CHAPTER 13

Ozone Depletion Potentials, Global Warming Potentials, and Future Chlorine/Bromine Loading

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CHAPTER 13

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Contents

SCIENTIFIC SUMMARY

Scientific indices representing the relative effects of different gases upon ozone depletion and climate forcing are presented. Several scenarios for future chlorine/bromine loading are described that are aimed at implementation of the Copenhagen Amendments of the Montreal Protocol and the consideration of possible further options. Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) are evaluated with improved models and input data, and their sensitivities to uncertainties are considered in greater detail than in previous assessments. Major new findings are as follows:

- *Peak levels of ozone-depleting compounds are expected at stratospheric altitudes in the late 1990s.* Because current emission estimates suggest that the tropospheric chlorine/bromine loading will peak in 1994, further reductions in emissions would not significantly affect the timing or magnitude of the peak stratospheric halogen loading expected later this decade (*i.e.*, about 3-5 years after the tropospheric peak).

- *Approaches to lowering stratospheric chlorine and bromine abundances are limited.* Further controls on ozone-depleting substances would be unlikely to change the timing or the magnitude of the peak stratospheric halocarbon abundances and hence peak ozone loss. However, there are four approaches that would steepen the initial fall from the peak halocarbon levels in the early decades of the next century:

  (i) If emissions of methyl bromide from agricultural, structural, and industrial activities were to be eliminated in the year 2001, then the integrated effective future chlorine loading above the 1980 level (which is related to the cumulative future loss of ozone) is predicted to be 13% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.

  (ii) If emissions of hydrochlorofluorocarbons (HCFCs) were to be totally eliminated by the year 2004, then the integrated effective future chlorine loading above the 1980 level is predicted to be 5% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.

  (iii) If halons presently contained in existing equipment were never released to the atmosphere, then the integrated effective future chlorine loading above the 1980 level is predicted to be 10% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.

  (iv) If chlorofluorocarbons (CFCs) presently contained in existing equipment were never released to the atmosphere, then the integrated effective future chlorine loading above the 1980 level is predicted to be 3% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.

- *Failure to adhere to the international agreements will delay recovery of the ozone layer.* If there were to be additional production of CFCs at, for example, 20% of 1992 levels for each year through 2002 and ramped to zero by 2005 (beyond that allowed for countries operating under Article 5 of the Montreal Protocol), then the integrated effective future chlorine loading above the 1980 level is predicted to be 9% more over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.

- *Production of CF_3 from dissociation of CFCs, HCFCs, and hydrofluorocarbons (HFCs) is highly unlikely to affect ozone.* ODPs of HFCs containing the CF_3 group (such as HFC-134a, HFC-23, and HFC-125) are highly likely to be less than 0.001, and the contribution of the CF_3 group to the ODPs of HCFCs (*e.g.*, from HCFC-123) and CFCs is believed to be negligible.

- *ODPs for several new compounds such as HCFC-225ca, HCFC-225cb, and CF_3I have been evaluated using both semi-empirical and modeling approaches,* and estimated to be 0.03 or less.

- *Both the direct and indirect components of the GWP of methane have been estimated using model calculations.* Methane's influence on the hydroxyl radical and the resulting effect on the methane response time lead to substantially longer response times for decay of emissions than OH removal alone, thereby increasing the GWP. In addition, indirect effects including production of tropospheric ozone and stratospheric water vapor were considered and are estimated to range from about 15 to 45% of the total GWP (direct plus indirect) for methane.

- *GWPs including indirect effects of ozone depletion have been estimated for a variety of halocarbons (CFCs, halons, HCFCs, etc.), clarifying the relative radiative roles of different classes of ozone-depleting compounds.* The net GWPs of halocarbons depend strongly upon the effectiveness of each compound for ozone destruction; the halons are highly likely to have negative net GWPs, while those of the CFCs are likely to be positive over both 20- and 100-year time horizons.

- *GWPs are not very sensitive to likely future changes in CO_2 abundances or major climate variables.* Increasing CO_2 abundances (from about 360 ppmv currently to 650 ppmv by the end of the 22nd century) could produce 20% larger GWPs for time horizons of the order of centuries. Future changes in clouds and water vapor are unlikely to significantly affect GWPs for most species.

- *GWPs for 16 new chemical species have been calculated, bringing the number now available to 38.* The new species are largely HFCs, which are being manufactured as substitutes for the CFCs, and the very long-lived fully fluorinated compounds, SF_6 and the perfluorocarbons.

13.1 INTRODUCTION

Numerical indices representing the relative impacts of emissions of various chemical compounds upon ozone depletion or global radiative forcing can be useful for both scientific and policy analyses. Prominent among these are the concepts of Chlorine/Bromine Loading, steady-state and time-dependent Ozone Depletion Potentials (ODPs), and Global Warming Potentials (GWPs), which form the focus of this chapter. Detailed descriptions of the formulations of these indices are provided later. Here we briefly review the broad definitions of these concepts and cite some of their uses and limitations:

Chlorine/Bromine Loading

Chlorine/bromine loading represents the amount of total chlorine and bromine in the troposphere or stratosphere. Stratospheric chlorine/bromine loading depends upon the surface emissions of gases such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and halons (which are based in large part upon industrial estimates of usage) and upon knowledge of the reactivity and hence the atmospheric lifetimes and chemical roles of those and related compounds. Recent depletions in stratospheric ozone in Antarctica and in the Arctic have been linked to anthropogenic halocarbon emissions (see Chapter 3), and the weight of evidence suggests that ozone depletions in midlatitudes are also related to the emissions of these compounds (see WMO, 1992 and Chapter 4 of this document). Thus, the chlorine/bromine loading is a key indicator of past and future changes in ozone. However, it should be recognized that chlorine/bromine loading is a measure only of changes in halogen content. It does not account for additional factors that could also affect the time-dependent changes in atmospheric ozone or the linearity of their relationship to chlorine/bromine loading (*e.g.*, carbon dioxide trends that can also affect stratospheric temperatures).

Ozone Depletion Potentials

Ozone Depletion Potentials (ODPs) provide a relative measure of the expected impact on ozone per unit mass emission of a gas as compared to that expected from the same mass emission of CFC-11 integrated over time (Wuebbles, 1983; WMO, 1990, 1992; Solomon *et al.*, 1992). Their primary purpose is for comparison of relative impacts of different gases upon ozone (*e.g.*, for evaluating the relative effects of choices among different CFC substitutes upon ozone). As in prior analyses, the ODP for each substance presented herein is based on the mass emitted into the atmosphere, and not on the total amount used. In some cases (such as emissions of CH_3Br in soil fumigant applications) not all of the compound used may be emitted into the global atmosphere (see Chapter 10). Steady-state ODPs represent the cumulative effect on ozone over an infinite time scale (also referred to here as "time horizon"). Time-dependent ODPs describe the temporal evolution of this ozone impact over specific time horizons (WMO, 1990, 1992; Solomon and Albritton, 1992; see Section 13.4.5). Atmospheric models and semi-empirical methods have been used in combination to best quantify these relative indices (Solomon *et al.*, 1992; WMO, 1992). As a relative measure, ODPs are subject to fewer uncertainties than estimates of the absolute percentage ozone depletion, particularly when only the ODP differences among various chlorinated gases are considered. Models used to evaluate ODPs now include better representations of midlatitude and polar vortex heterogeneous chemistry processes than those used earlier. Comparisons of model and semi-empirical methods reduce the uncertainties in ODPs. However, evaluations of ODPs are still subject to uncertainties in atmospheric lifetimes and in the understanding of stratospheric chemical and dynamical processes. The recent re-evaluation of the chemical rate and products for the reaction of $BrO + HO_2$ and resulting effects on ODPs for bromocarbons provide a graphic example of potential impacts of such uncertainties (see Section 13.4). Like chlorine/bromine loading, ODPs do not include other processes (such as changes in CO_2 and hence stratospheric temperatures) that could affect the future impacts of different gases upon ozone.

Global Warming Potentials

Global Warming Potentials provide a simple representation of the relative radiative forcing resulting from a unit mass emission of a greenhouse gas compared to a reference compound. Because of its central role in concerns about climate change, carbon dioxide has generally been used as the reference gas. However, because of the complexities and uncertainties associated with the carbon cycle, extensive effort has been put into evaluating the effects on GWPs from uncertainties in the time-dependent uptake of carbon dioxide emissions. As described in Chapter 4 of IPCC (1994), calculations made with climate models indicate that, for well-mixed greenhouse gases at least, the relationship between changes in the globally integrated adjusted radiative forcing at the tropopause and global-mean surface temperature changes is independent of the gas causing the forcing. Furthermore, similar studies indicate that, to first order, this "climate sensitivity" is relatively insensitive to the type of forcing agent (*e.g.*, changes in the atmospheric concentration of a well-mixed greenhouse gas such as CO_2, or changes in the solar radiation reaching the atmosphere). GWPs have a number of important limitations. The GWP concept is difficult to apply to gases that are very unevenly distributed and to aerosols (see, *e.g.*, Wang *et al.*, 1991, 1993). For example, relatively short-lived pollutants such as the nitrogen oxides and the volatile organic compounds (precursors of ozone, which is a greenhouse gas) vary markedly from region to region within a hemisphere and their chemical impacts are highly variable and nonlinearly dependent upon concentrations. Further, the indices and the estimated uncertainties are intended to reflect global averages only, and do not account for regional effects. They do not include climatic or biospheric feedbacks, nor do they consider any environmental impacts other than those related to climate. The direct GWPs for a number of infrared-absorbing greenhouse gases have been analyzed in this report, with a particular emphasis on a wide range of possible substitutes for halocarbons. The evaluation of effects on other greenhouse gases resulting from chemical interactions (termed indirect effects) has been more controversial. Underlying assumptions and uncertainties associated with both direct and indirect GWPs are discussed briefly in Section 13.5.

13.2 ATMOSPHERIC LIFETIMES AND RESPONSE TIMES

Atmospheric lifetimes or response times are used in the calculation of both ODPs and GWPs. The list of compounds considered in this assessment is an extension of those in WMO (1992), primarily reflecting the consideration of additional possible replacements for CFCs and halons. Additional compounds, such as the unusually long-lived perfluorocarbons and SF_6, are also included because of their potential roles as greenhouse gases and because some have been suggested as CFC and halon replacements.

After emission into the current or projected atmosphere, the time scale for removal (*i.e.*, the time interval required for a pulse emission to decay to 1/e of its initial perturbed value) of most ozone-depleting and greenhouse gases reflects the ratio of total atmospheric burden to integrated global loss rate. As such, the total lifetime must take into account all of the processes determining the removal of a gas from the atmosphere, including photochemical losses within the troposphere and stratosphere (typically due to photodissociation or reaction with OH), heterogeneous removal processes, and permanent removal following uptake by the land or ocean. In a few cases, the time scale for removal of a gas from the atmosphere cannot be simply characterized or is dependent upon the perturbation and/or the background atmosphere and other sources; in those cases (chiefly CO_2 and CH_4) we refer to removal of a pulse as the response time or decay response.

Alternatively, atmospheric lifetimes can be defined by knowledge of global source strengths together with the corresponding mean atmospheric concentrations and trends, but these are usually more difficult to define accurately. The atmospheric lifetime may be a function of time, due to changing photochemistry associated, for example, with ozone depletion or temperature trends, but these effects are likely to be small for at least the next several decades and will not be considered here.

The total lifetimes of two major industrially produced halocarbons, CFC-11 and CH_3CCl_3, have been reviewed and re-evaluated in a recent assessment (Kaye *et al.*, 1994). The empirically derived lifetime for CFC-11 determined in that study is 50 (±5) years (as compared to 55 years in the previous WMO [1992] assessment). As in previous assessments, the lifetimes presented here are not based solely upon model calculations, but use information from measurements to better constrain the lifetimes of these and other gases. The lifetime of CFC-11 is used here to normalize lifetimes for other gases destroyed by photolysis in the stratosphere (based upon scaling to the ratios of the lifetimes of each gas compared to that of CFC-11 obtained in the models discussed in Kaye *et al.*, 1994). This approach could be limited by the fact that different gases are destroyed in different regions of the stratosphere depending upon the wavelength dependence of their absorption cross sections (weakening the linearity of their comparison to CFC-11), particularly if stratospheric mixing is not rapid (see Plumb and Ko, 1992). Depending on absolute calibration factors used by different research groups, Kaye *et al.* (1994) derived a total lifetime for CH_3CCl_3 of either 5.7 (±0.3) years for 1990 or 5.1 (±0.3) years, respectively (see Prinn *et al.*, 1992), compared to 6.1 years in the earlier WMO (1992) assessment. Because of the current uncertainties in absolute calibration, we use a lifetime for CH_3CCl_3 of 5.4 years with an uncertainty range of 0.6 years in this report. From this total atmospheric lifetime, together with the evaluated loss lifetimes of CH_3CCl_3 due to the ocean (about 85 years, with an uncertainty range from 50 years to infinity; see Butler *et al.*, 1991) and stratospheric processes (40 ± 10 years), a tropospheric lifetime for reaction with OH of 6.6 years can be inferred (±25%). The lifetimes of other key gases destroyed by OH (*i.e.*, CH_4, HCFCs, and hydrofluorocarbons [HFCs]) can then be inferred relative to that of methyl chloroform (see, *e.g.*, Prather and Spivakovsky, 1990) with far greater accuracy than would be possible from a priori calculations of the complete tropospheric OH distribution. We note that a few of the newest CFC substitutes (namely, the HFCs -236fa, -245ca, and -43-10mee) have larger uncertainties in lifetimes since fewer kinetic studies of their chemistry have been reported to date. It is likely that methane is also destroyed in part by uptake to soil (IPCC, 1992), but this process is believed to be relatively slow and makes a small contribution to the total lifetime. Possible soil sinks are not considered for any other species.

The special aspects of the lifetime of methane and the response time of a pulse added to the atmosphere were defined in Chapter 2 of IPCC (1994), based largely upon Prather (1994). Those definitions are also employed here. Small changes in CH_4 concentrations can significantly affect the atmospheric OH concentration, rendering the response time for the decay of the added gas substantially longer than that of the ensemble (*i.e.*, longer than the nominal 10-yr lifetime for the bulk concentration of atmospheric CH_4 in the current atmosphere). This is due to the nonlinear chemistry associated with relaxation of the coupled OH-CO-CH_4 system (see Prather, 1994; Lelieveld *et al.*, 1993; and Chapter 2 of IPCC [1994] for further details). This effect was also discussed in IPCC (1990) and IPCC (1992) as an indirect effect on OH concentrations, and thus is not new. It arises through the fact that small changes in OH due to addition of a small pulse of CH_4 slightly affect the rate of decay of the much larger amount of CH_4 in the background atmosphere, thereby influencing the net removal of the added pulse. It is critical to note that the exact value of the CH_4 pulse response time depends upon a number of key factors, including the absolute amount of CH_4, size of the pulse, etc., making its interpretation complex and case-dependent. Here we consider small perturbations to the present atmosphere, and base the definition of the methane pulse response time to be used in calculation of the GWP upon the detailed explanation of the effect as presented in Prather (1994) and in Chapter 2 of IPCC (1994).

