.

Tables 4 and 5 detail preliminary steps of the calculations for HGWP. Table 4 shows the net IR radiative flux at the tropopause (@12 km) for tropospheric concentrations of 1ppbv as calculated by each model. Note that each of the model's calculations were based on different cloud assumptions (Du Pont used fixed 50% grey (albedo = 0.5) cloud cover while AER was based on a non-grey cloud with 48.5% cover). Table 5 shows the resulting values for Specific Surface Temperature Increases for each of the compounds. Each group's results correlate to each chemical's total band strengths, with compensation made by the

Table 4 Net IR Radiative Flux at the Tropopause
(at 12 km and 1 ppbv tropospheric mixing ratio)

Species	AER	Du Pont
CFC-11	0.175	0.133
CFC-12	0.248	0.158
CFC-113	0.223	0.163
CFC-114	0.258	0.181
CFC-115	0.204	0.164
HCFC-22	0.151	0.107
HCFC-123	0.140	0.092
HCFC-124	0.153	0.108
HFC-125	0.189	0.119
HFC-134a	0.135	0.095
HCFC-141b	0.109	0.076
HCFC-142b	0.144	0.101
HFC-143a	0.111	0.087
HFC-152a	0.092	0.059
CCl_4	0.080	0.063
CH_3CCl_3	0.038	0.033
[2 x CO_2]	4.41	3.87

Table 5 Specific Surface Temperature Increases
(warming resulting from 1 ppbv of each gas)

Species	Modeled Warming (°K/ppbv)		Normalized Warming # (°K/ppbv)		Lambda value, λ (°K/ppbv/Wm-2)	
	AER	Du Pont	AER	Du Pont	AER	Du Pont
CFC-11	0.135	0.084	0.088	0.102	0.771	0.632
CFC-12	0.202	0.102	0.131	0.124	0.815	0.647
CFC-113	0.174	0.103	0.113	0.125	0.780	0.632
CFC-114	0.208	0.115	0.135	0.139	0.806	0.635
CFC-115	0.170	0.107	0.110	0.130	0.833	0.652
HCFC-22	0.124	0.070	0.081	0.084	0.821	0.650
HCFC-123	0.111	0.059	0.071	0.072	0.793	0.644
HCFC-124	0.126	0.070	0.082	0.084	0.824	0.645
HFC-125	0.160	0.078	0.104	0.094	0.847	0.654
HFC-134a	0.114	0.061	0.074	0.074	0.844	0.647
HCFC-141b	0.086	0.048	0.056	0.059	0.789	0.637
HCFC-142b	0.120	0.066	0.078	0.080	0.833	0.651
HFC-143a	0.092	0.054	0.060	0.066	0.829	0.625
HFC-152a	0.076	0.038	0.049	0.046	0.826	0.649
CCl ₄	0.062	0.040	0.040	0.048	0.775	0.628
CH ₃ CCl ₃	0.027	0.020	0.018	0.025	0.710	0.618

Normalized by : $dT_s * 2 \text{ }^\circ\text{K}/(dT_s \text{ for } 2X \text{ CO}_2)$

where dT_s for $2X \text{ CO}_2$ is $3.08 \text{ }^\circ\text{K}$ using AER model

$1.651 \text{ }^\circ\text{K}$ using Du Pont model

radiative convective models for overlapping absorption by other IR active gases and for profile differences due to chemical reactivity. The inter-model differences are consistent with previously reported pattern (Owens et al., 1985) due primarily to different treatments of tropospheric feedbacks.

One can account for effects of the various feedback assumptions by normalizing the surface warming by the calculated surface warming from a doubling of carbon dioxide and a common warming of 2°C . The normalized results, shown in the middle two columns of Table 5, indicate good agreement between the two model results. All results are credible to 2 significant figures at best.

Also included on Table 5 are tabulations of the climate feedback factor, l , which is the ratio of the model calculated surface temperature change to the perturbation in the net radiative forcing. As seen from the table, these values are consistent for each of the models thereby validating the assumptions made for equivalency of the two forms of the HGWP definition.

