

# CHAPTER 5

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## A Focus on Information and Options for Policymakers

**Coordinating Lead Authors:**

J.S. Daniel  
G.J.M. Velders

**Lead Authors:**

O. Morgenstern  
D.W. Toohy  
T.J. Wallington  
D.J. Wuebbles

**Coauthors:**

H. Akiyoshi  
A.F. Bais  
E.L. Fleming  
C.H. Jackman  
L.J.M. Kuijpers  
M. McFarland  
S.A. Montzka  
M.N. Ross  
S. Tilmes  
M.B. Tully

**Contributors:**

S.O. Andersen  
U. Langematz  
P.M. Midgley



# CHAPTER 5

## A FOCUS ON INFORMATION AND OPTIONS FOR POLICYMAKERS

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## SCIENTIFIC SUMMARY

Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) are metrics frequently used to quantify the relative impacts of substances on ozone depletion and climate forcing. In Chapter 5, both ODPs and GWPs have been updated. The direct GWPs for some compounds presented here have not appeared previously in WMO/UNEP or Intergovernmental Panel on Climate Change (IPCC) assessments. Indirect GWPs have also been re-evaluated.

### Information for Policymakers

- **The Montreal Protocol is working. It has protected the stratospheric ozone layer from much higher levels of depletion by phasing out production and consumption of ozone-depleting substances (ODSs).** Simulations show that unchecked growth in the emissions of ODSs would have led to ozone depletion globally in the coming decades much larger than has been observed. Solar ultraviolet-B (UV-B) radiation at the surface would also have increased substantially.
- **The Montreal Protocol and its Amendments and Adjustments have made large contributions toward reducing global greenhouse gas emissions.** Because many ODSs are potent greenhouse gases, the Montreal Protocol has successfully avoided larger climate forcing. In 2010, the decrease of annual ODS emissions under the Montreal Protocol is estimated to be about 10 gigatonnes (Gt) of carbon dioxide-equivalent (GtCO<sub>2</sub>-eq) per year, which is about five times larger than the annual emissions reduction target for the first commitment period (2008–2012) of the Kyoto Protocol.
- **The accelerated hydrochlorofluorocarbon (HCFC) phase-out agreed to by the Parties to the Montreal Protocol in 2007 is projected to reduce cumulative HCFC emissions by 0.6–0.8 million ODP-tonnes between 2011 and 2050 and bring forward the year equivalent effective stratospheric chlorine (EESC) returns to 1980 levels by 4–5 years. In terms relevant to climate, the accelerated HCFC phase-out is projected to reduce emissions by 0.4–0.6 GtCO<sub>2</sub>-eq per year averaged over 2011 through 2050.** The actual climate benefit will be determined, in part, by the climate impact of the compounds used to replace the HCFCs. In comparison, global anthropogenic emissions of CO<sub>2</sub> were greater than 30 Gt per year in 2008.
- **EESC at midlatitudes is projected to return to 1980 levels in 2046 for the baseline (A1) scenario, 2–3 years earlier than projected in the previous Assessment.** This revision is primarily due to an improved understanding of lower stratospheric chlorine and bromine release from ODSs, along with contributions from smaller projected HCFC emissions, and despite larger projected emissions of carbon tetrachloride (CCl<sub>4</sub>) and a smaller 1980 mixing ratio of methyl bromide (CH<sub>3</sub>Br).
- **EESC in the Antarctic vortex is projected to return to 1980 levels around 2073 for the baseline (A1) scenario, 7–8 years later than projected in the previous Assessment.** This is primarily due to an improved understanding of lower stratospheric chlorine and bromine release from ODSs, with smaller contributions from changes in the emissions of CCl<sub>4</sub> and HCFCs and a smaller 1980 mixing ratio of CH<sub>3</sub>Br. The return to 1980 levels in the Antarctic vortex is about 26 years later than the return of midlatitude EESC to 1980 levels.
- **Due to the ongoing success of the Montreal Protocol and its Amendments and Adjustments in reducing the production, emissions, and abundances of controlled ODSs, other compounds and activities not controlled by the Montreal Protocol are becoming relatively more important to stratospheric ozone levels.**
- **Increasing abundances of radiatively important gases that are not controlled by the Montreal Protocol, especially CO<sub>2</sub>, methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O), are expected to significantly affect future stratospheric ozone levels** (see also Chapter 3). Under many IPCC future scenarios, it is projected that these gases will cause globally averaged ozone changes larger than those resulting from any of the ODS reduction cases explored in this chapter.