Table 13-1 shows the recommended total atmospheric lifetimes for all of the compounds considered here except methyl bromide (the reader is referred to Chapter 10 for a detailed discussion of the lifetime of this important gas). The response time of methane is also indicated. The lifetimes for many compounds have been modified relative to values used in WMO (1992; Table 6-2). The estimates for the lifetimes of many of the gases destroyed primarily by reaction with tropospheric OH (*e.g.*, HCFC-22, HCFC-141b, HCFC-142b, etc.) are about 15% shorter than in WMO (1992), due mainly to recent studies suggesting a shorter lifetime for CH_3CCl_3 based upon improved calibration methods and upon an oceanic sink (Butler *et al.*, 1991). Similarly, the estimates for the lifetimes of gases destroyed mainly by photolysis in the stratosphere (*e.g.*, CFC-12, CFC-113, H-1301) are about 10% shorter than in IPCC (1992) due to a shorter estimated lifetime for CFC-11 and related species. Lifetime estimates of a few other gases have also changed due to improvements in the understanding of their specific photochemistry (*e.g.*, note that the lifetime for CFC-115 is now estimated to be about 1700 years, as compared to about 500 years in earlier assessments). Fully fluorinated species such as SF_6, CF_4, and C_2F_6 have extremely long atmospheric lifetimes, suggesting that significant production and emissions of these greenhouse gases could have substantial effects on radiative forcing over long time scales. In contrast, CF_3I, which is being considered for use as a fire extinguishant and other applications, has an atmospheric lifetime of less than 2 days.

Table 13-1. Lifetimes and response times recommended for ODP and GWP calculations.

Gas	Lifetime or Response Time (yrs)	Reference
CFC-11	50 (±5)	2
CFC-12	102	3
CFC-13	640	1
CFC-113	85	3
CFC-114	300	1
CFC-115	1700	1
CCl_4	42	3
CH_3CCl_3	5.4 (±0.4)	2
$CHCl_3$	0.55	4
CH_2Cl_2	0.41	4
HCFC-22	13.3	4
HCFC-123	1.4	4
HCFC-124	5.9	4
HCFC-141b	9.4	4
HCFC-142b	19.5	4
HCFC-225ca	2.5	4
HCFC-225cb	6.6	4
CH_3Br	1.3	Chapter 10
CF_3Br (H-1301)	65	3
CF_2ClBr (H-1211)	20	3
HFC-23	250	10
HFC-32	6.0	4
HFC-125	36	4
HFC-134	11.9	5
HFC-134a	14	4
HFC-143	3.5	11
HFC-143a	55	4
HFC-152a	1.5	4
HFC-227ea	41	9
HFC-236fa	250	7
HFC-245ca	7	6
HFC-43-10mee	20.8	7
HFOC-125E	82	6
HFOC-134E	8	6
SF_6	3200	1
CF_4	50000	1
C_2F_6	10000	1
C_6F_{14}	3200	1
C_5F_{12}	4100	1
c-C_4F_8	3200	1
CF_3I	< 0.005	8
N_2O	120	3
CH_4 (pulse response)	14.5 ± 2.5	12

Table 13-1. Notes.

1. Ravishankara *et al.* (1993).
2. Prather, private communication 1993, based on NASA CFC report (Kaye *et al.,* 1994) and other considerations as described in text.
3. Average of reporting models in NASA CFC report (Kaye *et al.,* 1994). Scaled to CFC-11 lifetime.
4. Average of JPL 92-20 and IUPAC (1992) with 277 K rate constants for OH+halocarbon scaled against $OH+CH_3CCl_3$ and lifetime of tropospheric CH_3CCl_3 of 6.6 yr. Stratospheric lifetime from WMO (1992).
5. DeMore *et al.* (1993). Used 277 K OH rate constant ratios with respect to CH_3CCl_3, scaled to tropospheric lifetime of 6.6 yr for CH_3CCl_3.
6. Cooper *et al.* (1992). Lifetime values are estimates.
7. W. DeMore (personal communication, 1994) with 277 K rate constants for OH+halocarbon scaled against $OH+CH_3CCl_3$ and lifetime of tropospheric CH_3CCl_3 of 6.6 yr.
8. Solomon *et al.* (1994).
9. Brühl, personal communication based on data for the reaction rate constant with OH provided by Hoescht Chemicals, 1993; Zhang *et al.* (1994) and Nelson *et al.* (1993) with 277 K rate constants for OH+halocarbon scaled against $OH + CH_3CCl_3$ and lifetime of tropospheric CH_3CCl_3 of 6.6 yr.
10. Schmoltner *et al.* (1993) with 277 K rate constants for OH+halocarbon scaled against $OH+CH_3CCl_3$ and lifetime of tropospheric CH_3CCl_3 of 6.6 yr.
11. Barry *et al.* (1994) with 277 K rate constants for OH+halocarbon scaled against $OH+CH_3CCl_3$ and lifetime of tropospheric CH_3CCl_3 of 6.6 yr.
12. Prather (1994) and Chapter 2 of IPCC (1994).

The basis for the recommended lifetimes is described within the Table and its footnotes. These values are used for all calculations presented in this chapter.

13.3 CHLORINE/BROMINE LOADING AND SCENARIOS FOR CFC SUBSTITUTES

13.3.1 Equivalent Tropospheric Chlorine Loading

For the purposes of this report, a detailed assessment of those sources of tropospheric chlorine and bromine loading relevant to stratospheric ozone destruction was carried out. The approach taken is similar to that of Prather and Watson (1990) and previous assessment reports (WMO, 1992). This analysis is more complete in that it includes a description of the time delay between consumption and emission of the ozone-depleting substances. The time delays are based upon uses (*e.g.*, refrigeration, solvents, etc.). The procedure is also discussed in Daniel *et al.* (1994). The best understanding of the past history of emissions of fourteen of the most important halocarbons, together with current estimates of the lifetimes of these gases (Table 13-1) provides the input needed to evaluate past trends. The longest and most complete record of CFC emissions is contained in the industry-sponsored "Production, Sales and Atmospheric Release of Fluorocarbons" report (AFEAS, 1993). This report contains estimates of production in countries not covered in the industry survey. Recently, with declining global production in response to the Montreal Protocol, the fractional contribution to the total of this "unreported" production, a portion of which is in developing (Article 5) countries, has amounted to about 25%. Estimates of unreported production based on matching observed and calculated trends in the relevant trace gases are consistent with AFEAS estimates (see, *e.g.*, the detailed analysis in Cunnold *et al.*, 1994).

Expected uses and the corresponding release times for each of the gases are considered, in order to more accurately determine yearly emission amounts (AFEAS, 1993; Fisher and Midgley, 1993; Gamlen *et al.*, 1986; McCarthy *et al.*, 1977; McCulloch, 1992; Midgley, 1989; Midgley and Fisher, 1993). Possible time-dependent changes in release times (*e.g.*, for improved technologies) are not considered. For methyl bromide, a budget of natural and anthropogenic sources based upon

Chapter 10 is adopted. Anthropogenic sources of methyl bromide are assumed to be zero before 1931. A constant anthropogenic emission is assumed from 1931 to 1994 of 73 ktonnes/year (see Chapter 10). As noted in Chapter 10, it is possible that decreases in methyl bromide emissions associated with the declining use of gasoline additives could have offset some of the known increases in agricultural use of this compound during the 1970s and 1980s. However, precise information is not available. Although this assumption will affect the calculated historical contribution of methyl bromide to equivalent chlorine loading, because of the short lifetime of methyl bromide, it has very little effect on projected contributions. Anthropogenic emission of methyl bromide does not equal production, and this difference is explicitly considered in all calculations of methyl bromide's atmospheric loading and their impacts presented in this chapter.

The calculated contributions of methyl bromide and other bromocarbons to equivalent chlorine loading are more uncertain than that of other compounds. For the purpose of comparing the roles of chlorine- and bromine-containing gases once they reach the stratosphere, it is assumed that each bromine atom is 40 times more damaging to ozone than chlorine (see Section 13.4), allowing evaluation of an "equivalent tropospheric chlorine" that includes an estimate of the net ozone impact of bromocarbons. The enhanced effectiveness of bromine (hereafter referred to as α) depends in principle upon the amount of active chlorine present, making it a time-dependent quantity. However, in the next few decades (*i.e.*, until about 2020), the chlorine content of the stratosphere is expected to change relatively little, making α essentially constant during this period. Towards the middle and latter parts of the twenty-first century, decreases in chlorine abundances will likely lead to increases in the value of α, at least in polar regions. This follows from the fact that the reaction of ClO with itself represents an important ozone loss process in the Antarctic (and Arctic) that is dependent upon the square of the stratospheric chlorine abundance, while the reaction of ClO with BrO is linearly dependent upon the stratospheric chlorine abundance. Thus, as chlorine abundances decline, the reaction of ClO with BrO will become more important relative to ClO + ClO. This and other considerations discussed in Section 13.4 (particularly the role of the HO_2 + BrO reaction in the lower stratosphere) suggest that the adopted value of α of 40 is likely to be a low estimate. A higher value of α would increase the contributions of methyl bromide and the halons. The adopted methyl bromide lifetime of 1.3 years includes an ocean sink. If loss to the ocean were to be slower, the lifetime would be longer and the anthropogenic methyl bromide contribution would be larger. On the other hand, a faster ocean sink would decrease the contribution. Similarly, a decrease (increase) in the fractional emission of methyl bromide used for agricultural purposes would decrease (increase) the calculated contribution from that source. The budget of methyl bromide and its uncertainties are discussed in detail in Chapter 10 of this assessment.

Chlorinated solvents such as CH_2Cl_2, C_2Cl_4, and C_2HCl_3 were not explicitly considered in this analysis. Based upon emission estimates, WMO (1992) suggests that these species are present at about the 35, 32, and 1 pptv levels, respectively, within the current troposphere. Wang *et al.* (1994) present observations of C_2Cl_4 showing average abundances of only 7 pptv. The lifetimes of these gases may be long enough to allow a fraction to reach the stratosphere and thereby contribute to stratospheric chlorine loading. Schauffler *et al.* (1993) report tropospheric measurements of CH_2Cl_2 of about 30 pptv in 1992 and report direct measurements of this gas near the tropical tropopause of about 15 pptv, suggesting substantial transport to the stratosphere. While the abundances of these gases are presently small, increasing use would increase the abundances. At a growth rate of, for example, 3%/year, CH_2Cl_2 and C_2HCl_3 could reach abundances of 0.1 ppbv in 36 and 156 years, respectively. Thus, while these relatively short-lived gases probably contribute little to contemporary stratospheric chlorine loading, there is observational evidence of significant transport to the stratosphere for some species, and continued growth would lead to a greater contribution to stratospheric chlorine loading. On the other hand, a recent survey (P. Midgley, personal communication) indicates that industrial emissions of these gases in the U.S., Europe, and Japan have steadily decreased since 1984, so that current emissions are more likely to be decreasing than increasing.

Water-soluble emissions such as sea salt or volcanic HCl are effectively removed in clouds and rain (see, *e.g.*, Tabazadeh and Turco, 1993) and do not represent significant sources of stratospheric chlorine. Short-lived bromocarbons such as bromoform were also not considered here.

Equivalent chlorine loading was evaluated for eight cases to demonstrate impacts of various assumptions for future use of ozone-depleting substances. A complete description of the scenarios is provided in Table 13-2. Global compliance to the Copenhagen agreements is represented by case A. Estimates of future emissions of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are based on a detailed analysis of projected global demand for each gas carried out by the U.S. Environmental Protection Agency (EPA) to 2030 (D. Hufford, personal communication, 1993). Estimates beyond 2030 will depend on agreements for HCFC use in developing countries; no attempt is made to account for potential use and emissions beyond 2030. Such use would increase the HCFC equivalent chlorine loading. Figure 13-1 shows calculated tropospheric concentrations of HCFCs and HFC-134a based on the EPA analysis.

A complete phase-out of HCFCs after 2030 is assumed, after which time a 2.5%/year increase in HFC-134a is adopted (intended to represent not only HFC-134a itself but the combined impact of a class of hydrofluorocarbons that could be used as HCFC substitutes after 2030). These are important only insofar as their radiative forcing is concerned, since they do not significantly deplete stratospheric ozone (see Section 13.4). The use of shorter-lived or less infrared active gases could reduce the estimated radiative forcing from such compounds. Figure 13-1 shows a steep increase in the projected HFC concentrations in the latter part of the twenty-first century; the effect of such increases on radiative forcing is discussed further in Chapter 8.

Cases B through G demonstrate impacts relative to case A of continued CFC production outside international agreements, an accelerated HCFC phaseout, a methyl bromide phaseout or a 2%/year increase in industrial methyl bromide use, and complete recapture (as opposed to recycling) of halons, CFCs-11, -12, and -113 banked in existing equipment (*i.e.*, refrigeration, air-conditioning, fire extinguishants). Recapture illustrates the impact of potential use of non-ozone depleting substitutes that could reduce future emissions of these compounds. Case H is presented in order to compare the current (Copenhagen) agreements to the earlier London Amendments.

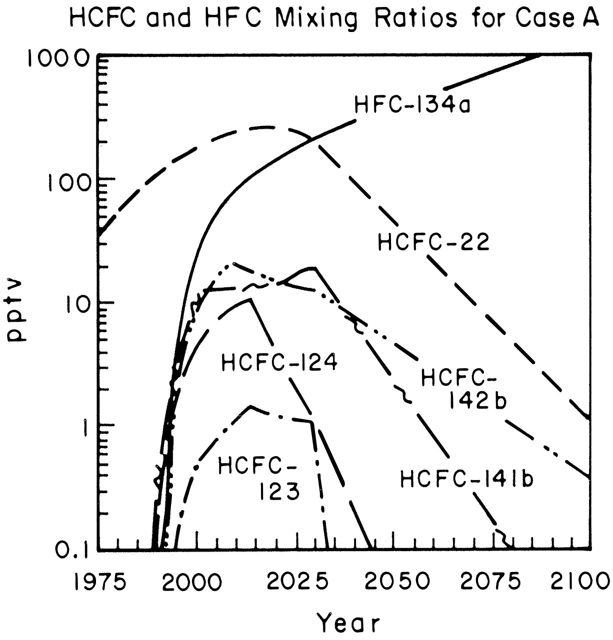

Figure 13-1. Calculated abundances of hydrofluorocarbons and hydrochlorofluorocarbons for case A.