One generalization at this point is drawn from this set of data. Whereas the total infrared band strengths

GLOBAL WARMING

Table 6 Halocarbon Global Warming Potentials Based on Modeled Lifetimes

Species	HGWP rel. to CFC11	
	AER	Du Pont
CFC-11	1.0	1.0
CFC-12	3.5	2.9
CFC-113	1.5	1.4
CFC-114	5.4	4.5
CFC-115	13.	8.2
HCFC-22	0.49	0.29
HCFC-123	0.026	0.015
HCFC-124	0.14	0.080
HFC-125	0.84	0.42
HFC-134a	0.39	0.22
HCFC-141b	0.12	0.073
HCFC-142b	0.51	0.29
HFC-143a	0.97	0.63
HFC-152a	0.045	0.024
CCl ₄	0.36	0.36
CH ₃ CCl ₃	0.026	0.022

are on the average comparable among the species, both the net IR flux and the specific surface warming values for HCFCs and HFCs on average are lower than values for CFCs by 40%. This lower value results from the fact that most hydrogenated halocarbons have bands that overlap the bands of both CH₄ and N₂O as well as water vapor unlike CFC-11 and CFC-12.

Because the total infrared band strengths for halocarbons are of the same order of magnitude (within a factor of 3x) and generally share the same amount of overlap with other radiatively active gases, the dT_s values have a similar range. However, once atmospheric lifetime factors are utilized to calculate HGWP values, the spread among chemicals is much more pronounced. Table 6 shows each modeling group's HGWP results with a range among chemicals of about 400X. Between modeling groups, the tropospheric sensitivity factor is removed since we are normalizing results to CFC11, yet substantial differences persist. Most of these differences are due to differences in modeled lifetimes. As previously reported in Fisher et al. (1989a), calculated lifetimes are only in fair agreement between models.

Since lifetime has a dominant factor on calculated HGWP, basing the HGWP values on a common reference set of lifetimes seems appropriate. Table 7 shows the results of such a rescaling. The reference lifetimes for CFCs are based on the estimates used in model calculations done for the WMO 1989 report. Reference lifetimes for HCFCs and HFCs are from the analysis of Prather (1989). As seen in this table, normaliza-

Table 7 Halocarbon Global Warming Potentials Based on a Common Set of Reference Lifetimes

Species	Reference* Lifetimes (Yrs)	AER	DuPont
CFC-11	60.	1.0	1.0
CFC-12	120.	3.4	2.8
CFC-113	90.	1.4	1.4
CFC-114	200.	4.1	3.7
CFC-115	400.	7.5	7.6
HCFC-22	15.3	0.37	0.34
HCFC-123	1.6	0.020	0.017
HCFC-124	6.6	0.10	0.092
HFC-125	28.1	0.65	0.51
HFC-134a	15.5	0.29	0.25
HCFC-141b	7.8	0.097	0.087
HCFC-142b	19.1	0.39	0.34
HFC-143a	41.0	0.76	0.72
HFC-152a	1.7	0.033	0.026
CCl ₄	50.	0.34	0.35
CH ₃ CCl ₃	6.3	0.022	0.026

* Lifetimes for CFCs are based on estimated lifetimes used in scenario development in WMO, 1989. Lifetimes for HCFCs and HFCs are based on Prather, 1989.

tion in this fashion diminishes differences between the two model's results. Furthermore, the HGWP values for fully halogenated CFCs range from 1.0 to 7.5 whereas the HCFC and HFC values range from 0.02 to 0.7.

5. SENSITIVITY TO TRACE GAS LEVELS

Calculated HGWP values have all been based on present day levels of trace gases of CO₂, CH₄, CO, and N₂O. Because the HGWP values are for consideration in future atmospheres as well as today's, we have examined the sensitivity of these parameters to changes in CO₂ and CH₄ to levels that might be achieved if current trends continue.

