Title

Global warming from chlorofluorocarbons and their alternatives: Time scales of chemistry and climate

Journal
Atmospheric Environment. Part A. General Topics, 27(4)

ISSN
09601686

Authors

Ko, Malcolm K.W.
Sze, Nien Dak
Molnar, Gyula
et al.

Publication Date
1993-03-01

DOI
10.1016/0960-1686(93)90215-K

Atmospheric Environment Vol. 27A. No. 4, pp. 581–587, 1993.
Printed in Great Britain.

0004-6981/93 $6.00+0.00

GLOBAL WARMING FROM CHLOROFLUOROCARBONS AND THEIR ALTERNATIVES: TIME SCALES OF CHEMISTRY AND CLIMATE

MALCOLM K. W. KO, NIEN DAK SZE and GYULA MOLNAR
Atmospheric and Environmental Research Inc., 840 Memorial Drive, Cambridge, MA 01730, U.S.A.

and

MICHAEL J. PRATHER*
National Aeronautics and Space Administration Headquarters, Washington, DC 20546, U.S.A.

(*First received* 27 *December* 1991 *and in final form* 21 *August* 1992)

Abstract—The halocarbons (chlorofluorocarbons, CFCs, and their replacement chemicals: the hydrochlorofluorocarbons, HCFCs, and the hydrofluorocarbons, HFCs) are greenhouse gases. The atmospheric accumulation of these gases is expected to add to the global warming predicted for expected increases of CO_2, CH_4, N_2O, tropospheric ozone and H_2O. Over the next decades, production of CFCs is scheduled to be phased out, while emissions of their alternatives are expected to increase. A simple model is used to illustrate the methodology for determining the time variations of the radiative forcing and temperature changes attributable to the direct greenhouse effect from potential emissions of the halocarbons. Although there are uncertainties associated with the lifetimes of the greenhouse gases, CFCs and their substitutes, the future growth rates of these gases, and the parameters used to simulate the response of the Earth–climate system, the method serves to illustrate an important aspect of the greenhouse warming issue beyond what is provided by the various greenhouse warming indices. Our results show that for likely substitution scenarios, the warming due to halocarbons will correspond to 4–10% of the total expected greenhouse warming at the year 2100. However, uncontrolled growth of the substitutes could result in an eight-fold increase in halocarbon production and a doubling of the halocarbon contribution by 2100.

Key word index: Greenhouse warming, global warming potential, halocarbons, CFC substitutes.

INTRODUCTION

The halocarbons (chlorofluorocarbons, CFCs, and their replacement chemicals: the hydrochlorofluorocarbons, HCFCs, and the hydrofluorocarbons, HFCs) are greenhouse gases (see Ramanathan, 1975; Wang *et al.*, 1976; WMO, 1986). Previous definitions used to characterize the greenhouse warming of trace gases tended to emphasize the integrated direct effect over a fixed period of time. The global warming potentials (GWPs) for the CFCs and their alternatives (Houghton *et al.*, 1990) are defined as the ratio of the integrated radiative forcing (not the surface warming) over a specified time horizon (20, 100 or 500 years) relative to that for the same mass of CO_2 emitted. Halocarbon global warming potentials (HGWPs) have been defined as the surface warming relative to CFC-11 at steady state for sustained emissions at the same constant rate (Fisher *et al.*, 1990). The question left unanswered by the GWPs, HGWPs and the similarly defined "discounted" global warming potentials (Lashof and Ahuja, 1990) is how the time scales of atmospheric chemistry and climate couple to produce a realized climate warming over the next century. The emissions of these gases are expected to vary so that their concentrations will continue to change without reaching steady state over the next century. At any given time, only part of the equilibrium temperature response corresponding to the instantaneous forcing is realized due to the large thermal inertia of the land–ocean–atmosphere system (Ramanathan, 1981; Hansen *et al.*, 1985; Houghton *et al.*, 1990). It could take decades or even centuries to reach equilibrium, even if a constant forcing were sustained.