The bottom panel of Figure 13-2 shows the contributions of the various gases considered here to the equivalent tropospheric chlorine versus time for case A. It shows that anthropogenic sources of chlorine and bromine are believed to have contributed much of the equivalent chlorine in today's troposphere. Direct measurements of chlorinated and brominated source gases have been obtained near the inflow region at the tropical tropopause on recent aircraft missions (Schauffler *et al.*, 1993). These reveal abundances of halocarbon source gases very close to those shown in Figure 13-2 for 1992. Further, concurrent measurements on-board the same aircraft confirm that HCl emitted at low altitudes from volcanoes, oceans, and other sources makes a very small contribution to the total chlorine injected in the tropical stratospheric inflow region (less than 0.1 ppbv; Schauffler *et al.*, 1993). Figure 13-2 also shows that equivalent chlorine is expected to maximize in the troposphere in 1994 under current agreements, and would return to levels near those believed to be present when Antarctic ozone depletion first became statistically significant compared to variability (*i.e.*, near 1980) around the middle of the twenty-first century if the emissions corresponding to case A are adopted. Since equivalent

Table 13-2. Scenarios for future chlorine and bromine loading.

Case	Description
Case A	Global Compliance to Montreal Protocol as Amended and Adjusted in Copenhagen (Protocol): CFCs, carbon tetrachloride, and methyl chloroform phased out in developed countries by 1996. Consumption in 1992 for Article 5 countries is assumed to be 5% of 1992 global production, growing to 10% of 1992 global production by 1996, constant to 2002, and a linear decline to zero by 2006. HCFC emissions based on U.S. EPA analysis as described in the test, and are consistent with limits under the Protocol. The halons in existing equipment (the "bank") as derived from McCulloch, 1992, are emitted in equal amounts over the period 1993 - 2000 for halon-1211 and the period 1993-2010 for halon-1301. Methyl bromide emissions are assumed constant over the period 1994 - 2100.
Case B	Production and Consumption Outside Protocol: Assumes continued production of CFC and carbon tetrachloride production at a rate equal to about 20% of 1992 global production through 2002 and then a linear decrease to zero by 2006. All other emissions as in case A.
Case C	Destruction of Halon Bank: Assumes all halons contained in existing equipment are completely recovered after 1994. All other emissions as in case A.
Case D	HCFC Early Phase-Out: Assumes that HCFC emissions cease on a global basis in 2004. All other emissions as in case A.
Case E	Methyl Bromide Increase: Assumes a 2%/year increase in agricultural emissions of methyl bromide until global agricultural emissions reach a maximum value three times that of the present. All other emissions as in case A.
Case F	Methyl Bromide Phase-Out: Assumes a 100% phase-out in all anthropogenic sources of methyl bromide emission except biomass burning (see Chapter 10) by 2001. All other emissions as in case A.
Case G	Destruction of CFC Bank: Assumes that all banked CFC-11 and CFC-12 in hermetically sealed and non-hermetically sealed refrigeration categories are completely recovered in 1995 and hence never released to the atmosphere. All banked CFC-113 is also assumed to be completely recovered. All other emissions as in case A.
Case H	London Amendments: Global compliance with the 1990 London Amendments to the Montreal Protocol rather than the 1992 Copenhagen Amendments.

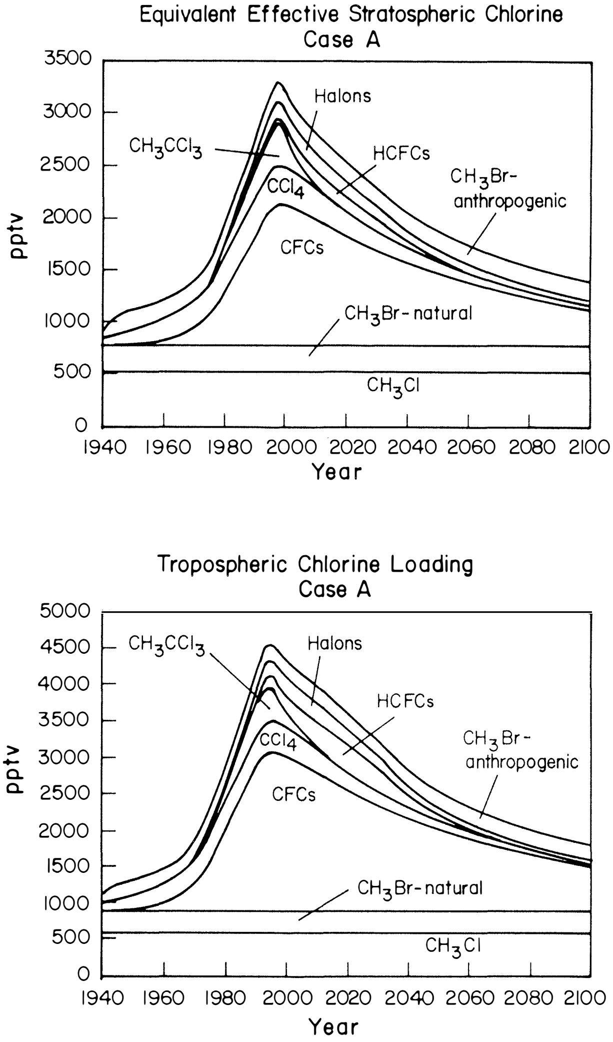

Figure 13-2. Contributions of various gases to the equivalent tropospheric (bottom) and stratospheric (top) chlorine versus time for case A.

tropospheric chlorine loading is expected to maximize in 1994, further controls would not reduce peak concentrations provided that global emissions continue to follow the requirements of the Protocol and its Amendments. However, consumption outside current Protocol agreements could increase the concentration.

13.3.2 Equivalent Effective Stratospheric Chlorine

Tropospheric chlorine loading alone does not determine the impact of a compound upon ozone loss, especially in the key region below about 25 km. Compounds that dissociate less readily within the stratosphere than others deliver less reactive chlorine, thereby decreasing their effectiveness from that indicated by their tropospheric loading. Examples of this behavior include HCFC-22 and HCFC-142b. Observations show that about 65% of the input of these gases to the stratosphere remains undissociated by the time they exit the stratosphere (see Solomon *et al.*, 1992), substantially reducing their impact on stratospheric ozone as compared to gases such as CCl_4, which undergo nearly complete dissociation while in the stratosphere. Here we evaluate the chlorine release in the lower stratosphere (below 25 km), since this is the region where most of the column-integrated ozone loss in the present atmosphere is observed to take place (WMO, 1992 and Chapter 1 of this document). The dissociation of many key compounds relative to a reference gas (CFC-11) in the lower stratosphere has been evaluated by Solomon *et al.* (1992) and by Daniel *et al.* (1994) using both observations and model calculations and is used here to define the equivalent effective stratospheric chlorine (EESC). In addition, a 3-year lag between tropospheric emission of halocarbons and stratospheric ozone impact is assumed, based in part on tracer studies (*e.g.*, Pollock *et al.*, 1992). Using these factors together with the estimate of α of 40 as discussed above, we define an "equivalent effective stratospheric chlorine" abundance that characterizes the impact of each source gas upon lower stratospheric ozone (similar to the "free halogen" defined in WMO, 1992). This definition is the same as that used for time-dependent ODPs discussed in Section 13.4.5.

The top panel of Figure 13-2 displays cumulative equivalent effective stratospheric chlorine for case A. Curves are lowered compared to tropospheric chlorine loading due to incomplete dissociation of the compounds. Peak chlorine loading occurs in 1997 as determined by the peak tropospheric loading that occurred three years earlier (bottom panel), suggesting that the maximum risk of ozone depletion has been determined by emissions occurring prior to 1995, assuming case A emissions.

Figure 13-3 shows the equivalent effective stratospheric chlorine represented by case A (Copenhagen Amendments) compared to the provisions of the original 1987 Montreal Protocol. The figure also illustrates what could have happened with no international agreements

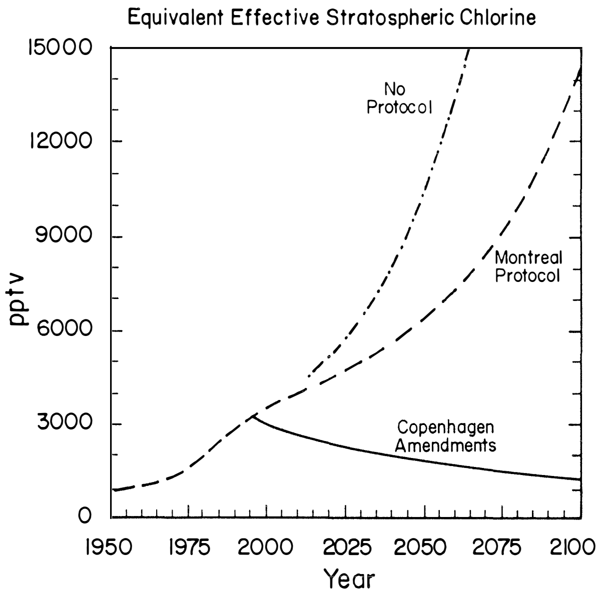

Figure 13-3. Estimated equivalent effective stratospheric chlorine represented by case A (Copenhagen Amendments) compared to the provisions of the original 1987 Montreal Protocol, and a case with no international agreements on ozone-depleting gases (where a 3%/year increase in global emissions of CFCs and methyl chloroform was assumed, less than known trends up to that time).

on ozone-depleting gases (where a 3%/year increase in global emissions of CFCs and methyl chloroform was assumed, less than known trends up to that time). The figure shows that without international agreements, equivalent effective stratospheric chlorine would likely reach values about twice as large as today's levels by 2030 and about three times today's levels by about 2050. Even with the provisions of the original Montreal Protocol, equivalent effective stratospheric chlorine would be likely to double by about the year 2060. Instead, under the current provisions, the stratospheric abundances of ozone-depleting gases are expected to begin to decrease within a few years.

One important measure of future ozone loss is the time integrated equivalent effective chlorine (pptv-year) to be expected from January 1, 1995, through the time when ozone depletion is likely to cease (*i.e.*, the integrated future ozone loss). Ozone depletion first became observable in a statistically significant sense in about 1980, making the return to equivalent effective chlorine for that year a reasonable proxy for the point where, all other things being equal, ozone depletion is likely to cease. For case A, for example, that point in time (referred to here as x) is expected to be reached in 2045. Table 13-3 presents the corresponding years for the other scenarios considered here. For evaluating cumulative long-term ecological impacts due to ozone depletion, it may also be useful to consider a similar integral beginning not in 1995 but in 1980 (thus integrating over the entire period when ozone depletion has been observed). A similar definition was used in WMO (1992), except that tropospheric values in 1985 were chosen as the reference point below which ozone depletion was assumed to cease, and the integral was performed from that point onwards rather than from 1995 onwards. Table 13-3 compares the percent differences from the base case A for each scenario for the following quantities: a) integrated equivalent effective stratospheric chlorine loading from 1995 until year x (the point when EESC drops below 1980 levels) and b) integrated equivalent effective stratospheric chlorine loading from 1980 until year x. Positive values denote integrated EESC levels that exceed the base case, while negative values indicate integrated EESC levels below the base Copenhagen scenario. The magnitudes of natural sources of chlorine and bromine (*e.g.*, from CH_3Cl and CH_3Br) do not influence these calculations, provided that they are not changing with time.

13.4 OZONE DEPLETION POTENTIALS

13.4.1 Introduction

Understanding of atmospheric chemical processes and the representation of these processes in models of global atmospheric chemistry and physics have improved since the WMO (1992) assessment. In particular, prior modeling analyses of ODPs were based largely on calculations including only gas phase chemistry, although a few calculations were carried out that included some of the chemistry occurring on background sulfuric acid aerosols. Some of the models used in the analysis presented here include representations of polar vortex processes (albeit in highly parameterized fashions) as well as most effects of heterogeneous chemistry on background sulfuric acid (but not volcanic) aerosols. The models still tend to underestimate the absolute

Table 13-3. Results of scenario calculations: integrated EESC differences (from case A) and the year when EESC drops below 1980 levels.

Scenario	Year (x) when EESC is expected to drop below 1980 value	Percent difference in $\int_{1995}^{x} \text{EESC}\,dt$ from case A.	Percent difference in $\int_{1980}^{x} \text{EESC}\,dt$ from case A.
A - Copenhagen	2045	0.0	0.0
B - Production outside of Protocol	2048	+9	+7
C - Destruction of halon bank	2043	-10	-7
D - HCFC early phase-out	2044	-5	-4
E - Methyl bromide increase	2057	+11	+9
F - Methyl bromide phase-out	2040	-13	-10
G - Destruction of CFC bank	2044	-3	-2
H - London Amendments	2055	+38	+30

ozone losses in the lowest part of the stratosphere (see Chapter 6); these limitations can affect ODPs, especially those for bromocarbons. The semi-empirical approach developed by Solomon *et al.* (1992) implicitly accounts for observed ozone destruction profiles both inside and outside of the polar vortices that are believed to reflect heterogeneous processes. While the semi-empirical approach is based upon limited data at low latitudes and high altitudes (above about 25 km), these limitations occur in regions that are believed to make relatively small contributions to the globally averaged ozone loss and hence to the ODP. Based upon these improvements in understanding, we did not explicitly evaluate chlorine loading potentials (a simpler but less complete index) in this report (see WMO, 1992).

13.4.2 Relative Effectiveness of Halogens in Ozone Destruction

A range of molecules are being considered as substitutes for the chlorofluorocarbons and halons. Some of these are non-halogenated compounds that result in no ozone loss, but others contain iodine or fluorine and could in principle deplete stratospheric ozone. It is also of interest to review the effectiveness of bromine relative to chlorine for ozone loss, which is critical for the ODPs of the halons and CH_3Br.

13.4.2.1 FLUORINE

It has long been assumed that atomic fluorine released from chlorofluorocarbons would be tied up in the form of HF and therefore unable to participate in catalytic cycles that significantly deplete ozone. For example, Stolarski and Rundel (1975) concluded that the catalytic efficiency for ozone depletion by fluorine atoms is less than 10^{-4} that of chlorine in the altitude range from 25 to 50 km. While recent estimates of the equilibrium constant, K_{eq}, for $F + O_2 \Leftrightarrow FO_2$ published in JPL (1992) suggest that FO_2 could have an appreciable thermal dissociation lifetime of the order of 1 day or longer in the stratosphere, it is unlikely that FO_x compounds can lead to significant ozone loss, as discussed in Chapter 12. Direct observations of HF and fluorine source gases (*e.g.*, Zander *et al.*, 1992) support the view that there are no large unrecognized reservoirs for fluorine. As in previous reports, we assume here that atomic fluorine and related species do not cause significant ozone depletion.