- **A nitrous oxide (N<sub>2</sub>O) ODP of 0.017 has been calculated. The anthropogenic ODP-weighted emission of N<sub>2</sub>O is larger than that of any current halogenated ODS emission.** The ODP of N<sub>2</sub>O is more uncertain than it is for halogenated substances, but it has been known since 1970 that N<sub>2</sub>O depletes stratospheric ozone. Reductions in N<sub>2</sub>O emissions would also reduce climate forcing.
- **Since the previous Assessment, new fluorocarbons have been suggested as possible replacements for potent HCFC and hydrofluorocarbon (HFC) greenhouse gases.** For example, HFC-1234yf (CF<sub>3</sub>CF=CH<sub>2</sub>) (ODP = 0; 100-year GWP = 4) is proposed to replace HFC-134a (CH<sub>2</sub>FCF<sub>3</sub>) (ODP = 0; 100-year GWP = 1370) in motor vehicle (mobile) air conditioning. Each new fluorocarbon proposed as a replacement will require an evaluation for ODP, GWP, atmospheric fate, safety, and toxicity for a thorough understanding of its potential environmental impact. Preliminary analyses of the atmospheric fate of HFC-1234yf indicate that global replacement of HFC-134a with HFC-1234yf at today's level of use is not expected to contribute significantly to tropospheric ozone formation or harmful levels of the degradation product TFA (trifluoroacetic acid). It is well established that TFA is a ubiquitous natural component of the hydrosphere, but uncertainties remain regarding its natural and anthropogenic sources, long-term fate, and abundances.

## Options for Policymakers

A new baseline scenario for ODSs is presented in Chapter 5 that reflects our current understanding of atmospheric mixing ratios, production levels, and bank sizes. Elimination of future emissions, production, and banks of various ODSs are applied to this scenario to evaluate the maximum impacts of various hypothetical phase-outs (see Table S5-1). The year EESC returns to 1980 levels, and integrated EESC changes, are two metrics used in the evaluation. The calculations of the years when EESC returns to the 1980 level in these hypothetical cases do not consider other effects such as changing atmospheric transport and lifetimes. An elimination of anthropogenic N<sub>2</sub>O emissions is also considered and compared to some ODS cases using globally averaged total ozone. In addition to the hypothetical cases discussed below, the impacts on stratospheric ozone of other activities, such as the use of automotive biofuels, commercial subsonic aircraft, and rocket launches, are considered in Chapter 5. These other activities are not expected to substantially affect stratospheric ozone now or in the near future.

- **Projections suggest that unmitigated HFC growth could result in GWP-weighted emissions up to 8.8 GtCO<sub>2</sub>-eq per year by 2050, comparable to the GWP-weighted emissions of chlorofluorocarbons (CFCs) at their peak in 1988.** The highest of these projections assumes that developing countries use HFCs with GWPs comparable to those currently used in the same applications in developed countries. The projected radiative forcing in 2050 from these compounds (up to 0.4 W/m<sup>2</sup>) can be reduced by using compounds with lower GWPs.
- **Options available for limiting future halocarbon emissions will have less impact on future ozone levels than what has already been accomplished by the Montreal Protocol.**
- **Leakage of CFCs and leakage of halons from the banks are the largest sources of current ODP-weighted emissions of ODSs.** A delay of four years, from 2011 to 2015, in the capture and destruction of the estimated CFC banks is currently thought to reduce the potential ozone and climate benefits from these actions by about 30%. The percentage impact of a four-year delay in the capture and destruction of the halon banks is similar.
- **Elimination of future CCl<sub>4</sub> emissions is now projected to have a larger impact on integrated EESC than was projected in the previous Assessment.** Recent observed CCl<sub>4</sub> mixing ratios have declined more slowly than previously projected. Extrapolation of this trend leads to larger future projected emissions in the baseline scenario and thus to the increased projected impact of the elimination of emissions.
- **The estimated impact on integrated EESC resulting from elimination of future HCFC production is slightly smaller than in the previous Assessment.** The recent growth in reported HCFC production in developing countries was larger than projected in the previous Assessment. This alone would have resulted in a larger projected HCFC