DESCRIPTION OF METHODOLOGY

The model-calculated climate forcing of a greenhouse gas can be expressed (Dickinson, 1982; Ramanathan, 1982; Ramanathan *et al.*, 1985; Fisher *et al.*, 1990; Houghton *et al.*, 1990) in terms of the model-calculated radiative forcing, $R(\mathrm{W\ m^{-2}\ ppbv^{-1}})$ which is the net radiative flux change ($\mathrm{W\ m^{-2}}$) at the tropopause due to the addition of 1 ppbv of the greenhouse gas to the atmosphere. This quantity is calculated as a radiative transfer problem for a fixed atmospheric

---

*Present address: Department of Geosciences, University of California, Irvine, CA 92717, U.S.A.

temperature and assumed scale height for each species. We assume, as in Houghton *et al.* (1990), that the surface temperature is in equilibrium with the radiative forcing in the year 1765. The change in forcing at the tropopause for a halocarbon species, j, at time, t, is defined relative to the corresponding reference value in the year 1765 as

$$\Delta F_j[t] \equiv R_j(f_j[t] - f_j[1765]), \tag{1}$$

where $f_j[t]$ is the tropospheric concentration of species, j, at time, t, and $f_j\,[1765] = 0$ for all halocarbons. The coefficients, R_js, for the halocarbons are given in Table 1. This forcing corresponds to the direct greenhouse forcing and exclude any indirect forcing that may arise due to the redistribution of other greenhouse gases. (See Houghton *et al.*, 1990; Ramaswamy *et al.*, 1992; WMO, 1992, chap. 7, for discussions of the indirect greenhouse effect.) In the calculations, the R_js for HCFCs and HFCs are held fixed and assumed to be independent of other trace gases and global temperature.

One can define an instantaneous equilibrium warming (Hansen *et al.*, 1989) for a given $\Delta F_j[t]$ at any time, t, by

$$\Delta T_j^e[t] = \Delta F_j[t]/B, \tag{2}$$

where B is the climate feedback parameter. The value of B depends on the physical and dynamical processes within the model such as the prediction of changes in water vapor, cloud cover and sea-surface temperatures for increased temperature. It may vary for different species because different vertical distributions of radiative forcing may lead to different feedbacks (Wang *et al.*, 1991; Molnar and Wang, 1992). However, we assume here that B is the same for all species.

There are many models with varying degrees of geophysical details that have been used to calculate the realized temperature response to a specified radiative forcing (Hansen *et al.*, 1984; Wigley and Schlesinger, 1985; Fisher *et al.*, 1990; Houghton *et al.*, 1990). If a time-dependent change in forcing at the tropopause ($\Delta F[t]$) is introduced, the instantaneous net imbalance at the tropopause (F^{net}) changes according to (Dickinson, 1986; WMO, 1986; Prather, 1989):

$$F^{\text{net}}[t] = \Delta F[t] - B\Delta T[t], \tag{3}$$

where $\Delta T[t]$ is the change in surface temperature relative to 1765 and B is the model climate feedback parameter as discussed above. One can solve for the time-dependent response, $\Delta T^{\text{d}}[t]$, using

$$\frac{\text{d}}{\text{d}t}\Delta T^{\text{d}}[t] = F^{\text{net}}[t]/C = \Delta F[t]/C - B\Delta T^{\text{d}}[t]/C, \tag{4}$$

where we have introduced C as the effective heat capacity or thermal inertia of the Earth. The exact value for C depends on the efficiency of heat exchange between the mixed-layer and the thermocline in the ocean. If there is limited heat exchange with the deep ocean, the effective heat capacity of the earth is estimated to be 10 W m^{-2} °C^{-1} yr, corresponding to the heat capacity of a 100 m deep mixed-layer (Hansen *et al.*, 1981). The value of C should be larger and could be a function of the surface temperature if ocean mixing responds to climate change. When C and ΔF are constant in time, a uniform forcing gives a solution for Equation (4) in the form

$$\Delta T^{\text{d}}[t] = \frac{\Delta F}{B}(1 - \exp(-t/\tau)), \tag{5}$$

where τ, defined as C/B, can be identified as the characteristic response time of the climate system. With the assumption that $\Delta F_j(t)$, B and C are independent of the absolute temperature and other species concentrations, we can linearly separate Equation (4) and ascribe a unique greenhouse warming for each species, ΔT_j^{d}, by

$$\frac{\text{d}}{\text{d}t}\Delta T_j^{\text{d}}[t] = (\Delta F_j[t] - B\Delta T_j^{\text{d}}[t])/C. \tag{6}$$

The sum of Equation (6) over all species results in Equation (4). The per cent contribution from the halocarbons is defined as

$$\sum_h \Delta T_h^{\text{d}}[t] \Big/ \sum_j \Delta T_j^{\text{d}}[t], \tag{7}$$

where subscript h is restricted to halocarbons and subscript j includes also CO_2, CH_4 and N_2O. Thus, this method also allows us to ascribe a unique warming to each greenhouse gas.