In contrast to atomic fluorine, FO, and FO_2, it has, however, recently been suggested (Li and Francisco, 1991; Biggs *et al.*, 1993) that the CF_3O_x group could be stable enough to undergo catalytic cycles that deplete ozone at a significant rate before being decomposed to less stable products that form HF. It has also been suggested that the $FC(O)O_x$ group could undergo similar chemistry (see Chapter 12). These free radical groups are produced upon decomposition of a number of HFCs and HCFCs, and even a few CFCs. Notably, it was suggested that such processes could compromise the use of HFC-134a as a substitute that does not damage the ozone layer. Briefly, the key chemical reactions are:

$$CF_3CFH_2 \text{ (HFC-134a)} + OH \text{ (multi-step)} \rightarrow CF_3 + \text{other products} \qquad (13\text{-}1)$$

$$CF_3 + O_2 + M \rightarrow CF_3O_2 \qquad (13\text{-}2)$$

$$CF_3O_2 + O_3 \rightarrow CF_3O + 2\,O_2 \qquad (13\text{-}3)$$

$$CF_3O + O_3 \rightarrow CF_3O_2 + O_2 \qquad (13\text{-}4)$$

The last two reactions constitute a catalytic cycle analogous to the OH and HO_2 reactions with ozone, and could in principle be an effective ozone loss cycle in the lower stratosphere. The key factors in terminating this catalytic chain are reactions that can break down the CF_3 group, forming either stable products or products that rapidly decompose to produce HF. Two such reactions have been identified:

$$CF_3O + NO \rightarrow CF_2O + FNO \qquad (13\text{-}5)$$

$$CF_3O + CH_4 \rightarrow CF_3OH + CH_3 \qquad (13\text{-}6)$$

Chapter 12 discusses recent measurements of these and other relevant kinetic rate constants in considerable detail. Direct laboratory measurements coupled with model calculations have shown that the chain-terminating reactions above are sufficiently fast, and the chain-propagating reactions sufficiently slow, that the Ozone Depletion Potentials relating to the presence of a CF_3 group are essentially negligible. Recently, Ravishankara *et al.* (1994) and Ko *et al.* (1994a) have examined the implications of these processes for the effectiveness of CF_3 radical groups for ozone loss relative to chlorine. Figure 13-4 shows the calculated efficiency of CF_3 as compared to chlorine from the Garcia-Solomon model used in the study of Ravishankara *et al.* for midlatitudes in winter. The figure illustrates that current laboratory measurements imply that the CF_3 group is at most about 1000 times less effective than chlorine for ozone destruction at 20 km in midlatitudes. While higher local values might be obtained in polar winter (where NO abundances are very small), the impacts of CF_3-related reactions on the globally averaged ODPs of CF_3-containing chlorofluorocarbons (such as CF_3Cl) and hydrochlorofluorocarbons (such as CF_3CHCl_2) are believed to be negligible, and the ODPs of HFCs such as HFC-134a and HFC-23 are highly likely to be less than 1×10^{-3} based upon current kinetic data (Ravishankara *et al.*, 1994).

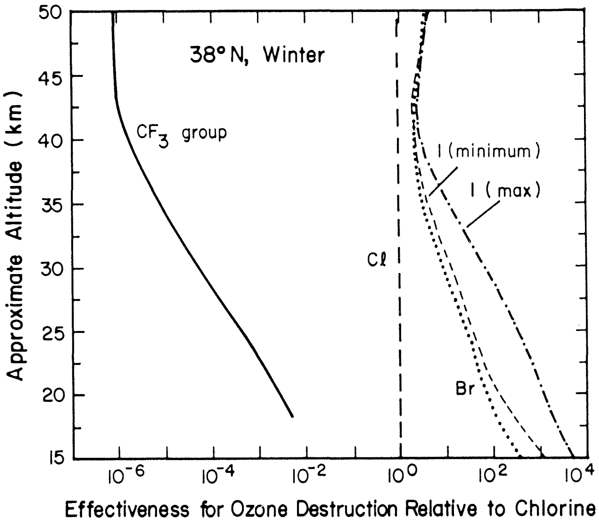

Figure 13-4. Calculated effectiveness of CF_3, bromine, and iodine in ozone destruction at midlatitudes relative to chlorine (based on results from Garcia-Solomon model as discussed in text).

13.4.2.2 BROMINE

The chemistry of atmospheric bromine is discussed further in Chapter 10. The understanding of the relative roles of bromine and chlorine in depleting ozone was discussed by Solomon *et al.* (1992), who noted that *in situ* and remote sensing measurements of ClO, BrO, and OClO strongly suggest that bromine is about 40 times more efficient than chlorine for Antarctic ozone loss. Assuming that the rate-limiting steps for ozone loss in the Antarctic are the reactions ClO + ClO and ClO + BrO, the value of α for Antarctic ozone loss can be derived as follows:

$$\alpha \approx \frac{2k(BrO)(ClO)/(Br_y)}{2k(ClO)(ClO)+2k(BrO)(ClO)/(Cl_y)} \qquad (13\text{-}7)$$

where the denominator represents the rate of ozone loss due to chlorine compounds per atom of chlorine available (*i.e.*, Cl released from all source gases, denoted here as Cl_y) and the numerator represents the rate of ozone loss due to bromine compounds per atom of bromine available (Br_y). Since the reaction ClO + ClO is believed to account for about 75% of the Antarctic ozone loss while ClO + BrO accounts for about 25% (see Solomon *et al.*, 1992 and references therein) and Cl_y is about 2.5 ppbv while Br_y is about 15 pptv in this region, the value of α for Antarctic ozone loss is about 40. Salawitch *et al.* (1990, 1993) pointed out that the lower absolute abundances of ClO observed in the Arctic as compared to Antarctica implies that bromine will be more effective for ozone loss there (*i.e.*, ClO + BrO will be more important compared to ClO + ClO).

Recent laboratory studies have confirmed and expanded understanding of the important role of bromine. Poulet *et al.* (1992) have shown that the kinetic rate constant for the reaction of BrO + HO_2 is about six times faster than previously believed at room temperature; this has been confirmed by the measurements of Bridier *et al.* (1993). As noted in WMO (1992), the importance of bromine for ozone loss could be substantially diminished if as much as 10% of the reaction between BrO + HO_2 were to yield HBr at the rate indicated by Poulet *et al.* (1992), while it would be *enhanced* if less than a few percent HBr is produced. The latter appears to be true based upon the study of Mellouki *et al.* (1994), who showed that the yield of HBr from this reaction is likely to be below 0.1% even at stratospheric temperatures based on new measurements and thermochemical data, a result consistent with modeling studies of the BrO gradient (Garcia and Solomon, 1994). Figure 13-4 shows the calculated effectiveness of bromine for ozone destruction relative to chlorine based upon the above photochemistry from the model of Garcia and Solomon (1994). The figure suggests that bromine is roughly 100 times more effective in the region of peak observed ozone loss (near 20 km). Very similar results have also been calculated with the Lawrence Livermore National Laboratory (LLNL) two-dimensional model. The figure illustrates that model calculations of the ODP for bromine-bearing compounds are likely to be quite sensitive to the altitude profile of ozone destruction. Since present models tend to underestimate the observed ozone losses in the lowest part of the stratosphere (see Chapter 6), where bromine is particularly efficient for ozone loss, this figure implies that the model-derived globally averaged values of α (weighted by the ozone loss distribution) will also be underestimates assuming present photochemical schemes.

Bromine's effectiveness for ozone loss in the lower stratosphere is related to the fact that a large fraction of the available Br_y resides in the ozone-depleting forms of Br and BrO. In contrast, only a very small fraction of available Cl_y resides in Cl and ClO except in the special case of polar regions. Thus, since all halogen atoms are very reactive (*e.g.*, with atomic oxygen, HO_2, and each other), bromine chemistry's effectiveness relative to chlorine will generally be driven by the fact that the BrO/Br_y ratio is on the order of 50-100 times larger than the ClO/Cl_y ratio in the lower stratosphere outside of polar regions. This in turn implies that the value of α is not very sensitive to which reactions are the dominant rate-limiting steps in ozone destruction, at least for current photochemical schemes (*e.g.*, ClO + BrO, HO_2 + BrO, HO_2 + ClO, etc.).

13.4.2.3 IODINE

The ability of reservoir molecules to sequester halogen radicals and thereby reduce their impact on ozone is inversely related to the size of the halogen atom. Thus fluorine rapidly forms HF, while chlorine forms HCl and $ClONO_2$. The bromine reservoirs (HBr and $BrONO_2$) are weakly bound, making BrO and Br effective ozone-destroying species as shown above. Iodine reservoirs such as HI, $IONO_2$, and others are known to be very readily dissociated by photolysis or reaction with OH, rendering any iodine that reaches the stratosphere at least as effective as bromine for ozone loss and very probably much more so. However, iodine source gases are very short-lived because of the relatively weak carbon-iodine bond. If the iodine source gases are short-lived enough, then anthropogenic releases (particularly at the surface at midlatitudes) may not reach the stratosphere in abundances sufficient to result in significant ozone loss. In this case, compounds such as CF_3I could represent useful substitutes for the halons.

The chemistry of iodine in the troposphere was discussed in detail by Chameides and Davis (1980). Recently, Solomon *et al.* (1994a, b) have considered the impact of iodine on stratospheric ozone compared to chlorine, based mainly on the iodine photochemistry considered in the kinetic evaluation of Atkinson *et al.* (1992). Solomon *et al.* (1994a, b) showed that current photochemical schemes imply that iodine is at least as effective as bromine for ozone destruction based upon the measured rate for HO_2 + IO (shown in Figure 13-4 as Iodine [minimum]). In addition, Solomon *et al.* (1994b) emphasized that several key chemical processes relating to iodine-catalyzed ozone destruction have not yet been quantified in laboratory studies, notably IO + ClO and IO + BrO. If these reactions were to take place relatively rapidly, iodine could be as much as 2000 times more effective than chlorine for ozone destruction near 20 km (denoted as Iodine [max] in Figure 13-4). This proposed chemistry does not significantly change the value of α, for the reasons discussed above. In combination with anthropogenic trends in ClO and BrO, as little as 1 pptv of iodine in the lower stratosphere due to the very large natural sources of compounds such as methyl iodide could be significant for lower stratospheric ozone loss (Solomon *et al.*, 1994b). These considerations are taken into account in the estimate of the ODP for CF_3I presented in Solomon *et al.* (1994a) and later in this chapter. In spite of these large efficiencies, the very short lifetime of CF_3I (less than 2 days; see Solomon *et al.*, 1994a) results in an estimated upper limit for the steady-state ODP for surface emissions of this compound of only 0.008. Other iodine-bearing compounds, such as C_2F_5I, would likely have similar ODPs.

13.4.3 Breakdown Products of HCFCs and HFCs

In the calculation of the ODPs for HCFCs presented here, it is assumed that chlorine atoms will be promptly released (and hence able to participate in ozone destruction) once the parent molecule is broken down. Concern has been raised that the ODPs of some HCFCs could be enhanced if the tropospheric breakdown products contain chlorine and have atmospheric lifetimes comparable to or longer than the precursor HCFC (WMO, 1990, 1992) and thus potentially be transported to the stratosphere. Particular attention has been focused on the carbonyl and PAN-like compounds. The chemistry of these intermediates is discussed in detail in Chapter 12, where it is shown that photolysis and heterogeneous removal (in clouds and rain) likely makes the tropospheric abundances of these intermediates too small to affect ODPs or GWPs.

On the other hand, Kindler *et al.* (1994) showed that the stratospheric lifetime of the phosgene ($COCl_2$) produced by the dissociation of such compounds as CCl_4 and CH_3CCl_3 is long enough to imply a *reduction* of perhaps 10-15% in the ODPs for CCl_4 and CH_3CCl_3. Similarly, fluorophosgene (COFCl) is a product of the degradation of HCFC-141b. The lifetime of this species is also believed to be rather long in the stratosphere, suggesting a similar reduction in the ODP of HCFC-141b. These chemical processes have not been included in the ODP estimates discussed below.

13.4.4 Model-Calculated and Semi-Empirical Steady-State ODPs

Model-derived ODPs have been determined for a range of compounds using the two-dimensional models at LLNL (D. Wuebbles and K. Patten), Atmospheric and Environmental Research, Inc. (AER; D. Weisenstein and M. Ko), and Universita' Degli Studi-L'Aquila (G. Visconti and G. Pitari). In addition, the ODPs of some bromocarbons were evaluated in the Oslo model (I. Isaksen *et al.*) and some HCFCs were considered in the Indian Institute of Technology (IIT)/Delhi one-dimensional model (M. Lal *et al.*). The National Oceanic and Atmospheric Administration/National Center for Atmospheric Research (NOAA/NCAR) two-dimensional model was used to analyze the ODPs for HFC-134a, HFC-23, HFC-125, and CF_3I (Ravishankara *et al.*, 1994; Solomon *et al.*, 1994a). Each of these models used updated kinetics (based primarily on JPL, 1992), with the exception that the L'Aquila results do not include the new BrO + HO_2 rate. These models also account for the effects of heterogeneous chemistry on background stratospheric sulfate aerosols and most include a representation of polar vortex processes. The ODPs presented in Table 13-4 use results from the models normalized to the atmospheric lifetimes in Table 13-1. They agreed to within 10% in most cases and within 30% in all cases examined; the results from reporting models were averaged. In the AER 2-D model (D. Weisenstein, private

Table 13-4. Steady-state ODPs derived from 2-D models and from the semi-empirical approach. ODPs are normalized based on recommended atmospheric lifetimes in Section 13.2.

Trace Gas	Model-Derived ODP	Semi-Empirical ODP
CFC-11	1.0	1.0
CFC-12	0.82	0.9
CFC-113	0.90	0.9
CFC-114	0.85	
CFC-115	0.40	
CCl_4	1.20	
CH_3CCl_3	0.12	0.12
HCFC-22	0.04	0.05
HCFC-123	0.014	0.02
HCFC-124	0.03	
HCFC-141b	0.10	0.1
HCFC-142b	0.05	0.066
HCFC-225ca	0.02	0.025
HCFC-225cb	0.02	0.03
HFC-134a	$< 1.5 \times 10^{-5}$	$< 5 \times 10^{-4}$
HFC-23	$< 4 \times 10^{-4}$	
HFC-125	$< 3 \times 10^{-5}$	
CH_3Br (1.3 yr lifetime)	0.64	0.57
CF_3Br (H-1301)	12	13
CF_2ClBr (H-1211)	5.1	5
CF_3I		< 0.008
CH_3Cl	0.02	

communication, 1993), the derived ODP for CH_3Br increased by 33% due to the change from the old to the new kinetic rate constant for the reaction between BrO and HO_2, illustrating the key role of this reaction as discussed above. The factors influencing the ODP for CH_3Br and their possible uncertainties are discussed further in Chapter 10. The best estimate of the lifetime for CH_3Br is about 1.3 years as discussed in Chapter 10, rather than the value of 2 years used in the WMO (1992) report. Thus, the increased chemical effectiveness of bromine for ozone loss is approximately cancelled by the decreased lifetime in deriving an ODP for CH_3Br. Model-derived ODPs for the long-lived CFCs and halons shown in Table 13-4 are slightly smaller than in the WMO (1992) assessment, probably because of changes in atmospheric lifetimes and the consideration of polar processes.