The trace gas changes and the resulting calculated changes in lifetimes, surface temperature rises, and HGWP values (from the AER model) are shown in Table 8. Calculated changes in surface temperature for tested CFCs and HCFCs were compared to a reference atmosphere including the assumed gas perturbation.

GLOBAL WARMING

Table 8 Sensitivity Study
Variation in Trace Gas Levels and Impact on HGWP values (AER 1-D model)

Atmosphere		Species			
		CFC-11	CFC-12	HCFC-22	HCFC-123
Lifetime (yrs)	Present Day	60	125	20	2.1
	CH ₄ (1.6 → 3.2 ppb)	60	126	23	2.5
	CO ₂ (340 → 680 ppm)	61	128	20	2.1
dT _s (°C/ppb)	Present Day	0.14	0.20	0.12	0.11
	CH ₄ (1.6 → 3.2 ppb)	0.14	0.20	0.12	0.11
	CO ₂ (340 → 680 ppm)	0.12	0.17	0.12	0.11
HGWP	Present Day	1.0	3.5	0.49	0.026
	CH ₄ (1.6 → 3.2 ppb)	1.0	3.5	0.56	0.031
	CO ₂ (340 → 680 ppm)	1.0	3.4	0.49	0.027

As seen in Table 8, trace gas changes have little effect on HGWP values. CO₂ has the greatest effect on CFC radiative forcing because the albedo feedback is weaker in the warmer atmosphere. As a result, the radiative forcing for CFCs -11 and -12 is weakened somewhat. Methane affects the chemical lifetimes of the HCFCs, resulting in slightly greater HGWP values for these compounds.

6. TIME DEPENDENCE OF RELATIVE GLOBAL WARMING

Since the HGWP parameter is based on steady state effects, it does not describe the relative time-dependent effects of constituents on warming. Even though the HGWP is an equivalent measure of the cumulative warming during its lifetime for each unit mass emitted, the transient response to a constant emission level is also of interest.

The calculated warmings for a number of halocarbons are shown in Figure 2. As seen, the calculated warming reaches an asymptote rapidly for the HCFCs, but requires longer periods to approach steady state for CFCs. These response patterns echo the respective patterns for increases in atmospheric abundances for each species, as seen in Figure 3.

Relative warmings are shown in Figure 4. For HCFCs, the relative effects are at a maximum at very short times. One can easily show (using L'Hospital's rule), that the initial relative value is the ratio of the value of the Specific Surface Temperature Increase (°C /ppb) / molecular weight -- relative to the corresponding ratio for CFC-11. Thus the relative effects are on the order unity at times when the individual effects are small. However, as atmospheric concentrations build and chemistry differences affect