Table 1. Lifetimes and forcing at the tropopause for the species

Species	Lifetime* (years)	$R \equiv \Delta F$/ppb† (W m^{-2} ppb^{-1})
F-11	60	0.18
F-12	120	0.25
F-113	90	0.22
F-114	200	0.26
F-115	400	0.20
F-22	15	0.15
CCl_4	50	0.08
CH_3CCl_3	6	0.038
HCFC (115 amu)	15‡	0.14
HFC (100 amu)	25‡	0.14

*Reference lifetime from Prather and Watson (1990).
†AER model result as reported in Fisher *et al.* (1990).
‡Assumed.

We use the above method to calculate the transient response of the globally averaged temperature ($\Delta T_j^{\text{d}}[t]$) to the radiative forcing of the individual gas ($\Delta F_j[t]$) by adopting values for the climate feedback parameter, B and the characteristic response time of the climate system, τ. The values cited for B for a doubling of CO_2 from energy-balance models and general circulation models range from 0.9 to 2.5 W m^{-2} °C^{-1} (Cess *et al.*, 1989; Houghton *et al.*, 1990), corresponding to a warming of 4.9–1.8 °C for a forcing of 4.4 W m^{-2} from CO_2 doubling. Previous models (Hansen *et al.*, 1984; Wigley and Schlesinger, 1985) assumed that oceanic uptake of heat below the mixed layer is by diffusion and showed that τ is proportional to K/B^2, where K is the effective thermal diffusivity of the ocean. For example, with $K = 1$ $cm^2 s^{-1}$ and $B = 1.4$ W m^{-2} °C^{-1}, Hansen *et al.* (1984) calculated $\tau = 55$ years. We adopt here values of 1.4 W m^{-2} °C^{-1} for B and 40 years for τ. Results for different values of B and τ will be discussed.

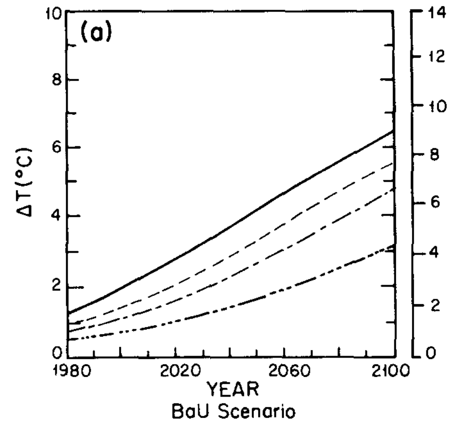
Figure 1 shows the calculated $\Delta T^e[t]$ and $\Delta T^d[t]$ relative to 1765 due to CO_2, CH_4 and N_2O using the radiative forcing given for the business as usual (BaU) case and case D in table 2-7 of the IPCC report (Houghton *et al.*, 1990). These two cases correspond to concentrations for CO_2, N_2O and CH_4 in the year 2100 of 825 ppmv, 415 ppbv and 4.0 ppmv; and 450 ppmv, 370 ppbv and 1.5 ppmv respectively. The calculations used $B = 1.4$ W m^{-2} °C^{-1} and response times of 20, 40 and 100 years. As expected for the case with monotonically increasing forcing, ΔT^d always lags behind ΔT^e (Wigley and Schlesinger, 1985). Our results are similar to those reported in Houghton *et al.* (1990) which uses a 1-D energy-balance climate model with an upwelling-diffusion ocean (Schlesinger and Jiang, 1991). The calculated warmings in 1980 for values of B between 1.0 and 3.0 W m^{-2} °C^{-1} ranges from 0.35 to 1.2 °C (not shown), bounding the value of 0.5 °C derived from observed trends (Houghton *et al.*, 1990).