As discussed in WMO (1992), Solomon *et al.* (1992) have formulated a semi-empirical approach for determining ODPs based mainly upon observations rather than models. These semi-empirical ODPs have been updated using the atmospheric lifetimes discussed in Section 13.2, along with some updates in the observed fractional dissociation of halocarbons in the stratosphere (Daniel *et al.*, 1994). Table 13-4 gives the semi-empirical steady-state ODPs based on this analysis. The effectiveness of bromine relative to chlorine for ozone loss in this analysis was assumed to be 40; as indicated in Section 13.4, this value is likely to be too low in the region where bromine emissions are most effective in destroying ozone at midlatitudes, suggesting that the semi-empirical ODPs for CH_3Br and the halons may be underestimated. A value of α of 80 is plausible in the lower stratosphere (see Chapter 10 and Garcia and Solomon, 1994), and would approximately double the ODPs of these compounds.

13.4.5 Time-Dependent Effects

While steady-state Ozone Depletion Potentials describe the integrated impact of emission of a halocarbon upon the ozone layer compared to CFC-11, it is also of interest to consider the time dependence of these effects (WMO, 1990, 1992; Solomon and Albritton, 1992). Time-dependent ODPs can be used to provide insight into the effect of a mix of compounds upon the short-term future of the ozone layer (*e.g.*, the next few decades, when peak chlorine and bromine loading are expected to occur), while steady-state ODPs indicate integrated effects over longer time scales. We describe below in more detail than in previous reports the physical processes that control the expected time dependence of ODPs for various chemicals. We then present updated time-dependent Ozone Depletion Potentials for several molecules of interest based upon new kinetic information and lifetimes as discussed in this report.

A simple semi-empirical framework for understanding the physical reasons for time-dependence of ODPs was presented by Solomon and Albritton (1992), who showed that the following equation can be used to approximate the time-dependent ODP at any point in the stratosphere:

$$ODP_X(t) = \left\{\frac{F_X}{F_{CFC-11}}\right\} \cdot \frac{M_{CFC-11}}{M_X} \cdot \frac{n_X}{3} \cdot \alpha \cdot \frac{\int_{t_s}^{t} e^{-(t-t_s)/\tau_x}\,dt}{\int_{t_s}^{t} e^{-(t-t_s)/\tau_{CFC-11}}\,dt} \qquad (13\text{-}8)$$

The term in brackets, $\{F_x/F_{CFC-11}\}$, denotes the fraction of the halocarbon species, x, injected into the stratosphere that has been dissociated compared to that of CFC-11 (obtained from measurements of both). M_x, M_{CFC-11}, τ_x, and τ_{CFC-11} indicate the molecular weights and atmospheric lifetimes of species x and CFC-11, respectively, while n_x is the number of chlorine or bromine atoms in the molecule (and note that CFC-11 contains 3 chlorine atoms per molecule). Also, t_s is the time required for a molecule to be transported from the surface to the region of the stratosphere in question, and t is time. In the following figures, the time refers to the time since reaching the lower stratosphere at middle-to-high latitudes (which is believed to be on the order of three years). In principle, the above equation should be integrated over the entire stratosphere in order to derive the globally averaged time-dependent ODP. In practice, however, the ozone column depletion observed in the current atmosphere is dominated by the region below 25 km. Further, mixing processes imply compact linear correlations between many of the long-lived halocarbon source gases in this region (Plumb and Ko, 1992), making the term in brackets, $\{F_x/F_{CFC-11}\}$, very nearly a constant over broad regions of the lower stratosphere (see Daniel *et al.*, 1994).

Using the above equation, together with the revised lifetimes of Table 13-1, updated values of $\{F_x/F_{CFC-11}\}$ where available from Daniel *et al.* (1994), and a value of α of 40 for bromocarbons and 2000 for iodocarbons, semi-empirical time-dependent ODPs were deduced. In addition, the instantaneous (*i.e.*, not integrated) relative ozone loss was also considered. Figure 13-5 shows instantaneous time-dependent relative ozone loss rates (compared to CFC-11) for several molecules of interest here. The time axis on the figure refers to the time since reaching the stratosphere, not the total time (which is about 3-5 years longer; see Pollock *et al.*, 1992). The instantaneous ozone loss rates relative to CFC-11 for the first few years are determined largely by the values of α for bromocarbons or iodocarbons and by the values of $\{F_x/F_{CFC-11}\}$ and n_x for chlorocarbons. Over longer time scales, the short-lived compounds are removed from the atmosphere, and the slope of their decay depends upon the relative values of τ_x and τ_{CFC-11}. Note, for example, that HCFC-141b (which contains 2 chlorine atoms) initially destroys roughly 2/3 as much ozone as CFC-11. It has a lifetime of about 10 years, and therefore its instantaneous ozone loss drops to very small values within a few decades. The ozone-depleting effects of pulsed injections of compounds with shorter lifetimes (such as HCFC-123) decay much faster. A

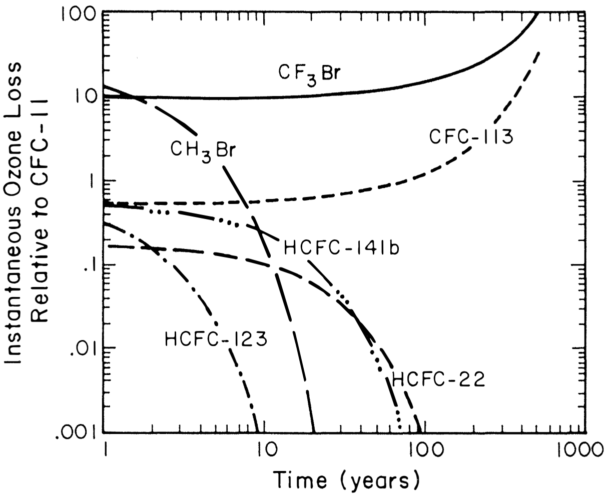

Figure 13-5. Instantaneous time-dependent relative ozone loss rates (compared to CFC-11) for several compounds of interest. Note that the x-axis refers to the time since reaching the stratosphere, not the total time.

compound with a lifetime longer than that of CFC-11 (such as CFC-113) has an impact on the ozone layer relative to CFC-11 that grows for time scales longer than the 50-year lifetime of CFC-11, because of the decay of the reference gas. The behavior of CH_3Br is qualitatively similar to that of HCFC-123, but it has a very large initial ozone impact because of the value of α, making its relative ozone loss in the first few years close to 10 times that of CFC-11 (approximately $\alpha/3$).

The time-dependent Ozone Depletion Potentials are simply the time integrals of the instantaneous relative ozone loss rates shown in Figure 13-5. These are illustrated in Figure 13-6. Note, for example, the growth of the ODP for CFC-113 for time scales longer than about 100 years, at which time more CFC-113 remains to destroy ozone than the reference gas, CFC-11. The time-dependent ODP for a very short-lived gas such as HCFC-123 has large values for the first five years. However, by the end of the first five years, HCFC-123 is destroying very little ozone (Figure 13-5), because it has been nearly completely removed from the atmosphere. The reference gas, CFC-11, is continuing to destroy ozone, so that the cumulative value of the denominator in Equation 13-8 continues to increase. It is this slow increase in the denominator that controls when the ODPs for short-lived gases such as HCFC-123 reach their steady-state values. The steady-state ODP for HCFC-123 therefore asymptotes to a value below 0.02 in about 100 years. A calculation of the time-dependent ODPs for CH_3Br using the Oslo model gave values of 5.6, 2.3, and 1.5 for time scales of 10, 20, and 30 years, respectively, very similar to the semi-empirical values shown in Figure 13-6. In the above calculations, a lifetime of 2.0 years was used for CH_3Br. The ODPs for this gas would be about 30% smaller over long time scales if a lifetime of 1.3 years was employed.

Figure 13-6 includes an upper-limit estimate of the time-dependent ODP for surface releases of CF_3I, based on the framework described in Solomon *et al.* (1994a). The calculated upper limit to the ODP for this gas is about 0.08 in the first five years and asymptotes to a value below 0.01 in about 100 years.

Although the ODP concept has primarily been applied to the relative effects of halocarbons on stratospheric ozone, there have also been several recent attempts to determine ODPs for emissions of other gases. For example, Ko *et al.* (1994b) have evaluated an ODP for chlorine emitted directly into the stratosphere from launch of the U.S. Space Shuttle. They derive a time-dependent ODP that is quite large initially (but is also dependent on the definition of what constitutes a mass emission, the choice being emission of HCl only or

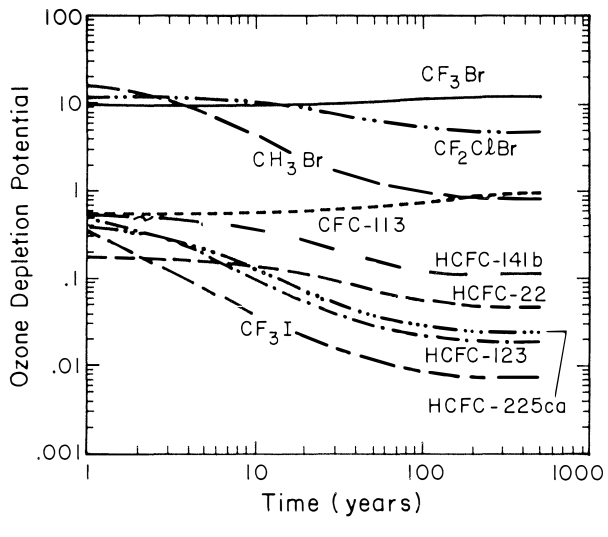

Figure 13-6. Time-dependent Ozone Depletion Potentials for several compounds of interest. Note that the x-axis refers to the time since reaching the stratosphere, not the total time.

the total fuel load). The effect from the Space Shuttle decays quite rapidly due to removal of the emitted HCl from the stratosphere.

Since the ozone layer is believed to respond relatively rapidly to changes in chlorine and/or bromine loading (time scale of about 3-5 years or less), time-dependent Ozone Depletion Potentials provide an appropriate measure of the expected ozone response to changing inputs of source gases relative to the reference molecule. On the other hand, steady-state Ozone Depletion Potentials may be applicable to evaluation of associated long-term biological impacts, where the ecosystem response may take place over many decades of exposure to changes in ultraviolet radiation resulting from ozone changes.

13.5 GLOBAL WARMING POTENTIALS

13.5.1 Introduction

This section addresses the numerical indices that can be used to provide a simple representation of the relative contribution of an atmospheric trace gas to greenhouse warming, drawing heavily on the information in the earlier ozone assessments (WMO, 1990, 1992), the climate-system reports of the Intergovernmental Panel on Climate Change (IPCC, 1990, 1992, 1994), and recent journal publications. The major objective of the text that follows is to update the information on radiative forcing indices. To this end, we describe the calculations of the indices contained herein, discuss the sensitivity of the results to some of the specifications and assumptions, and present the resulting numerical indices and their uncertainties.

As in the case of ODPs, calculating the relative alteration in radiative forcing due to the change in greenhouse gas A compared to that due to a change in greenhouse gas B can be evaluated more accurately than the absolute climate response due a change in a single greenhouse gas alone. In the following, we briefly discuss some key factors that contribute to GWPs.

Common to all greenhouse gases are three major factors – two technical and one user-oriented – that determine the relative contribution of a greenhouse gas to radiative forcing and hence are the primary input in the formulation, calculation, and use of radiative forcing indices:

Factor 1: The strength with which a given species absorbs longwave radiation and the spectral location of its absorbing wavelengths. Chemical species differ markedly in their abilities to absorb longwave radiation. Overlaps of the absorption spectra of various chemical species with one another (especially H_2O, CO_2, and, to a lesser extent, O_3) are important factors. In addition, while the absorption of infrared radiation by many greenhouse gases varies linearly with their concentration, a few important ones display nonlinear behavior (*e.g.*, CO_2, CH_4, and N_2O). For those gases, the relative radiative forcing will depend upon concentration and hence upon the scenario adopted for the future trace-gas atmospheric abundances. A key factor in the greenhouse role of a given species is the location of its absorption spectrum relative to the region in the absorption of atmospheric water vapor through which most outgoing planetary thermal radiation escapes to space. Consequently, *other things being equal*, chemical species that have strong absorption band strengths in the relatively weak water-vapor "window" are more important greenhouse gases than those that do not. This is illustrated in Figure 13-7, which shows how the instantaneous radia-

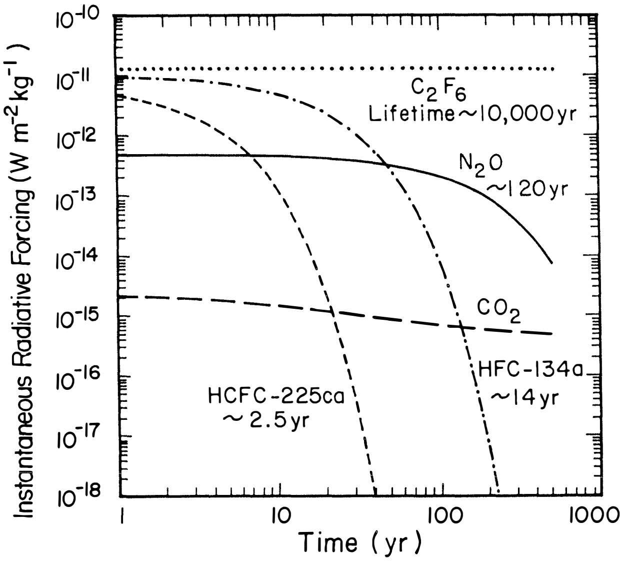

Figure 13-7. Instantaneous radiative forcing (W m^{-2} kg^{-1}) versus time after release for several different greenhouse gases. The CO_2 decay response function is based upon the Bern carbon cycle model with fixed CO_2 concentrations.

tive forcings due to the pulse emission of one kilogram of various long-lived gases with differing absorption properties change as the concentrations decay away in time after they have become well mixed (*e.g.*, about a year after injection into the atmosphere). The relevant point here is on the left-hand scale at t = 1, namely, that the radiative forcing of an equal emission of the various gases can differ by as much as four orders of magnitude. Laboratory studies of molecular radiative properties are a key source of the basic information needed in the calculation of radiative forcing indices. The status of such spectroscopic data of greenhouse gases is discussed in detail in Chapter 8 and in Chapter 4 of IPCC (1994).

Factor 2. The lifetime of the given species in the atmosphere. Greenhouse gases differ markedly in how long they reside in the atmosphere once emitted. Clearly, greenhouse gases that persist in the atmosphere for a long time are more important, other things being equal, in radiative forcing than those that are shorter-lived. This point is also illustrated in Figure 13-8. As shown, the initial dominance of the radiative forcing at early times can be overwhelmed by the lifetime factor at later times.

The relative roles of the strength of radiative absorption and lifetimes on GWPs, as shown in Figures 13-7 and 13-8, parallel those of chemical effectiveness and lifetimes on ODPs, as illustrated in Figures 13-5 and 13-6.