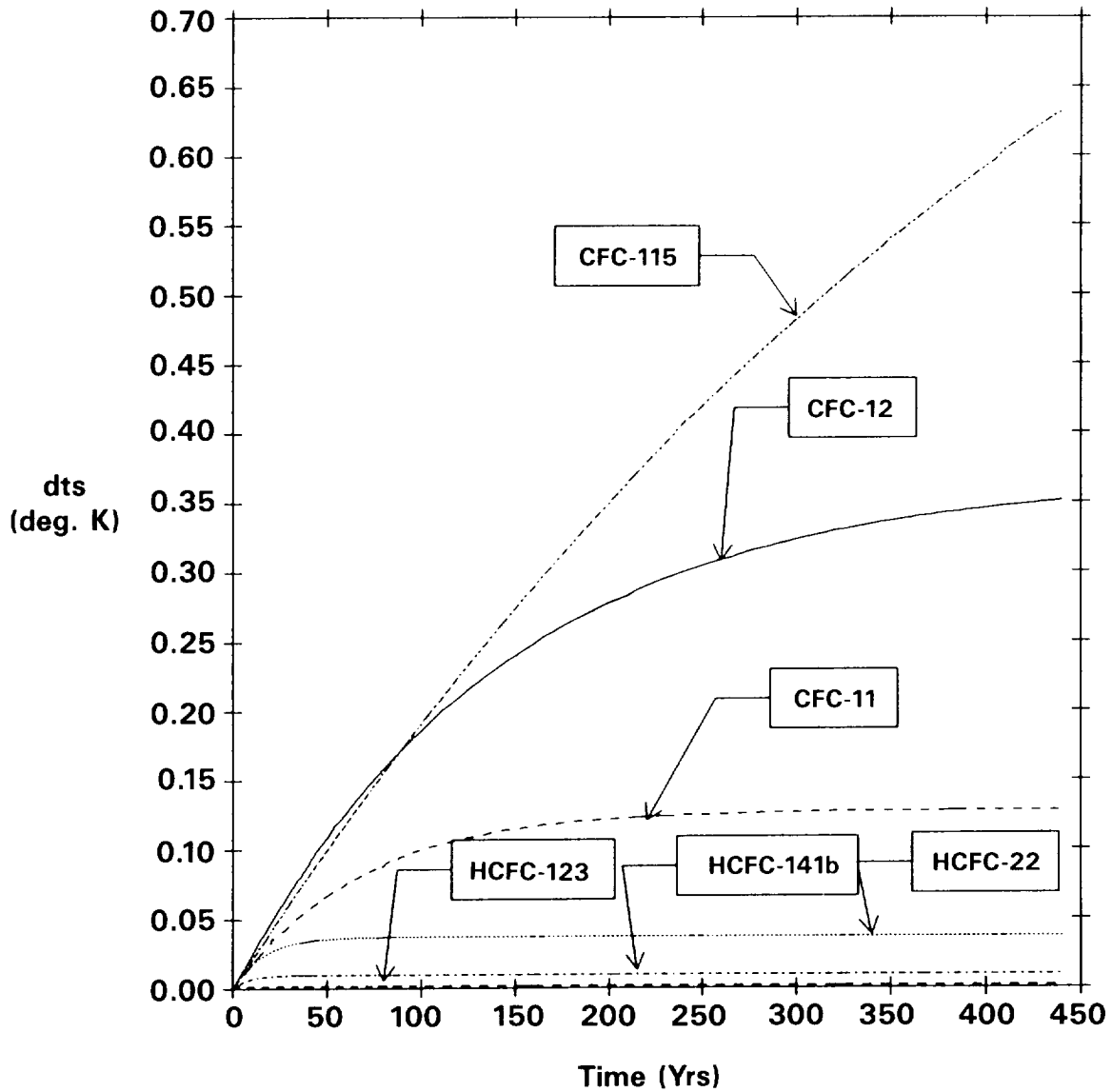


Figure 2. Change of Calculated Warming Following a Step Change of Emission of Specified Gas at 5×10^{18} kg/yr [Du Pont 1-D Model]