SCENARIOS FOR CALCULATION

Over the next decades, production of CFCs is scheduled to be phased out, while emissions of their alternatives are expected to increase (Montreal Protocol, 1987; London Amendment, 1990). Prather and Watson (1990) examined the time-dependent response of atmospheric chlorine concentrations to different strategies for CFC phase-out and alternative CFC replacement. They focussed on peak chlorine levels and the subsequent rate of decrease in atmospheric chlorine content. To obtain the radiative forcing, it is necessary to calculate the time-dependent tropospheric concentrations of the halocarbons from the given emission scenarios. These are calculated using the method described in Prather and Watson (1990) by equating emission rates with production rates. More accurate treatment would account for use and banking of halocarbons between production, use and emissions (Wigley, 1988). The atmospheric lifetimes that are used in the calculations are taken from Prather and Watson (1990) and are given in Table 1. These are current best estimates of the lifetimes based on model calculations and observations. The typical uncertainty range is about a factor of 1.5 to 2.

Production rates prior to 1985 are taken from CMA (1990) for CFC-11 and CFC-12, Midgley (1989) for CH_3CCl_3, and WMO (1986) for CFC-113, CFC-114, CCl_4 and HCFC-22. Production rates for 1985 are taken from Prather and Watson (1990). A 4% per year growth in production (i.e. emission) is assumed for CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, CH_3CCl_3, CCl_4 and HCFC-22 between the years 1985 and 1990. Production for all species is assumed to remain constant between 1990 and 2000. Although additional information is now available to update the production rates after 1985, we decided to keep the previous assumptions so that they can be compared directly with the scenarios used in Prather and Watson (1990) and WMO (1992).

Most of the scenarios assumed phase-out of the HCFCs by 2030 in order to meet the goal of reducing chlorine content below 2 ppbv by the year 2075. We assume that concern over ozone depletion will lead to a phase-out of HCFCs around the year 2030; however, no such restriction is assumed for the HFCs since they contain no chlorine. The calculations performed are



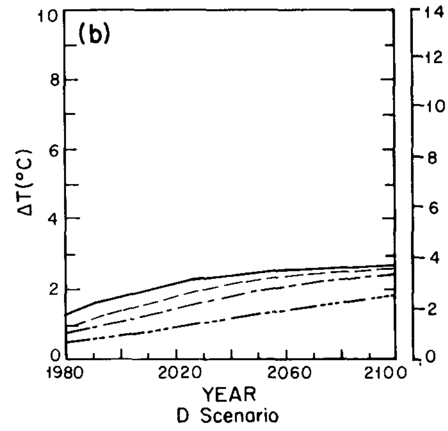


Fig. 1. Calculated equilibrium (——) and realized surface warming (°C) due to increases in CO_2, CH_4 and N_2O for the business as usual (BaU) scenario (a) and scenario D (b) in Houghton *et al.* (1990). The forcing ($\Delta F[t]$) can be read off the equilibrium curve using the scale on the right. The temperature responses are calculated with $B = 1.4$ Wm^{-2} °C^{-1} and $\tau = 24$ (- - -), 40 (-·-·-) and 100 (- ··· - ···) years.

Table 2. Summary of emission scenarios

Scenario 1	Stop emissions of halocarbons (CFC + CCl_4, + CH_3CCl_3 + HCFC-22) after 2000, no substitutes
Scenario 2	Continuous emissions of halocarbons at 1990 rates (2214 ktons yr^{-1}) after 2000
Scenario 3	Stop emissions of halocarbons after 2000; 50% substitution of 1985 emissions of 1820 ktons yr^{-1} with 80:20 split between HCFCs and HFCs; 3% per year growth in emissions for both HCFCs and HFCs; stop HCFC emissions in 2030; HFCs continue to grow at 3% per year
Scenario 4	Stop emissions of halocarbons after 2000; 100% substitution of 1985 emissions with 80:20 split between HCFCs and HFCs; emissions for both HCFCs and HFCs held constant; stop HCFC emissions in 2030; HFCs continue as before
Scenario 5	Same as scenario 3 except that HFC emissions replace HCFC emissions in 2030 and continue to grow at 3% per year

intended to illustrate the climate response to the range of parameters that define the scenarios.