Factor 3. The time period over which the radiative effects of the species are to be considered. Since many of the responses of the Earth's climate to changes in radiative forcing are long (*e.g.*, the centennial-scale warming of the oceans), it is the *cumulative* radiative forcing of a greenhouse gas, rather than its instantaneous value, that is of primary importance to crafting a relevant radiative forcing index. As a consequence, such indices involve an integral over time. Rodhe (1990) has noted that the choice of time interval can be compared to cumulative-dosage effects in radiology. IPCC (1990, 1992) used integration *time horizons* of 20, 100, and 500 years in calculating the indices. Figure 13-8 shows the integrals of the decay functions in Figure 13-7 for a wide range of time horizons. It illustrates the need for the user of the radiative forcing indices to select the time period of consideration. A strongly absorbing, but short-lived, gas like HCFC-225ca will contribute more radiative forcing in the short term than a weaker-absorbing, but longer-lived, gas like N_2O; however, in the longer term, the reverse is true. Methane is a key greenhouse gas discussed extensively below; its integrated radiative forcing would lie below that of N_2O and reach a plateau more quickly because of its shorter lifetime.

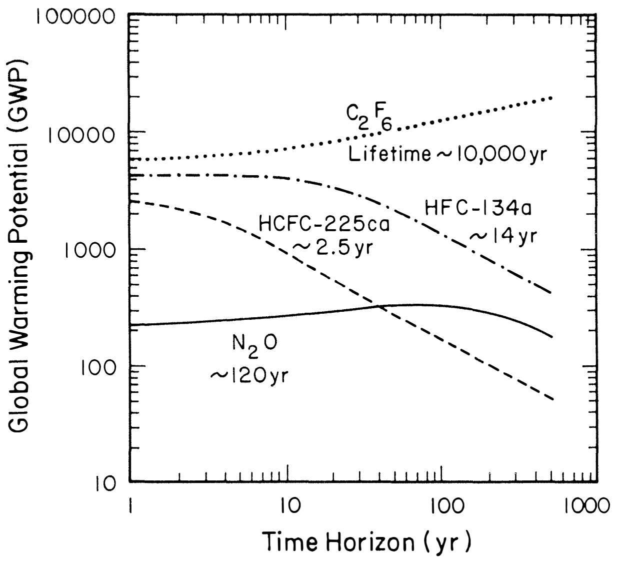

Figure 13-8. Global Warming Potentials (GWPs) for a range of greenhouse gases with differing lifetimes, using CO_2 as the reference gas.

The spread of numerical values of the radiative forcing indices reported in Section 13.5.2 below largely reflects the influence of these three major factors. In addition to these direct radiative effects, some chemical species also have indirect effects on radiative forcing that arise largely from atmospheric chemical processes. For example, important products of the oxidative removal of CH_4 are water vapor in the stratosphere and ozone in the troposphere, both of which are greenhouse gases. These are discussed in Section 13.5.4.

13.5.2 Radiative Forcing Indices

13.5.2.1 FORMULATION

The primary radiative forcing indices used in scientific and policy assessments are the Global Warming Potential (GWP) and Absolute Global Warming Potential (AGWP). Other possible formulations are described and contrasted with those in IPCC (1994).

Global Warming Potential

Based on the major factors summarized above, the relative potential of a specified emission of a greenhouse gas to contribute to a change in future radiative forcing, *i.e.*, its GWP, has been expressed as the time-integrated radiative forcing from the instantaneous release of 1 kg of a trace gas expressed relative to that of 1 kg of a reference gas (IPCC, 1990):

$$\mathrm{GWP}(x) = \frac{\int_0^{TH} a_x \cdot [x(t)]dt}{\int_0^{TH} a_r \cdot [r(t)]dt} \tag{13-9}$$

where TH is the time horizon over which the calculation is considered; a_x is the climate-related radiative forcing due to a unit increase in atmospheric concentration of the gas in question; [x(t)] is the time-decaying abundance of a pulse of injected gas; and the corresponding quantities for the reference gas are in the denominator. The adjusted radiative forcings per kg, a, are derived from infrared radiative transfer models and are assumed to be independent of time. The sensitivity of these factors to some climate variables (H_2O, clouds) is discussed later. As noted above, a_r is a function of time when future changes in CO_2 are considered. Time-dependent changes in a_x or lifetimes are not explicitly considered here. The trace gas amounts, [x(t)] and [r(t)], remaining after time t are based upon the atmospheric lifetime or response time of the gas in question and the reference gas, respectively.

The reference gas has been taken generally to be CO_2, since this allows a comparison of the radiative forcing role of the emission of the gas in question to that of the dominant greenhouse gas that is emitted as a result of human activities, hence of the broadest interest to policy considerations. However, the atmospheric residence time of CO_2 is among the most uncertain of the major greenhouse gases. Carbon dioxide added to the atmosphere decays in a highly complex fashion, showing an initial fast decay over the first 10 years or so, followed by a more gradual decay over the next 100 years or so, and a very slow decline over the thousand-year time scale, mainly reflecting transfer processes in the biosphere, ocean, and deep ocean sediments, respectively. Because of these different time constants, the removal of CO_2 from the atmosphere is quite different from that of other trace gases and is not well described by a single lifetime (Moore and Braswell, 1994). Wuebbles *et al.* (1994b) and Wigley (1993) have also noted the importance of uncertainties in the carbon cycle for calculations of GWPs when CO_2 is used as the reference. Furthermore, CO_2 is also recirculated among these reservoirs at an exchange rate that is poorly known at present, and it appears that the budget of CO_2 is difficult to balance with current information. As a result, when CO_2 is used as the reference gas, the numerical values of the GWPs of all greenhouse gases are apt to change in the future (perhaps substantially) simply because research will improve the understanding of the removal processes of CO_2. While recognizing these issues, Caldeira and Kasting (1993) discuss feedback mechanisms that tend to offset some of these uncertainties for GWP calculations.

Absolute Global Warming Potential

Wigley (1993; 1994a, b) has emphasized the uncertainty in accurately defining the denominator for GWP calculations if CO_2 is used as the reference molecule, and suggested the use of "Absolute" or AGWPs given simply by the integrated radiative forcing of the gas in question:

$$\mathrm{AGWP}(x) = \int_0^T a_x \cdot [x(t)]\,dt \quad \mathrm{W \cdot yr \cdot kg^{-1} \cdot m^{-2}} \tag{13-10}$$

The advantage of this formulation is that the index is specific only to the gas in question. An important disadvantage is that the absolute value of radiative forcing depends upon many factors that are poorly known, such as the distributions and radiative properties of clouds (*e.g.*, Cess *et al.*, 1993).

Based upon the recommendation of the co-authors of Chapter 1 from IPCC (1994), we use the results from the carbon cycle model of Siegenthaler and co-workers ("Bern" model) for the decay response of CO_2 for the GWP calculations presented here. The fast initial (first several decades) decay of added CO_2 calculated in current carbon cycle models reflects rapid uptake by the biosphere and is believed to be an important improvement compared to that used in IPCC (1990, 1992). This change in decay decreases the integrated radiative forcing of CO_2 and thereby acts to increase the estimated GWPs of all gases (see IPCC, 1994). We present AGWPs for CO_2 needed for conversion of the results to other units and other CO_2 decay functions (*e.g.*, to show the impact of the choice of the denominator on GWP values).

13.5.2.2 Sensitivity to the State of the Atmosphere

To provide realistic evaluations of GWPs for specified time horizons and estimate their uncertainties, future changes in the radiative properties of the atmosphere must be considered. Some of these changes to the present state can be estimated based upon scenarios (*e.g.*, CO_2 concentrations), while others are dependent upon the evolution of the entire climate system and are poorly known (*e.g.*, clouds and water vapor). In IPCC (1990), the composition of the background atmosphere used in the GWP calculations was the present-day abundances of CO_2, CH_4, and nitrous oxide (N_2O), which were assumed constant into the future. However, likely changes in CO_2, CH_4, or N_2O concentrations will lead to future changes in the radiative forcing per molecule of those gases (and perhaps others whose spectral bands overlap with them), as noted previously. The radiative properties of CO_2 are particularly sensitive to changes in concentration, since the large optical depth of CO_2 in the current atmosphere makes its radiative forcing depend logarithmically on concentration (see WMO, 1992 and Chapter 8 of this document). Thus, the forcing for a particular incremental change of CO_2 will become smaller in the future, when the atmosphere is expected to contain a larger concentration of the gas. In the case of CH_4 and N_2O, there is a square-root dependence of the forcing on their respective concentrations (IPCC, 1990); hence, just as for CO_2, the forcings due to a specified increment in either gas are expected to become smaller for future scenarios. For the other trace gases considered here, the present and likely future values are such that the direct radiative forcing is linear with respect to their concentrations and hence is independent of the scenario.

IPCC (1994) showed in detail that the dependence of the AGWP of CO_2 upon choice of future atmospheric CO_2 concentrations is not a highly sensitive one. A constant atmosphere at pre-industrial values (280 ppmv) would yield values different by less than about 20% for all time horizons. Similarly, the increasing CO_2 concentrations in a future scenario stabilizing at 650 ppmv would yield GWP values that are smaller by 15% or less. The decreases in the radiative forcing per molecule due to the increasing CO_2 atmospheric abundance appear to be opposite in sign to those due to the changed CO_2 decay response (see Caldeira and Kasting, 1993, and Wigley, 1994a).

IPCC (1994) and this report also considered the possible evolution of the radiative forcing of CH_4 and N_2O and the interplay between the spectral overlap of these two gases using the IS92a scenario published in the Annex of IPCC (1992). If the calculations were made with the IS92a CH_4 and N_2O scenarios rather than with the constant current values, the direct GWPs of CH_4 would decrease by 2 to 3%, and the 20-, 100-, and 500-yr GWPs of N_2O would decrease by 5, 10, and 15%, respectively. The impact of the adopted future scenarios for CO_2, CH_4, and N_2O on the radiative forcing of other trace species was not considered.

Water Vapor

While it is likely that water vapor will change in a future climate state, the effect of such changes upon the direct GWPs of the great majority of molecules of interest here is expected to be quite small. For example, the model of Clerbaux *et al.* (1993) was used to test the sensitivity of the direct GWP for CH_4 to changes in water vapor. Even for changes as large as 30% in water vapor concentration, the calculated GWP of CH_4 changed by only a few percent (C. Granier, personal communication, 1993). For many other gases whose radiative impact occurs largely in the region where water vapor's absorption is relatively weak, similar or smaller effects are likely.

Clouds

Clouds composed of water drops or ice crystals possess absorption bands in virtually the entire terrestrial infrared spectrum. By virtue of this property, they modulate considerably the infrared radiation escaping to space from the Earth's surface and atmosphere. Since cloud tops generally have lower temperatures than the Earth's surface and the lower part of the atmosphere, they reduce the outgoing infrared radiation. This reduction depends mainly on cloud height and optical depth. The higher the cloud, the lower is its temperature and the greater its reduction in infrared emission. On the other hand, higher clouds (in particular, high ice clouds) tend to have low water content and limited optical depths. Such clouds are partially transparent, which reduces the infrared trapping effect.

The absorption bands of several trace gases overlap significantly with the spectral features of water drops and ice crystals, particularly in the "window" region. Owing to the relatively strong absorption properties of clouds, the absolute radiative forcing of many trace molecules is diminished in the presence of clouds. However, it is important to note that the impact of changes in clouds upon GWPs depends upon the difference between the change in radiative forcing of the gas considered and that of the reference gas, not the absolute change in radiative forcing of the gas alone. IPCC (1994) shows that the model calculations of Granier and co-workers suggest that the presence or absence of clouds results in changes of the relative radiative forcings of the molecules considered here of at most about 12%. Thus, uncertainties in future cloud cover due to climate change are unlikely to substantially impact GWP calculations.

13.5.3 Direct GWPs

New direct GWPs of many gases were calculated for IPCC (1994) and for this report with the radiative transfer models developed at the National Center for Atmospheric Research – NCAR (Briegleb, 1992; Clerbaux *et al.*, 1993), Lawrence Livermore National Laboratory – LLNL (Wuebbles *et al.*, 1994a, b), the Max Planck Institut für Chemie – Mainz (C. Brühl *et al.*, 1993; Roehl *et al.*, 1994), the Indian Institute of Technology (Lal and Holt, 1991, updated in 1993), and the University of Oslo (Fuglestvedt *et al.*, 1994). The radiative forcing a-factors adopted are those given in Chapter 8 of this report and in IPCC (1994). Some of these values are apt to be amended in the near future (see Chapter 4 of IPCC, 1994). Table 13-5 presents a composite summary of those results. In addition, it presents results from the studies of Ko *et al.* (1993) and Stordal *et al.* (personal communication, 1994) for SF_6, and from Solomon *et al.* (1994a) for CF_3I. With the exception of CF_3I, all of the molecules considered have lifetimes in excess of several months and thus can be considered reasonably well-mixed; only an upper limit rather than a value is presented for CF_3I. For those species addressed in IPCC (1992), a majority of the GWP values are larger, typically by 10-30%. These changes are largely due to (i) changes in the CO_2 reference noted above and (ii) improved values for atmospheric lifetimes.

Several new gases proposed as CFC and halon substitutes are considered here for the first time, such as HCFC-225ca, HCFC-225cb, HFC-227ea, and CF_3I. Table 13-5 also includes for the first time a full evaluation of the GWPs of several fully fluorinated species, namely SF_6, CF_4, C_2F_6, and C_6F_{14}. SF_6 is used mainly as a heat transfer fluid for electrical equipment (Ko *et al.*, 1993), while CF_4 and C_2F_6 are believed to be produced mainly as accidental by-products of aluminum manufacture. C_6F_{14} and other perfluoroalkanes have been proposed as potential CFC substitutes. The very long lifetimes of the perfluorinated gases (Ravishankara *et al.*, 1993) lead to large GWPs over long time scales.

The uncertainty in the GWP of any trace gas other than CO_2 depends upon the uncertainties in the AGWP of CO_2 and the AGWP of the gas itself. The uncertainties in the relative values of AGWPs for various gases depends upon the uncertainty in relative radiative forcing per molecule (estimated to be about 25% for most gases, as shown in Chapter 8) and on the uncertainty in the lifetimes of the trace gas considered (which are likely to be accurate to about 10% for CFC-11 and CH_3CCl_3 and perhaps 20-30% for other gases derived from them). Combining these dominant uncertainties (in quadrature) suggests uncertainties in the direct AGWPs for nearly all of the trace gases considered in Table 13-5 of less than ±35%. Uncertainties in the AGWPs for CO_2 depend upon uncertainties in the carbon cycle (see Chapter 1 of IPCC, 1994) and on the future scenario for CO_2. The effect of the latter uncertainty is likely to be relatively small, as shown in Chapter 5 of IPCC (1994).