GLOBAL WARMING

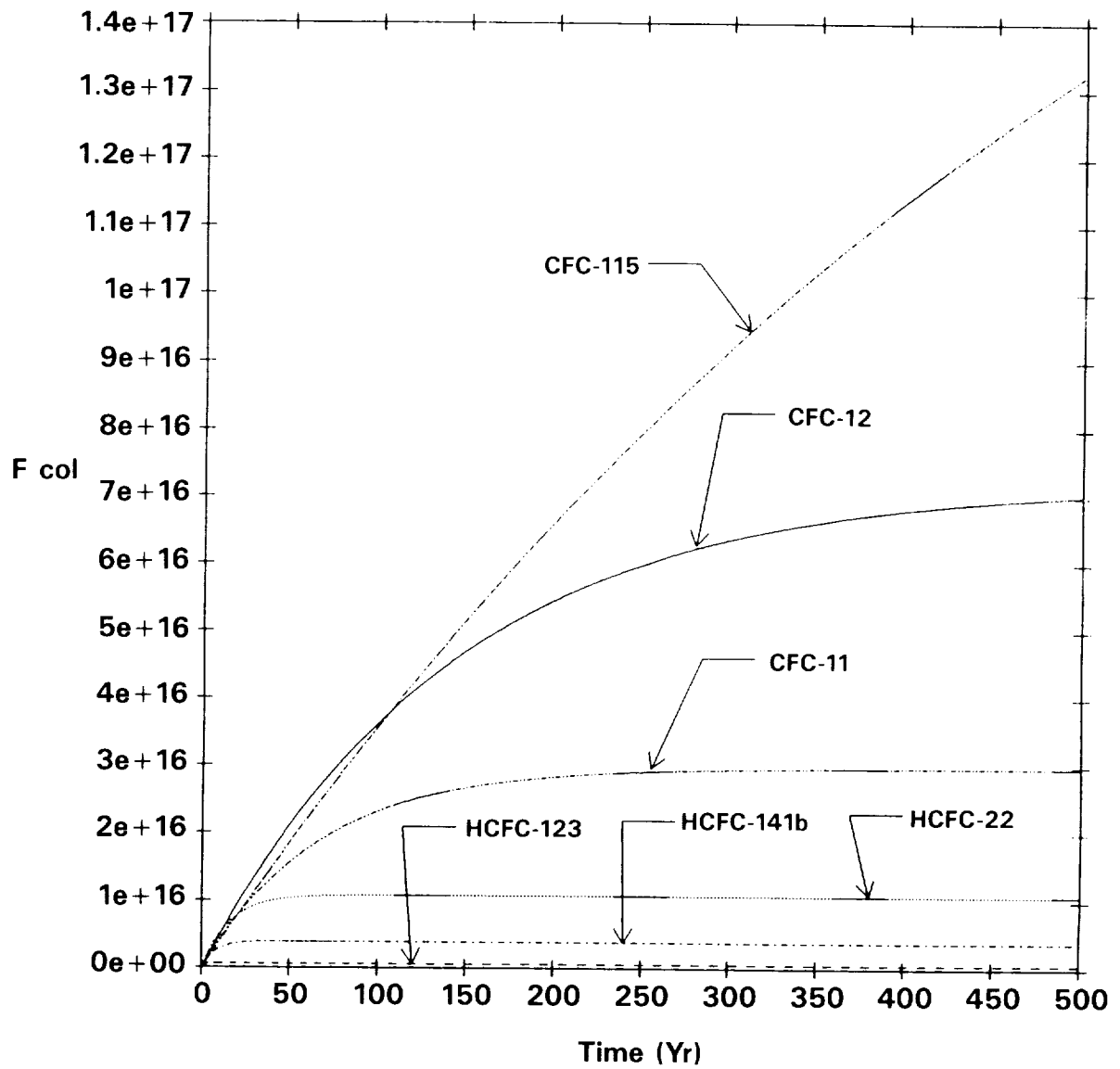


Figure 3. Column of (hydro) Chlorofluorocarbons Following Step Change of Emission of Specified Gas at 5.0×10^{18} kg/yr. [Du Pont 1-D Model]