Definition of emission scenarios after 2000 are given in Table 2. Substitution levels referred to in scenarios 3–5 apply to replacement of the 1985 emissions (100% = 1820 ktons y^{-1}), using an 80:20 split between HCFCs and HFCs. The findings of the technological review panel for the Montreal Protocol (UNEP, 1992) indicated that the demand for CFC products will diminish by one-third due to conservation; another third will be met by non-halocarbon alternatives; and the remaining third will be met by halocarbon products, with a 75:25 split between HCFCs and HFCs. The 80:20 split assumed here corrects for the continued use or substitution of current non-CFC halocarbons (e.g. CH_3CCl_3 and HCFC-22) used in refrigeration, foam blowing and cleaning. Although the properties of these chemicals are similar to those of the HCFCs, we assume that they will also be replaced by a mix of HCFCs and HFCs. Scenario 3 is identified here as the most likely scenario, incorporating a 50% substitution of current halocarbon usage with a 3% per year growth for both HCFCs and HFCs after the year 2000. The 3% per year value reflects the assumption of no growth in CFC alternatives in the developed world and a 10% per year growth in developing countries. The zero growth in CFC alternative does not imply a stagnant economy for the developed world; we expect that conservation, improved efficiency, recovery practice and not-in-kind technology will continue to hold the usage fixed despite growth in applications.

Rather than considering specific individual substitutes, we will use a proxy substitute as in Prather and Watson (1990). The lifetimes of the HCFCs and HFCs range from 2 to 20 years and 2 to 40 years, respectively (Derwent and Volz-Thomas, 1990; Prather, 1990; Prather and Spivakovsky, 1990; Fisher *et al.*, 1990). We adopt conservative values of 15 and 25 years for the proxy HCFC and HFC. It is also assumed that the forcing for all proxy substitutes are 0.14 W m^{-2} $ppbv^{-1}$ corresponding to the averages of the HCFC and HFC values reported in Fisher *et al.* (1990).

RESULTS

The integrated nature of the realized warming smooths over short-term fluctuations in forcing, as seen by comparing equilibrium warmings (Fig. 2a) and realized warmings (Fig. 2b) for four selected halocarbon scenarios calculated with $B = 1.4\ W m^{-2} {}^{\circ}C^{-1}$ and $\tau = 40$ years. In scenario 2, where the emissions of CFCs, CCl_4, CH_3CCl_3 and HCFC-22 were continued indefinitely past 1990 at the sum total of 2214 ktons yr^{-1}, the calculated warming continues to increase, reaching 0.55 and 0.7 °C by 2100 for the realized and equilibrium values, respectively, with the realized warming lagging behind the equilibrium warming. In contrast, for scenario 1 with a complete phase-out of halocarbons after the year 2000, the realized warming reaches a smooth maximum of 0.15 °C about 40 years after the peak equilibrium value of 0.25 °C. Thus, the realized warming is committed for a longer time and the calculated warming of 0.11 °C is 50% greater than the equilibrium value of 0.08 °C at 2100.

In scenario 3, all halocarbon emissions after 2000 are replaced by 728 ktons yr^{-1} of HCFCs and 182 ktons yr^{-1} of HFCs. With the 3% per year growth, the HFC emissions reach 3500 ktons yr^{-1} by the year 2100. The warming in this case is smaller than that in case 2, despite the much larger emissions of HFCs around 2100. The lack of a minimum in the realized warming for scenario 3 underscores the complex relation between the climate response and the instantaneous forcing. Comparison of the warmings for scenarios 1 and 3 indicates that the CFCs left in the atmosphere from emissions before 2000 are still responsible for 50% of the calculated halocarbon warming by 2100 in this scenario.

For comparison, we included a case (scenario 4) which represents 100% substitution of the 1985 production by HCFCs and HFCs with no growth and phase-out of HCFCs in 2030. Because of the shorter lifetime and smaller forcing, the warming is significantly smaller compared to scenario 2. In scenario 5, the HCFC emissions at 2030 are replaced by HFC emissions which are assumed to grow at 3% per year.

The calculated realized warming exceeds that of scenario 2 by 2080 reaching 0.8 °C by 2100 (not shown) when the total emissions are 17, 500 ktons yr^{-1}, or a factor of 8 larger than the 1985 emissions.