The reference gas for the GWPs in Table 13-5 is the CO_2 decay response from the "Bern" carbon cycle model (Chapter 1 of IPCC, 1994). The GWPs calculations were carried out with background atmospheric trace gas concentrations held fixed at 354 ppmv.

The direct GWPs given in Table 13-5 can be readily converted to other frameworks such as AGWPs, GWPs for a changing atmosphere, and GWPs using as reference either a specific carbon cycle model or the three-parameter fit employed in IPCC (1990, 1992). Table 13-6 presents the relevant factors to carry out such conversions:

- To convert to AGWP units, the numbers in Table 13-5 should be multiplied by the AGWP for the

Table 13-5. Global Warming Potentials (mass basis), referenced to the AGWP for the adopted carbon cycle model CO_2 decay response and future CO_2 atmospheric concentrations held constant at current levels. Only direct effects are considered, except for methane.

Species	Chemical Formula	Global Warming Potential (Time Horizon) 20 years	100 years	500 years
<u>CFCs</u>				
CFC-11	$CFCl_3$	5000	4000	1400
CFC-12	CF_2Cl_2	7900	8500	4200
CFC-13	$CClF_3$	8100	11700	13600
CFC-113	$C_2F_3Cl_3$	5000	5000	2300
CFC-114	$C_2F_4Cl_2$	6900	9300	8300
CFC-115	C_2F_5Cl	6200	9300	13000
<u>HCFCs, etc.</u>				
Carbon tetrachloride	CCl_4	2000	1400	500
Methyl chloroform	CH_3CCl_3	360	110	35
HCFC-22 (†††)	CF_2HCl	4300	1700	520
HCFC-141b (†††)	$C_2FH_3Cl_2$	1800	630	200
HCFC-142b (†††)	$C_2F_2H_3Cl$	4200	2000	630
HCFC-123 (††)	$C_2F_3HCl_2$	300	93	29
HCFC-124 (††)	C_2F_4HCl	1500	480	150
HCFC-225ca (††)	$C_3F_5HCl_2$	550	170	52
HCFC-225cb (††)	$C_3F_5HCl_2$	1700	530	170
<u>Bromocarbons</u>				
H-1301	CF_3Br	6200	5600	2200
<u>Other</u>				
HFC-23 (†)	CHF_3	9200	12100	9900
HFC-32 (†††)	CH_2F_2	1800	580	180
HFC-43-10mee (†)	$C_4H_2F_{10}$	3300	1600	520
HFC-125 (††)	C_2HF_5	4800	3200	1100
HFC-134 (†)	CHF_2CHF_2	3100	1200	370
HFC-134a (†††)	CH_2FCF_3	3300	1300	420
HFC-152a (††)	$C_2H_4F_2$	460	140	44
HFC-143 (†)	CHF_2CH_2F	950	290	90
HFC-143a (††)	CF_3CH_3	5200	4400	1600
HFC-227ea (†)	C_3HF_7	4500	3300	1100
HFC-236fa (†)	$C_3H_2F_6$	6100	8000	6600
HFC-245ca (†)	$C_3H_3F_5$	1900	610	190
Chloroform (††)	$CHCl_3$	15	5	1
Methylene chloride (††)	CH_2Cl_2	28	9	3
Sulfur hexafluoride	SF_6	16500	24900	36500
Perfluoromethane	CF_4	4100	6300	9800
Perfluoroethane	C_2F_6	8200	12500	19100
Perfluorocyclo-butane	$c\text{-}C_4F_8$	6000	9100	13300
Perfluorohexane	C_6F_{14}	4500	6800	9900
Methane*	CH_4	62 ± 20	24.5 ± 7.5	7.5 ± 2.5
Nitrous oxide	N_2O	290	320	180
Trifluoroiodo-methane	CF_3I	< 5	$<< 1$	$<<< 1$

*	Includes direct and indirect components (see Section 13.5.4.2).
(†††)	Indicates HFC/HCFCs in production now and likely to be widely used (see Chapter 4 of IPCC, 1994).
(††)	Indicates HFC/HCFCs in production now for specialized end use (see Chapter 4 of IPCC, 1994).
(†)	Indicates HFC/HCFCs under consideration for specialized end use (see Chapter 4 of IPCC, 1994).

Table 13-6. Absolute GWPs (AGWPs) (W m^{-2} yr $ppmv^{-1}$).*

Case	Time Horizon		
	20 year	100 year	500 year
CO_2, Bern Carbon Cycle Model, fixed CO_2 (354 ppmv)	0.235	0.768	2.459
CO_2, Bern Carbon Cycle Model, S650 scenario	0.225	0.702	2.179
CO_2, Wigley Carbon Cycle Model, S650 scenario	0.248	0.722	1.957
CO_2, Enting Carbon Cycle Model, S650 scenario	0.228	0.693	2.288
CO_2, LLNL Carbon Cycle Model, S450 scenario	0.247	0.821	2.823
CO_2, LLNL Carbon Cycle Model, S650 scenario	0.246	0.790	2.477
CO_2, LLNL Carbon Cycle Model, S750 scenario	0.247	0.784	2.472
CO_2-like gas, IPCC (1990) decay function, fixed CO_2 (354 ppmv)	0.267	0.964	2.848

*Multiply these numbers by 1.291×10^{-13} to convert from per ppmv to per kg.

adopted Bern carbon cycle model, fixed CO_2 (354 ppmv) scenario (*i.e.*, Line 1 in Table 13-6) and multiplied by 1.291×10^{-13} to convert the AGWP of CO_2 from per ppmv to per kg.

- To convert to GWP units using one of the other indicated carbon cycle models and/or trace-gas future scenarios, the numbers in Table 13-5 should be multiplied by the AGWP for the adopted Bern carbon cycle model, fixed CO_2 (354 ppmv) scenario (Line 1) and divided by the AGWP value in Table 13-6 for the carbon cycle model and/or scenario in question.
- To convert to GWPs that are based on the same reference as was used in IPCC (1990,1992), the numbers in Table 13-5 should be multiplied by the AGWP for the adopted Bern carbon cycle model, fixed CO_2 (354 ppmv) scenario (Line 1) and divided by the AGWP value in Table 13-6 for the CO_2-like gas, IPCC (1990) decay function, fixed CO_2 (354 ppmv) (*i.e.*, last line in Table 13-6).

13.5.4 Indirect Effects

13.5.4.1 General Characteristics

In addition to the direct forcing caused by injection of infrared-absorbing gases to the atmosphere, some compounds can also modify the radiative balance through indirect effects relating to chemical transformations. When the full interactive chemistry of the atmosphere is considered, a very large number of possible indirect effects can be identified (ranging from the production of stratospheric water vapor as an indirect effect of H_2 injections to changes in the HCl/ClO ratio and hence in ozone depletion resulting from CH_4 injections).

The effects arising from such processes are difficult to quantify in detail (see Chapter 2 of IPCC, 1994), but many are highly likely to represent only small perturbations to the direct GWP and to global radiative forcing. As noted above for ODPs, recent work has shown that the production of products such as fluoro- and chlorophosgene and organic nitrates from the breakdown of CFCs and HCFCs is unlikely to represent a substantial indirect effect on the GWPs of those species, due to the rapid removal of these water-soluble products in clouds and rain (see Chapter 12 and Kindler *et al.*, 1994). Similarly, the addition of HCFCs and HFCs to the atmosphere can, in principle, affect the oxidizing capacity of the lower atmosphere and hence their lifetimes, but the effect is completely negligible for reasonable abundances of these trace gases.

Table 13-7 summarizes some key stratospheric and tropospheric chemical processes that do represent important indirect effects for GWP estimates. The current state of understanding of these processes is examined in detail in Chapters 2 and 5 of IPCC (1994). It is particularly difficult to calculate GWPs of short-

Table 13-7. Important indirect effects on GWPs.

Species	Indirect Effect	Sign of Effect on GWP
CH_4	Changes in response times due to changes in tropospheric OH	+
	Production of tropospheric O_3	+
	Production of stratospheric H_2O	+
	Production of CO_2 (for certain sources)	+
CFCs, HCFCs,	Depletion of stratospheric O_3	-
Bromocarbons	Increase in tropospheric OH due to enhanced UV	-
CO	Production of tropospheric O_3	+
	Changes in response times due to changes in tropospheric OH	+
	Production of tropospheric CO_2	+
NO_x	Production of tropospheric O_3	+
NMHCs	Production of tropospheric O_3	+
	Production of tropospheric CO_2	+

lived gases with localized sources, such as NO_x and non-methane hydrocarbons. Further, lack of detailed knowledge of the distributions of these and other key tropospheric gases complicates calculations of indirect effects relating to tropospheric ozone production (see Chapters 5 and 7). It is, however, important to recognize that ozone processes in the upper troposphere are more effective for radiative forcing than those near the surface (see Chapter 8), emphasizing chemical processes occurring in the free troposphere.

We present here the indirect GWP effect of tropospheric ozone production only for CH_4. Additional GWP quantification (*e.g.*, for tropospheric ozone precursors such as CO, non-methane hydrocarbons (NMHCs), and NO_x) must await further study of the model intercomparisons described in Chapter 2 of IPCC (1994) and improved field, laboratory, and theoretical characterization of the processes involved in tropospheric ozone production. Reliable radiative forcing indices for gases that form atmospheric aerosols (*e.g.*, sulfur dioxide, SO_2) cannot currently be formulated meaningfully, chiefly because of the lack of understanding of many of the processes involved (*e.g.*, composition of the aerosols, radiative properties, etc.) and because of uncertainties regarding the climate response to the inhomogeneous spatial distributions of the aerosols (see Chapter 3 of IPCC, 1994). For the first time, an estimate of the effects from depletion of ozone on halocarbon GWPs is also presented in this chapter, drawing upon (i) the extensive discussion on ODPs and photochemical considerations behind them in Section 13.4, (ii) the discussion of the relationship between radiative forcing due to ozone change and climate sensitivity in Chapter 8, and (iii) the available scientific literature.

13.5.4.2 INDIRECT EFFECTS UPON THE GWP OF CH_4

Recent research studies of the indirect effects on the GWP of methane include those of Hauglustaine *et al.* (1994a, b), Lelieveld and Crutzen (1992), Lelieveld *et al.*, (1993), and Brühl (1993). In this report, we consider those results together with inputs from Chapters 2 and 4 of IPCC (1994). The relative radiative forcing for methane itself compared to CO_2 on a per-molecule basis is given in Table 4.2a of IPCC (1994) and is used here. Eight multi-dimensional models were used to study the chemical response of the atmosphere to a 20% increase in methane, as discussed in Section 2.9 of IPCC (1994). The calculated range of ozone increases from the full set of tropospheric models considered in that study provides insight regarding the likely range in ozone production.

Uncertainties in these calculations include those related to the NO_x distributions employed in the various models, formulation of transport processes, and other factors discussed in detail in Chapter 2 of IPCC (1994). The estimated uncertainty in the indirect GWP for CH_4 from tropospheric ozone production given below is based upon the calculated mid-to-upper tropospheric ozone response of the models to the prescribed methane perturbation at northern midlatitudes and consideration of the current inadequacies in the understanding of many relevant atmospheric processes. The calculated ozone changes from the model simulations derived for a 20% increase in methane imply an indirect effect that is about 25 ± 15% of the direct effect of methane (or 19 ± 12% of the total), using the infrared radiative code of the LLNL model. A similar number is estimated in Chapter 4 of IPCC (1994). This upper end of this range is close to that presented in IPCC (1990).

Release of CH_4 leads to increased stratospheric water vapor through photochemical oxidation; estimates of this indirect effect range are on the order of 5% or less of the direct effect of methane (4% of the total) based on the discussion in Chapter 4 of IPCC (1994); current results from the LLNL, NCAR, and Mainz radiative/photochemical two-dimensional models; and the published literature (*e.g.*, Lelieveld and Crutzen, 1992; Lelieveld *et al.*, 1993; Brühl, 1993; Hauglustaine *et al.*, 1994a, b). We adopt 5% of the direct effect in the table below, which is smaller than the value quoted in IPCC (1990).

Each injected molecule of CH_4 ultimately forms CO_2, representing an additional indirect effect that would increase the GWPs by approximately 3 for all time horizons (see IPCC, 1990). However, as noted by Lelieveld and Crutzen (1992), this indirect effect is unlikely to apply to biogenic production of CH_4 from most sources (*e.g.*, from rice paddies), since the ultimate source of the carbon emitted as CH_4 in this case is CO_2, implying no net gain of carbon dioxide. While non-biogenic methane sources such as mining operations do lead indirectly to a net production of CO_2, this methane is often included in national carbon production inventories. In this case, consideration of CO_2 production in the GWP could lead to "double-counting," depending upon how the GWPs and inventories are combined. As shown in IPCC (1994), most human sources of methane are biogenic, with another large fraction being due to coal mines and natural gas. Thus, the indirect effect of CO_2 production does not apply to much of the CH_4 inventory, and is not included in the table below (in contrast to IPCC (1990), where this effect was included).

As in Table 13-5, the GWPs were calculated relative to the CO_2 decay response of the Bern carbon cycle model with a constant current CO_2 and CH_4 atmosphere. Table 13-8 summarizes the composite result for methane GWPs, its uncertainty, and considers the breakdown of the effects among various contributing factors. The ranges in CH_4 GWPs shown in Table 13-8 reflect the uncertainties in response time, lifetime, and indirect effects, as discussed below. We assume a lifetime of methane in the background atmosphere of 10 ± 2 years (which is consistent with the budget given in IPCC, 1994). However, the response time of an added pulse is assumed to be much longer (12-17 years based upon Chapter 2 of IPCC, 1994). The total GWPs reported in IPCC (1990) including indirect effects are within the ranges shown in Table 13-8. The longer response time adopted here for methane perturbations is responsible for a large part of the change in methane GWP values compared to the nominal values including direct effects only in the IPCC (1992) report (although the fact that indirect effects were likely to be comparable to the direct effect was noted). This change is based entirely on the analysis presented in Chapter 2 of IPCC (1994) used to define the methane response time for this report (see Prather, 1994). The decay response has been thoroughly tested only for small perturbations around a background state and continuing input flux approximately representative of today's atmosphere. It would be different if, for example, large changes in methane emissions were to occur in the near future. It is also believed to be sensitive to other chemical factors such as the sources of carbon monoxide. The GWP determined in this manner is similarly valid for relatively small perturbations, *e.g.*, those that would be required to stabilize concentrations at current levels rather than continuing the small trend (order 1%/year) observed in the past decade (see Chapter 2). However, the GWP shown in Table 13-8 cannot be used to estimate the radiative forcing that occurred since preindustrial times, when methane concentrations more than doubled.

Table 13-8. Total GWP for CH_4, including indirect effects, referenced to the AGWP computed for the CO_2 decay response of the Bern carbon cycle model and future CO_2 atmospheric concentrations held constant at current levels.