**Table S5-1. Summary of hypothetical cases for accelerating the recovery of the ozone layer and reducing carbon-equivalent emissions.** The table below shows the reductions in integrated EESC and integrated CO<sub>2</sub>-eq emissions relative to the baseline (A1) scenario that can be achieved in several hypothetical cases. The EESC excess above 1980 levels is integrated from 2011 until the time EESC returns to the 1980 level (before 2050). Any potential contribution from very short-lived substances is neglected.

| Substance or Group of Substances                      | Reductions (%) in Integrated EESC (equivalent effective stratospheric chlorine) |                  | Reduction in Cumulative GWP-Weighted Emissions from 2011 to 2050 (Gt of CO <sub>2</sub> -equivalent) |                        |
|---|---|------------------|--|------------------------|
|   | 2011  | 2015             | 2011   | 2015                   |
| <i>Bank capture and destruction in 2011 and 2015:</i> |   |                  |  |                        |
| CFCs  | 11  | 7.0              | 7.9  | 5.5                    |
| Halons  | 14  | 9.1              | 0.4  | 0.3                    |
| HCFCs   | 4.8   | 5.3 <sup>1</sup> | 4.9  | 5.5 <sup>1</sup>       |
| <i>Production elimination after 2010:</i>             |   |                  |  |                        |
| HCFCs   |   | 8.8              |  | 13.2                   |
| CH <sub>3</sub> Br for quarantine and pre-shipment    |   | 6.7              |  | 0.002                  |
| <i>Total emissions elimination after 2010:</i>        |   |                  |  |                        |
| CCl <sub>4</sub> <sup>2</sup>                         |   | 7.6              |  | 0.9                    |
| CH <sub>3</sub> CCl <sub>3</sub>                      |   | 0.1              |  | 0.004                  |
| HFCs  |   | 0.0              |  | Up to 170 <sup>3</sup> |

<sup>1</sup> The impact of a 2015 HCFC bank recovery is larger than a 2011 bank recovery because this calculation assumes destruction of the bank in only a single year, and because the bank in 2015 is larger than the bank in 2011 owing to continued annual production that is larger than the annual bank release.

<sup>2</sup> Banks are assumed to be zero. Emissions include uncertain sources such as possible fugitive emissions and unintended by-product emissions.

<sup>3</sup> Strongly dependent on future projections and does not consider HFC-23 emissions. HFCs are not controlled by the Montreal Protocol, but are included in the basket of gases of the Kyoto Protocol.

production in the new baseline scenario compared to the previous Assessment, but is projected to be more than compensated for by the accelerated HCFC phase-out agreed to by the Parties to the Montreal Protocol in 2007. Projections suggest that total emissions of HCFCs will begin to decline in the coming decade due to measures already agreed to under the Montreal Protocol.

- **The elimination of all emissions of chlorine- and bromine-containing ODSs after 2010 would shift the year EESC reaches the 1980 level by about 13 years, from 2046 to 2033.** In terms relevant to climate, this would reduce emissions of these substances by about 0.7 GtCO<sub>2</sub>-eq per year averaged over 2011 through 2050. Future production of HCFCs and the sum of the current banks of CFCs plus HCFCs contribute about equally to this number. In comparison, global anthropogenic emissions of CO<sub>2</sub> were greater than 30 Gt per year in 2008.
- **A phase-out of methyl bromide emissions from quarantine and pre-shipment (QPS) applications beginning in 2011 would shift the year EESC reaches the 1980 level earlier by 1.5 years compared to continued use at current levels.** Continuing critical-use exemptions (CUEs) indefinitely at the approved 2011 level would delay the return of EESC to 1980 levels by 0.2 years.
- **Elimination of anthropogenic emissions of very short-lived substances (VSLS) could shift the year EESC reaches the 1980 level earlier by almost 3 years,** if anthropogenic VSLS contribute 40 parts per trillion of EESC to the stratosphere. It remains unclear, however, how VSLS emissions reductions at different surface locations would affect their contribution to stratospheric chlorine. VSLS are not controlled by the Montreal Protocol.