The percentage contribution of the halocarbons to the total realized warming for two different IPCC scenarios shown in Fig. 1 are depicted in Figs 3a and 3b, respectively. The calculated warming (for CO_2, CH_4 and N_2O alone) is a factor of 1.8 smaller in scenario D by the year 2100 and the relative contributions from CFCs and CFC substitutes are larger by a corresponding amount. Results for other values of B (not shown) are very similar indicating that the percentage warming is not sensitive to the choice of B and τ. Contribution from the halocarbons would be limited to 12–18% of the total warming in scenario D, even if emissions were allowed to continue indefinitely at the 1990 rates. A complete phase-out of CFCs in 2000 without substitutes would limit this fraction to less than 10% in the next century leading to stabilization of the halocarbon-induced greenhouse warming both in absolute value and relative to the likely CO_2-generated warming. The warming for scenario 3 corresponds to 10–13% of the total warming in the year 2040, and 4–6 or 6–10% in the year 2100, depending on the assumptions made for other trace gases. Finally, continued growth in the emissions of the CFC substitutes beyond 2030 (scenario 5) could lead to a warming in the year 2100 that approaches 30% of the combined effects of CO_2, N_2O and CH_4 in scenario D.

The above results will be different if the actual atmospheric lifetimes are different from those listed in Table 1. For example, longer lifetimes for the halocarbons would result in larger warming. The exact effect has to be evaluated on a case-by-case basis as new information on the individual lifetimes becomes available. An estimate can be made as follows. In both scenarios 1 and 2, the warming in 2100 is dominated by the contribution from CFC-12. If the actual lifetime for CFC-12 were 1.5 times longer than listed, the calculated forcing at 2100 would be 35 and 15% larger for scenarios 1 and 2, respectively.

CONCLUDING REMARKS

We limited our discussion to the direct greenhouse effects of the trace gases. Indirect effects attributable to the degradation products of the greenhouse gas (e.g. CO_2 and H_2O from oxidation of CH_4) and redistribu-

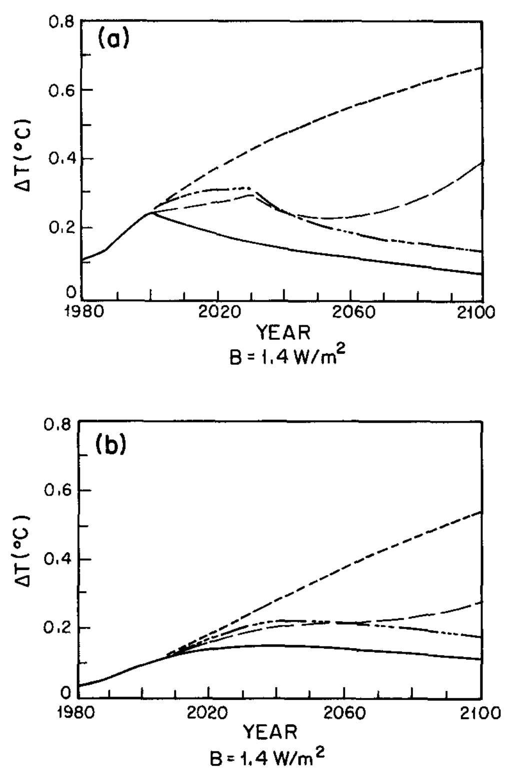
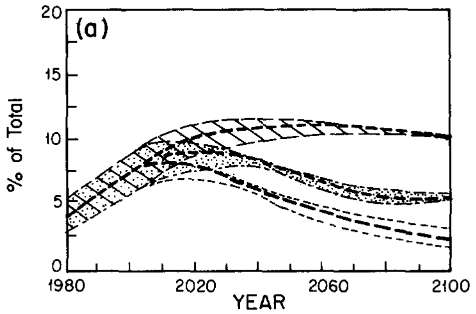
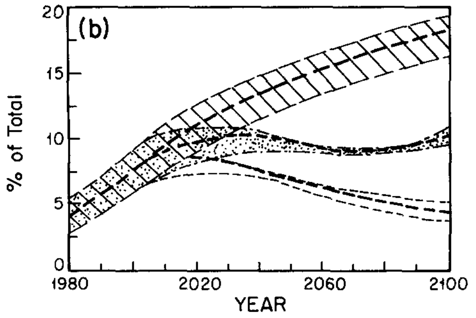


Fig. 2. Calculated equilibrium (a) and realized warmings (b) due to different halocarbon scenarios. The warmings are calculated using $B = 1.4$ Wm^{-2} °C^{-1} and $\tau = 40$ years. Scenario 1 (——), scenario 2 (- - - -), scenario 3 (– – – –) and scenario 4 (- ··· - ···). See Table 2 and text for discussion of halocarbon scenarios.