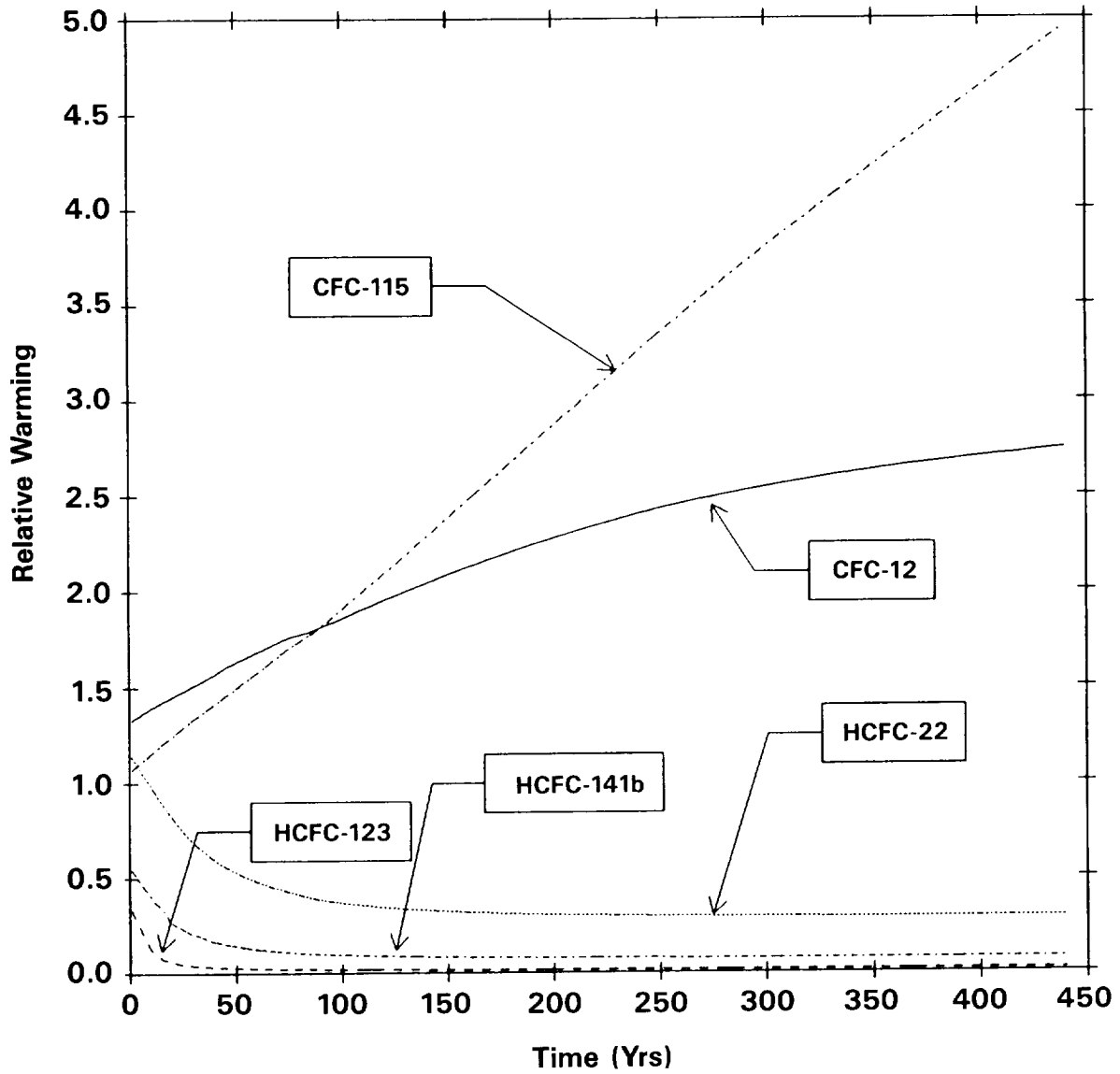


Figure 4. Calculated Relative Warming Following a Step Change of Emission of Specified Gas (CFC-11 Reference) [Du Pont 1-D Model]