GWP	Time Horizon 20 year	 100 year	 500 year
Total CH_4 GWP, including indirect effects and 12-17 year response time	42-82	17-32	5-10
Fraction of total GWP due to tropospheric O_3 change	19 ± 12%	19 ± 12%	19 ± 12%
Fraction of total GWP due to stratospheric H_2O change	4%	4%	4%

13.5.4.3 NET GLOBAL WARMING POTENTIALS FOR HALOCARBONS

Chlorofluorocarbons effectively absorb infrared radiation and have been estimated to have accounted for as much as about 25% of the anthropogenic direct radiative forcing of the Earth's climate system over the period from 1980 to 1990 (IPCC, 1990). Improved understanding of the impact of ozone depletion on global radiative forcing has, however, markedly altered this picture (WMO, 1992; IPCC, 1992). It is now clear that the large ozone depletions observed in the lower stratosphere are likely to influence temperatures near the tropopause (Lacis *et al.*, 1990; Ramaswamy *et al.*, 1992), implying that in addition to their *direct* greenhouse warming, the *indirect* effect of ozone depletion is significant for estimating the GWPs of ozone-destroying gases. Ramaswamy *et al.* (1992) and WMO (1992) concluded that the globally averaged *decrease* in radiative forcing at the tropopause due to ozone depletion approximately balanced the globally averaged *increase* in direct radiative warming in the troposphere related to the direct forcing due to halocarbons during the decade of the 1980s. While changes in ozone have been reported in the upper troposphere (see Chapter 1), these are probably due to factors other than halocarbon increases (*e.g.*, changes of CO, NO_y, etc.) and do not affect the inference of halocarbon GWPs so long as the vertical profile of ozone depletion can be characterized. If such changes were to mask the vertical extent of halocarbon-induced ozone loss, then the cooling tendency ascribed to halocarbons could be underestimated. Updated estimates of halocarbon radiative forcing are provided in Chapter 8 of this report, IPCC (1994), and Schwarzkopf and Ramaswamy (1993). Daniel *et al.* (1994) have considered the indirect effects of ozone depletion in analyses of the GWPs for halocarbons. They concluded that the indirect effect varies greatly for different kinds of halocarbons (*e.g.*, halons, CFCs, HCFCs), a result that will be discussed further below.

Several recent studies have addressed the degree to which the radiative heating due to additions of a quasi-uniformly distributed tropospheric gas such as a CFC may be equated with the spatially inhomogeneous cooling at the tropopause due to ozone depletion for the purposes of evaluating a net climate response (*e.g.*, Molnar *et al.*, 1994). Some studies suggest that ozone depletion may result in important dynamical changes that modulate the realized climate response (Molnar *et al.*, 1994). For the purposes of the present analysis, it will be assumed that the indirect and direct radiative effects of halocarbons can be compared to one another in a globally averaged sense, an assumption that is currently being tested with detailed three-dimensional models (see Chapter 8 and IPCC, 1994).

Model calculations show that radiative cooling is a strong function of the vertical profile of the ozone loss (Schwarzkopf and Ramaswamy, 1993; Wang *et al.*, 1993). This implies that it will be difficult to calculate these effects using a fully interactive two-dimensional chemistry-dynamics model, since these tend to underestimate the ozone losses observed in the critical lowest part of the stratosphere (see, *e.g.*, Hauglustaine *et al.*, 1994a). Satellite and ozonesonde observations (see Chapter 1) can, however, be used to characterize the shape of the ozone loss profile fairly well. It has been shown by Schwarzkopf and Ramaswamy (1993) that the uncertainty in the globally averaged ozone cooling is on

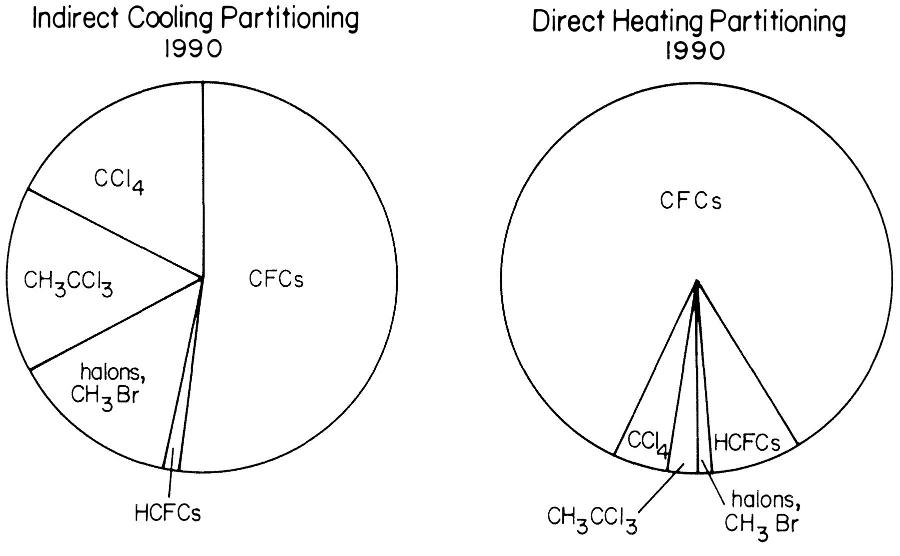

Figure 13-9. Contributions of various gases to the total estimated radiative cooling (indirect) and heating (direct) due to halocarbons in 1990 (Adapted from Daniel *et al.*, 1994). The adopted value of α for these calculations is 40.

the order of ±30% for a broad range of assumptions regarding the magnitude of the ozone depletion observed during the 1980s in the lowest part of the stratosphere (*i.e.*, below the region where satellite data exist). This estimate does not, however, include the enhanced ozone depletions that have been obtained in 1992 and 1993, nor does it consider the large changes in ozone observed by the Stratospheric Aerosol and Gas Experiment (SAGE) near the tropical tropopause (see Chapter 1). Insofar as these may be halocarbon-induced, these effects would tend to increase the global cooling and hence decrease the GWPs of ozone-depleting gases shown below.

Daniel *et al.* (1994) combined estimates of radiative cooling for the 1980s and their uncertainties (from the work of Schwarzkopf and Ramaswamy, 1993) with the detailed evaluation of past and future equivalent effective stratospheric chlorine for each halocarbon described in Section 13.3 to examine the net radiative forcing that can be attributed to each halocarbon. They emphasized that both Antarctic and midlatitude total ozone depletions appear to be quite small prior to about 1980, but to increase rapidly after that time, suggesting that a "threshold" for ozone destruction may have been reached. They assumed that the indirect radiative cooling for each halocarbon depends linearly upon its contribution to the total equivalent effective stratospheric chlorine whenever the latter lies above this threshold value. Possible nonlinearities associated, for example, with temperature feedbacks between ozone depletion and polar stratospheric cloud frequencies have therefore been neglected in this study. The impact of changing UV radiation due to ozone depletion upon OH and hence tropospheric chemistry has also not been considered here.

Insofar as significant ozone loss likely occurs only for total equivalent effective stratospheric chlorine levels above a certain threshold, the total indirect radiative cooling caused by any halocarbon depends upon the abundances of others and cannot be specified independent of scenario. This implies that GWPs for halocarbons based upon the indirect effects estimated for injection of an infinitesimally small amount of added gas can no longer be used to directly calculate the net radiative impact of the true amount of that gas in the Earth's atmosphere; this limitation is similar to that for methane discussed above.

Figure 13-9 shows an estimate of the contributions of various gases to the total estimated radiative cooling (indirect) and heating (direct) due to halocarbons in 1990 (Daniel *et al.*, 1994). A key point noted by Daniel *et al.* (1994) is that the CFCs are likely to be responsible for a much larger fraction of the estimated heating than

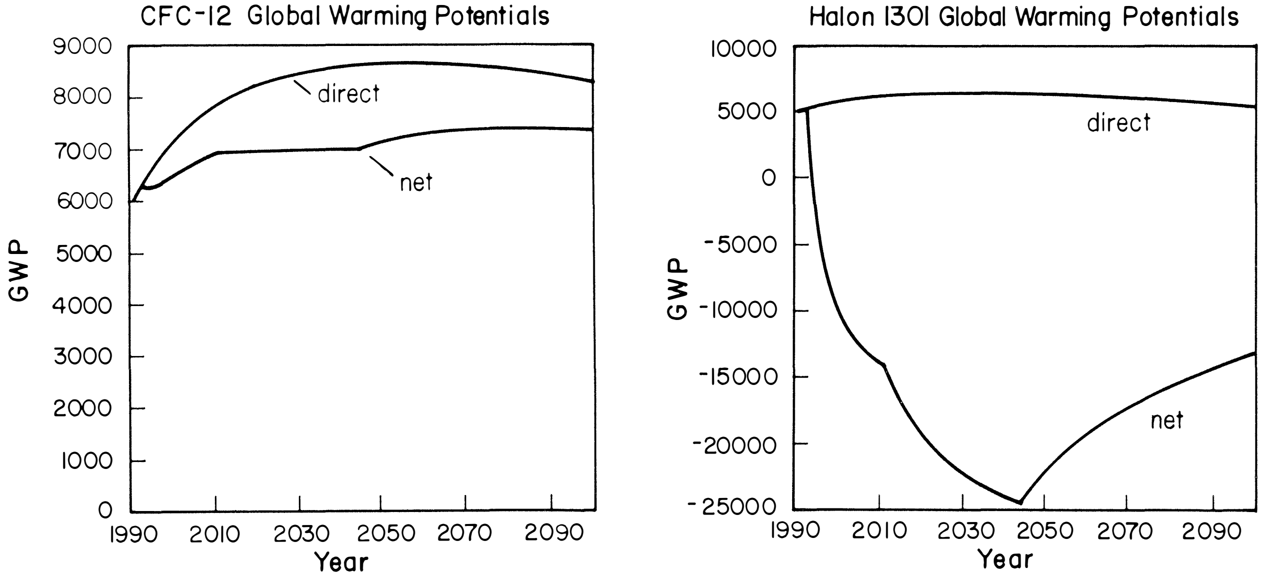

Figure 13-10. Calculated time-dependent GWPs for CFC-12 and halon-1301, adapted from the study of Daniel *et al.* (1994), for the basic Copenhagen scenario described in Section 13.3 (case A) and assuming a value of α of 40. The denominator used in these calculations is based upon the carbon cycle model as discussed in the text.

of the cooling, while for compounds such as the halons and anthropogenic CH_3Br, the situation is reversed. This is due to the enhanced effectiveness of brominated compounds compared to chlorinated species for ozone loss (see Section 13.4.2), by about a factor of 40. CCl_4 and CH_3CCl_3, while not as effective as the bromocarbons for ozone destruction, contain several chlorine atoms per molecule and release them readily in the stratosphere, making them relatively effective ozone destroyers (and hence cooling agents) as well. This introduces a new factor that would have to be dealt with in the use of such indices in policy decisions, underscoring the difficulty of considering gases with multiple, and very different, environmental impacts using a single simple index. Multiple impacts could require more sophisticated policy tools.

Figure 13-10 shows calculated GWPs for CFC-12 and halon-1301 as a function of time horizon adapted from the study of Daniel *et al.* (1994), for the base Copenhagen scenario (case A) described in Section 13.3, assuming a value of α of 40, and using the Bern *et al.* carbon cycle model results for the denominator as in IPCC (1994). As suggested by Figure 13-10, the net GWP of CFC-12 remains positive while that of halon-1301 becomes large and negative when indirect effects are considered in this framework. Daniel *et al.* (1994) considered the following key uncertainties in deriving the GWPs for halocarbons: (i) variations in the scenario for future concentrations of ozone-depleting gases, as in the scenarios of Section 13.3, (ii) uncertainties in the globally-averaged relative efficiency of bromine for ozone loss as compared to chlorine (α, assumed to lie between 40 and 200), and (iii) uncertainties in the magnitude of the cooling in the lower stratosphere due to uncertainties in the ozone loss profile (estimated to be about ±30% as noted above). They found that the GWPs were not as sensitive to the adopted range of possible scenarios for future concentrations of halocarbons nor to the exact values of the thresholds or scenarios assumed as to the uncertainties in the absolute value of the cooling and the value of α. This is consistent with the rather small differences in key aspects of the various scenarios shown in Table 13-3. The GWPs for bromocarbons were found to be extremely sensitive to the chosen value of α, while those for CFCs were quite sensitive to the adopted uncertainty in the total absolute radiative cooling in the 1980s. Table 13-9 shows the range of 20- and 100-year net GWPs derived for the halocarbons including indirect

Table 13-9. Net GWPs per unit mass emission for halocarbons including indirect effects (adapted from Daniel et al., 1994). Relative to CO_2 using Bern model for decay function (as in IPCC, 1994).

	Time Horizon = 2010					Time Horizon = 2090				
	Uncertainty in scenario, α		Uncertainty in cooling		Direct	Uncertainty in scenario, α		Uncertainty in cooling		Direct
compound	min	max	min	max		min	max	min	max	
CFC-11	1900	2900	1300	3000	5000	1400	1800	640	2200	4000
CFC-12	6300	6900	6100	6900	7900	6900	7100	6500	7400	8500
CFC-113	3200	3800	2800	3800	5000	3300	3500	2800	3800	5000
HCFC-22	3900	4000	3800	4000	4300	1500	1500	1500	1600	1700
HCFC-142b	3800	3900	3700	4000	4200	1800	1800	1700	1800	2000
CH_3Br	-18600	-4900	-6400	-3300		-5700	-1500	-2000	-1000	
H-1301	-97200	-22400	-31000	-13800	6200	-87300	-21600	-31200	-14200	5600
H-1211	-92400	-21500	-29600	-13400		-50600	-13600	-18800	-8900	
HCFC-141b	910	1200	690	1200	1800	270	370	180	390	630
CH_3CCl_3	-780	-450	-1100	-420	360	-260	-150	-360	-140	110
CCl_4	-1800	-520	-2500	-430	2000	-1500	-1100	-2400	-630	1400
HCFC-123	120	170	67	180	300	37	52	20	54	93
HCFC-124	1300	1400	1300	1370	1500	410	430	390	430	480
HFC-134a	3300	3300	3300	3300	3300	1300	1300	1300	1300	1300

effects from these sensitivity studies and compares them to GWPs for the direct effect only (adapted from Daniel *et al.*, 1994 for the denominator used here).

The range of values in the table underscores the uncertain nature of these estimates due to uncertainties in α and in the total absolute radiative cooling (*i.e.*, ozone loss distribution), but also illustrates systematic differences between various broad classes of compounds that are more robust. In particular, the CFCs and HCFCs are highly likely to be net warming agents. CCl_4 and CH_3CCl_3 are likely to be nearly "climate neutral," while halons and methyl bromide are believed to be net cooling agents. The impact of the implementation of the Copenhagen Amendments on radiative forcing and hence on climate change will depend upon the time-dependent mix of these gases and their substitutes in the future (see Chapter 8).

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