Scenario BaU used for "background"



Scenario D used for "background"

Fig. 3. Per cent contribution of halocarbons to total realized greenhouse warming. Warmings relative to BaU (a) and scenario D (b). See Table 2 and text for discussion of scenarios. The heavy set curves are calculated using $B = 1.4$ W m^{-2}°C^{-1} and $\tau = 40$ years. Each heavy set curve is bounded by two light set curves that are calculated with $\tau = 24$ and 100 years. The scenarios are: scenario 1, unshaded; scenario 2, hatched; scenario 3, dimpled.

tion of ozone (e.g. ozone changes in the upper troposphere associated with CH_4 increases and ozone changes in the lower stratosphere associated with N_2O and CFC emissions) could modify the global warming effects in a significant way (see Houghton *et al.*, 1990; Ramaswamy *et al.*, 1992; WMO, 1992). These effects could be accounted for in the method described here by incorporating the indirect radiative forcing changes and different values of B_j for each species. However, with B_j different for different species, Equation (4) can no longer be separated into its components as in Equation (6), making it less straightforward to quantify the per cent contribution from each species.

While the limitations of this simple approach are quite obvious, it provides an efficient method for evaluating the likely transient climate response to CFC phase-out and substitution, similar to the approach of using chlorine loading to estimate ozone impact (Prather and Watson, 1990). In view of the importance of transient effects in the calculated global warming, we recommend that formulation of the control policy for these chemicals be based on consideration not only of static equilibrium indices such as HGWPs and GWPs, but also of the time evolution of the expected warming.

Acknowledgement—We thank Dr R. T. Watson for discussions. Work at AER Inc. was supported by the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS).

REFERENCES

Cess R. D. *et al.* (1989) Interpretation of cloud climate feedback as produced by atmospheric general circulation models. *Science* **245**, 513–516.

CMA (Chemical Manufacturers Association) (1990) Production, sales and release of CFC-11 and CFC-12 through 1988. CMA, Washington, DC.

Derwent R. G. and Volz-Thomas A. (1990) The tropospheric lifetimes of halocarbons and their reactions with OH radicals: an assessment based on the concentration of ^{14}CO. In *Scientific Assessment of Stratospheric Ozone*: 1989 *World Meteorological Organization, Global Ozone Research and Monitoring Project*. Report No. 20, WMO, Geneva.

Dickinson R. E. (1982) Modeling climatic changes due to carbon dioxide increases. In *Carbon Dioxide Review* (edited by Clark W. C.), pp. 101–133. Clarendon Press, New York.

Dickinson R. E. (1986) How will climate change? In *The Greenhouse Effect, Climate Change, and Ecosystems* (edited by Bolin B., Doos B. R., Jagger J. and Warrick R. A.), pp. 207–270. Wiley, Chichester.

Fisher D. A., Hales C. H., Wang W.-C., Ko M. K. W. and Sze N. D. (1990) Model calculations of the relative effects of CFCs and their replacements on global warming. *Nature* **344**, 513–516.

Hansen J., Johnson D., Lacis A., Lebedeff S., Lee P., Rind D. and Russell G. (1981) Climate impact of increasing atmospheric carbon dioxide. *Science* **213**, 957–964.

Hansen J., Lacis A., Rind D., Russell G., Stone P., Fung I., Ruedy R. and Lerner J. (1984) Climate sensitivity: analysis of feedback mechanisms. In *Climate Processes and Climate Sensitivity*, Maurice Ewing Series 5 (edited by Hansen J. E. and Takasashi T.). American Geophysical Union, Washington, DC.

Hansen J., Russell G., Lacis A., Fung I., Rind D. and Stone P. (1985) Climate response times: dependence on climate sensitivity and ocean mixing. *Science* **229**, 857–859.

Hansen J., Lacis A. and Prather M. (1989) Greenhouse effect of chlorofluorocarbons and other trace gases. *J. geophys. Res.* **94**, 16417–16421.