## 5.1 SUMMARY OF PREVIOUS ASSESSMENT AND KEY ISSUES TO BE ADDRESSED IN THE CURRENT ASSESSMENT

The benefits of the Montreal Protocol and its Amendments and Adjustments to both stratospheric ozone and climate have been well documented. Controls on the production and consumption of ozone-depleting substances have been so successful, in fact, that remaining options for further reducing future emissions of ozone-depleting substances (ODSs) are not expected to be as effective in reducing future ozone depletion and climate forcing as what has already been accomplished. As the ability to make further ODS reductions becomes more limited and ODS emissions continue to decline, other processes and anthropogenic activities are expected to become relatively more important in affecting future ozone evolution.

The majority of this chapter is devoted to assessing the impacts of various ozone-relevant processes and activities on ozone depletion and climate forcing. It serves primarily as an update to Chapter 8 of the previous Assessment (Daniel and Velders et al., 2007). In that chapter, future equivalent effective stratospheric chlorine (EESC) projections were updated with the goal of providing a more accurate estimate of the time when the impact of ODSs on stratospheric ozone depletion would return to its 1980 level. The most significant updates resulted from improved bank estimates of chlorofluorocarbon-11 (CFC-11) and CFC-12. For the first time, bank estimates were available from a bottom-up method, leading to more reliable future projections. Before the previous Assessment, banks were estimated from the cumulative difference between production and emissions, a technique thought to be characterized by large uncertainties. The value for the relative effectiveness of bromine compared with chlorine was also increased to be consistent with the latest literature, making methyl bromide ( $\text{CH}_3\text{Br}$ ) emissions and halon banks more important relative to the chlorine-containing ODSs than they would have been otherwise. Using the updated EESC projections, the impacts of eliminating future production, bank release, and emissions of several compound groups were quantified. It was found that the elimination of future hydrochlorofluorocarbon (HCFC) emissions could reduce future EESC more than the elimination of emissions of any other compound group. In 2007, the Parties to the Montreal Protocol decided to accelerate the production and consumption phase-out of the HCFCs. The previous Assessment was also the first assessment that presented dates for the return of EESC to 1980 levels relevant to both the midlatitude and Antarctic stratosphere.

In the current chapter, Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) for ODSs and their replacements are updated. New scenarios are generated to explore the potential impacts of some current

hypothetical ODS and nitrous oxide ( $\text{N}_2\text{O}$ ) emissions reductions on future ozone depletion and climate forcing. These new scenarios incorporate updated bottom-up bank estimates and the latest ODS mixing ratio observations. The impact of the 2007 HCFC accelerated phase-out is also quantified. This chapter assesses some additional processes and activities that are expected to affect future ozone levels through mechanisms that do not necessarily involve the emission of chlorine- and bromine-containing source gases. Some of these processes could affect future ozone levels more than future emissions of controlled ODSs. We also discuss the impact of the Montreal Protocol on climate forcing where appropriate. For example, in addition to the climate forcing of ODSs, we assess the impact of future hydrofluorocarbon (HFC) abundances on climate because these chemicals are commonly used as replacement compounds for ODSs. Finally, since the previous Assessment, additional work has been published that investigates the impact of the Montreal Protocol on both ozone and climate. These studies support our understanding that the Montreal Protocol and its Amendments and Adjustments have averted many profound changes to Earth and its atmosphere.

Uncertainties remain in our ability to evaluate the effects of human activities on future ozone levels. Where appropriate, we identify gaps in our understanding that inhibit a precise quantification of ozone impacts.