GLOBAL WARMING

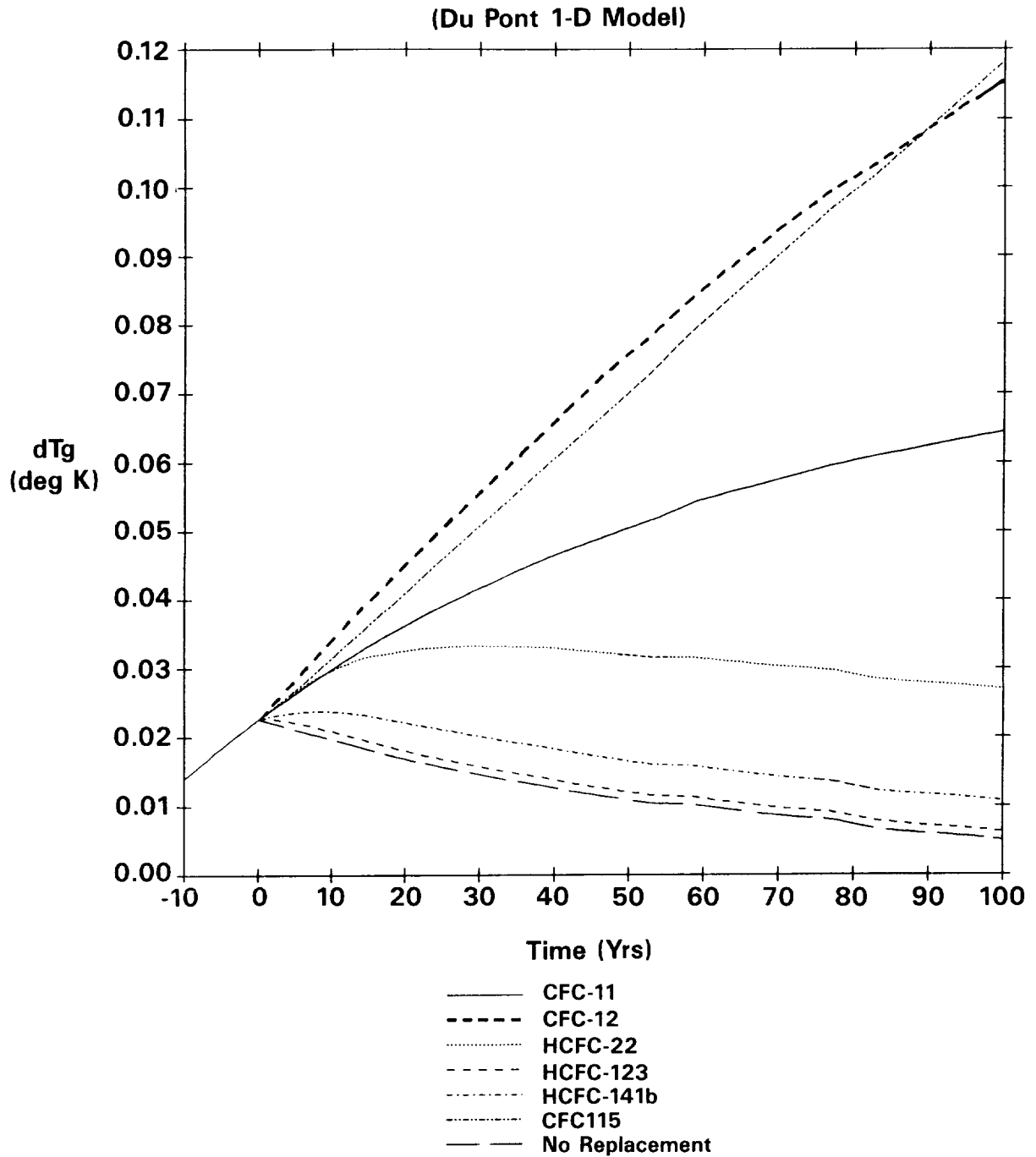


Figure 5. Transient Calculated Global Warming; lb/for/lb replacement of CFC-11 with various species at $t = 0$ and constant emission.

GLOBAL WARMING

the relative amount in the atmosphere, the relative effects either grow or decrease depending on whether the lifetimes are longer or shorter than that of CFC-11. As seen in Figure 4, the HCFCs have lifetimes shorter than the lifetime of the reference gas and have relative effects that asymptotically approach the HGWP value with a time constant equal to the lifetime of CFC-11. Longer lived species have relative effects that grow with time asymptotically approaching their HGWP value with time constant of THEIR OWN lifetime.