Houghton J. T., Jenkins G. J. and Ephraums J. J. (Eds) (1990) *Scientific Assessment of Climate Change*. Cambridge University Press, Cambridge.

Lashof D. A. and Ahuja D. R. (1990) Relative contributions of greenhouse gas emissions to global warming. *Nature* **344**, 529–531.

London Amendment to the Montreal Protocol (1990) UNEP.

Midgley P. (1989) The production and release to the atmosphere of 1.1, 1-trichloroethane (methyl chloroform). *Atmospheric Environment* **23**, 2663–2665.

Montreal Protocol (1987) On substances that deplete the ozone layer final act. UNEP.

Molnar G. and Wang W.-C. (1992) Effects of cloud optical property feedbacks on the greenhouse warming. *J. Clim.* **5**, 814–821.

Prather M. J. (1989) *Proc. Workshop An Assessment Model for Atmospheric Composition*, NASA/Goddard Institute for Space Studies, New York, 10–13 January 1988. NASA conference publication 3023.

Prather M. J. (1990) Tropospheric hydroxyl concentrations and the lifetimes of hydrochlorofluorocarbons (HCFCs). In *Scientific Assessment of Stratospheric Ozone*: 1989 *World Meteorological Organization, Global Ozone Research and Monitoring Project*. Report No. 20, WMO, Geneva.

Prather M. J. and Spivakovsky C. M. (1990) Tropospheric OH and the lifetimes of hydrochlorofluoro-carbons. *J. geophys. Res.* **95**, 18723–18729.

Prather M. J. and Watson R. T. (1990) Stratospheric ozone depletion and future levels of atmospheric chlorine and bromine. *Nature* **344**, 729–734.

Ramanathan V. (1975) Greenhouse effect due to chlorofluorocarbons: climatic implications. *Science* **190**, 50.

Ramanathan V. (1981) The role of ocean–atmosphere interactions in the CO_2 climate problem. *J. atmos. Sci.* **38**, 918–930.

Ramanathan V. (1982) Commentary on climatic effects of minor atmospheric constituents. In *Carbon Dioxide Review*: 1982 (edited by Clark W. C.). Clarendon Press, New York.

Ramanathan V., Cicerone R. J., Singh H. B. and Kiehl J. T. (1985) Trace gas trends and their potential role in climate change. *J. geophys. Res.* **90**, (D3), 5547–5566.

Ramaswamy V., Schwarzkopf M. D. and Shine K. P. (1992) Radiative forcing of climate from halocarbon-induced global stratospheric loss. *Nature* **355**, 810–812.

Schlesinger M. E. and Jiang X. (1991) Revised projection of future greenhouse warming. *Nature* **300**, 219–221.

UNEP (United Nations Environmental Programme) (1992) Montreal Protocol on substances that deplete the ozone layer, 1991 assessment. Report of the Technology and Economic Assessment Panel.

Wang W. C., Yung Y. L., Lacis A. A., Mo T. and Hansen J. E. (1976) Greenhouse effects due to man-made perturbations of trace gases. *Science* **194**, 685–690.

Wang W.-C., Dudek M. P., Liang X.-Z. and Kiehl J. T. (1991) Inadequacy of effective CO_2 as a proxy in simulating the greenhouse effect of other radiatively active gases. *Nature* **350**, 573–577.

Wigley T. M. L. (1988) Future CFC concentrations under the Montreal Protocol and their greenhouse effect. Implications. *Nature* **335**, 333.

Wigley T. M. L. and Schlesinger M. E. (1985) Analytical solution for the effect of increasing CO_2 on global mean temperature. *Nature* **315**, 649–652.

WMO (World Meteorological Association) (1986) *Atmospheric Ozone* 1985: *Assessment of Our Understanding of the Processes Controlling Its Present Distribution and Change.* WMO report no. 16, WMO, Geneva.

WMO (World Meteorological Association) (1990) *Scientific Assessment of Stratospheric Ozone*: 1989 *World Meteorological Organization, Global Ozone Research and Monitoring Project.* Report No. 20, WMO, Geneva.

WMO (World Meteorological Association) (1992) *Scientific Assessment of Ozone Depletion, World Meteorological Organization, Global Ozone Research and Monitoring Project.* Report No. 25, WMO, Geneva.