## 5.2 METRICS USED TO QUANTIFY OZONE AND CLIMATE IMPACTS

### 5.2.1 Background

Halocarbons and other long-lived gases released from Earth's surface become mixed in the lower atmosphere and are transported into the stratosphere by atmospheric dynamical processes. They are removed from the atmosphere by photolysis, reaction with excited-state oxygen atoms ( $\text{O}(^1\text{D})$ ) and hydroxyl radicals (OH) (the latter typically only for unsaturated compounds or those containing C-H bonds), and for some compounds, uptake by the oceans and/or land (see Chapter 1). Halocarbons that are transported intact to the stratosphere can react or undergo photolysis and release their degradation products there directly. Some fraction of the degradation products from halocarbons that react before leaving the troposphere can also be transported to the stratosphere. The final degradation products are inorganic halogen species containing fluorine, chlorine, bromine, and iodine atoms. The fraction of the inorganic halogen present in the stratosphere as X atoms ( $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ) and XO largely determines the efficiency of ozone destruction there. Fluorine atoms, for

example, exist as F and FO in very small relative quantities because fluorine species are rapidly converted into hydrogen fluoride (HF), a stable reservoir species that does not react with ozone. This prevents fluorine from contributing to ozone destruction to any significant degree (Ravishankara et al., 1994; Wallington et al., 1995). Iodine atoms participate in catalytic ozone destruction cycles, but rapid tropospheric loss of iodine-containing compounds reduces the amount of iodine reaching the stratosphere from surface emissions (see Chapter 1). Thus, it is primarily chlorine- and bromine-containing compounds that lead to ozone depletion. Halocarbons also absorb terrestrial radiation (long-wavelength infrared radiation emitted from Earth's surface and by the atmosphere) and contribute to the radiative forcing of climate.

Simple metrics have been widely used to quantify the contribution of individual compounds to stratospheric ozone depletion and climate change. ODPs and GWPs are the most established metrics and have been used in past climate and ozone assessments (IPCC, 1990, 1995, 1996, 2001, 2007; IPCC/TEAP, 2005; WMO, 1989, 1991, 1995, 1999, 2003, 2007). They have qualities that are particularly useful in policy discussions. Specifically, they are simple and transparent concepts that are straightforward to estimate and communicate. They approximate the integrated impact of the emission of a given gas relative to that for the emission of the same mass of a reference compound (generally CFC-11 for ODPs and carbon dioxide (CO<sub>2</sub>) for GWPs). Some uncertainties in translating emissions into absolute environmental impacts tend to cancel, and the relative benefits of controlling emissions of different gases are highlighted when using such indices. ODPs and GWPs have found widespread use in international agreements such as the Montreal Protocol and Kyoto Protocol and in national regulatory discussions.

Both steady-state and time-dependent ODPs can provide valuable information about the potential for ozone destruction by a compound. **Steady-state ODPs are defined as the change in global ozone for a sustained unit mass emission of a specific compound relative to the change in global ozone for the sustained unit mass emission of CFC-11 (CFCl<sub>3</sub>)** (Fisher et al., 1990; Solomon et al., 1992; Wuebbles, 1983). For compounds that are removed by linear processes, this is equivalent to assuming an emission pulse and integrating over the entire decay of the compound (Prather, 1996; 2002). CFC-11 was a widely used industrial compound in the 1970s and 1980s and so has been chosen as a convenient reference gas (Fisher et al., 1990; Wuebbles, 1981; Wuebbles, 1983). Steady-state ODPs have no time dependence and are frequently calculated using chemical transport models. The accuracy of the calculation depends on the model's ability to simulate the distribution of the considered compound and the associated ozone loss. However, because the ODPs are

defined relative to the ozone loss caused by CFC-11, it is generally expected that for chlorocarbon compounds ODPs demonstrate less sensitivity to photochemical modeling errors than do absolute ozone loss calculations. Steady-state ODPs are normally derived relative to a fixed atmosphere; there would be differences in some ODPs if calculations were made for a future atmosphere with different background composition. ODPs with some time horizon, referred to as time-dependent ODPs (Solomon and Albritton, 1992), are more analogous to GWPs and provide information regarding the different timescales over which the compound and reference gas (CFC-11) liberate chlorine and bromine into the stratosphere. Compounds that have shorter (longer) atmospheric lifetimes than CFC-11 have ODPs that decrease (increase) with increasing integration time. Semi-empirical ODPs have also been developed (Solomon et al., 1992) so steady-state and time-dependent ODPs could have an observational basis. Some semi-empirical steady-state values have been revised in this chapter to reflect updates to fractional release values and to some lifetimes. In previous assessments, the semi-empirical approach and model calculations have been shown to yield similar values for most gases.