Another perspective on the transient response is to consider the replacement of compounds and the resulting transitions in calculated warming. Figure 5 shows the results of a simple set of substitution scenarios performed using the Du Pont model. These calculations were meant to estimate the warming changes resulting from substitution of various gases for CFC-11 at time, $t = 0$. Current level and growth (in atmospheric concentrations) for CFC-11 were used, namely 260 pptv and 4.0%/yr. Emission levels were assumed constant. Compounds are substituted on an equal mass basis. Results for all HCFCs fall within the envelope bounded by the no replacement results and the results for continued emission of CFC-11 and show a negative trend in warming within a few years of substitution. Results for CFC-12 and CFC-115 on the other hand show continued positive slope exceeding the CFC-11 no-substitution case for all times.

UNCERTAINTIES

Uncertainties in the the effectiveness of gases to produce global warming fall into two general classes -- those that are generalized to the total greenhouse effect and those that are specific to the individual species considered here.

There are a number of problems that need to be resolved in the modeling of greenhouse warming. The radiative properties of the earth's surface such as changes in the surface and ice cover albedos, and changes in cloud cover and composition need to be quantified as a function of surface warming. Changes in the temperature structure of the atmosphere will affect the convective patterns and chemistry of the stratosphere. The coupling of oceans (as heat reservoirs) and ocean currents to surface temperature changes will also affect the timing and location of the warming. Research is being carried out worldwide to understand these questions which apply to ALL trace gases that affect the future radiative balance of the earth.

Uncertainties also exist regarding the CFCs, HCFCs, and HFCs and their influence on the radiative balance. The temperature dependence of the absorptances of individual species need to be resolved and parameterized for use in climate models. The chemical processes affecting both lifetimes and atmospheric profiles are also the subject of continuing research.

Resolution of questions related to the general greenhouse warming will directly affect the modeled timing and magnitude of global warming, whereas resolution of the radiative and chemical parameterizations for halocarbons will have a direct effect on the HGWP values for these species.

7. ACKNOWLEDGMENTS

The authors are grateful for the support received for this work from AFEAS , (Alternative Fluorocarbon Environmental Acceptability Study).

X. IMPACT ON PHOTOCHEMICAL OXIDANTS INCLUDING TROPOSPHERIC OZONE

An Assessment of Potential Impact of Alternative Fluorocarbons on Tropospheric Ozone

Hiromi Niki

Centre for Atmospheric Chemistry
Department of Chemistry
York University
4700 Keele Street, North York
Ontario, Canada M3J 1P3

EXECUTIVE SUMMARY

One type of tropospheric impact of the alternative halocarbons may arise from their possible contribution as precursors to the formation of O₃ and other oxidants on urban and global scales. In the present assessment the following specific issues related to tropospheric oxidants are addressed:

1. Is it likely that the HFCs and HCFCs would contribute to production of photochemical oxidants in the vicinity of release?
2. On a global basis, how would emissions of HCFCs and HFCs compare to natural sources of O₃ precursors?

Since almost all CFCs are emitted in urban environments, the first question deals primarily with urban "smog" formation. Salient features of chemical relationships between oxidants and their precursors as well as the relevant terminologies are described briefly in order to provide a framework for the discussion of these two issues.

Based on an analysis of the atmospheric concentrations of various O₃ precursors, and their atmospheric reactivity and O₃ forming potential, the maximum projected contributions of the alternative fluorocarbons to O₃ production in both urban and global atmospheres have been derived as follows:

1: Urban Atmosphere (values in parenthesis in units of 10⁻³% of the total contribution of all O₃ precursors):

HFCs: CH₃CHF₂-152a (59), CH₂FCF₃-134a (8), CHF₂CF₃-125 (4)

HCFCs: CHClF₂-22 (8), CH₃CClF₂-142b (6), CH₃CHClF-124 (16),

CH₃CCl₂F-141b (13), CHClCF₃-123 (59)

2: Global Atmosphere (values in parenthesis in units of 10⁻³% of the total contribution of all O₃ precursors):

HFCs: CH₃CHF₂-152a (92), CH₂FCF₃-134a (11), CHF₂CF₃-125 (7)

HCFCs: CHClF₂-22 (11), CH₃CClF₂-142b (10), CH₃CHClF-124 (25),

CH₃CCl₂F-141b (20), CHClCF₃-123 (92)