The advantages and disadvantages of the ODP metric have been discussed in previous WMO/UNEP reports (WMO, 1989, 1991, 1995, 1999, 2003, 2007). The projected importance of non-halocarbon emissions to future ozone levels presents new challenges to the ODP concept and raises questions about their continued comprehensiveness. Emissions occurring in the stratosphere or upper troposphere from aviation and rockets present special challenges to the ODP concept, but may be able to be treated in a manner similar to how very-short-lived species are treated (as a function of where and when emissions occur). ODPs are discussed in more detail in Section 5.2.2 below.

Calculation of the GWP of a compound requires knowledge of its radiative efficiency and global lifetime. The change in net radiation at the tropopause caused by a given change in greenhouse gas concentration or mass is referred to as radiative efficiency. Radiative efficiency has units of Watts per square meter per part per billion (W m<sup>-2</sup> ppb<sup>-1</sup>) or Watts per square meter per kilogram (W m<sup>-2</sup> kg<sup>-1</sup>); it is calculated using radiative transfer models of the atmosphere and depends upon the strength and spectral position of a compound's absorption bands as well as atmospheric structure, surface temperature, and clouds. The Absolute Global Warming Potential (AGWP) for time horizon  $t'$  is defined as

$$\text{AGWP}_x(t') = \int_0^{t'} F_x \cdot x(t) dt \quad (5-1)$$

where  $F_x$  is the radiative efficiency of species  $x$ ,  $x(t)$  describes the decay with time of a unit pulse of compound  $x$ , and  $t'$  is the time horizon considered.  $F_x$  is given in terms

of  $\text{W m}^{-2} \text{kg}^{-1}$  or in  $\text{W m}^{-2} \text{ppb}^{-1}$ . The AGWP usually has units of  $\text{W m}^{-2} \text{kg}^{-1} \text{yr}$  and quantifies the future integrated radiative forcing over the time horizon of a unit mass pulse emission of a greenhouse gas. To compare the relative integrated effect of various compounds on climate, the GWP metric was developed. The GWP for time horizon  $t'$  (IPCC, 1990; 2001; 2007) can be defined as

$$\text{GWP}_x(t') = \frac{\text{AGWP}_x(t')}{\text{AGWP}_{\text{CO}_2}(t')} = \frac{\int_0^{t'} F_x \exp\left(-t/\tau_x\right) dt}{\int_0^{t'} F_{\text{CO}_2} R(t) dt} \quad (5-2)$$

where  $F_{\text{CO}_2}$  is the radiative efficiency of  $\text{CO}_2$ ,  $R(t)$  is the response function that describes the decay of an instantaneous pulse of  $\text{CO}_2$ , and the decay of the pulse of compound  $x$  has been rewritten assuming it obeys a simple exponential decay curve with a response time of  $\tau_x$ . The pulse response terms lead to a dependence of GWPs on the integration time horizon; compounds that decay more quickly (slowly) than the reference ( $\text{CO}_2$ ) have GWPs that decrease (increase) with increasing time horizon. As shown in equations (5-1) and (5-2), the most common definition of GWPs applies to pulsed emissions. However, GWPs have also been developed to evaluate the effect of sustained emissions (Berntsen et al., 2005; Johnson and Derwent, 1996).

We note that GWP is not the only metric available to compare the climatic impacts of different gases. The science of alternative metrics was considered by an Intergovernmental Panel on Climate Change (IPCC) expert panel recently (IPCC, 2009), which noted that metric design depends critically on the policy goal, and that “the GWP was not designed with a particular policy goal in mind.” Furthermore, the choice of time horizon used in calculating GWPs is not determined purely by climate science considerations. Rather, the choice often depends on what information is useful to decision makers, based in part on the time horizon of the impacts and on the values they consider most important. In an effort to account for the impact of the choice of time horizon, typically three time horizons have been considered (20, 100, and 500 years) when reporting GWPs.

The GWP index has three major advantages over most other indices used to measure the contribution of greenhouse gases to global warming: transparency, simplicity, and widespread acceptance. However, it also has several disadvantages (see, e.g., IPCC, 2009 and references therein). There is growing recognition of the limitations of the GWP metric especially when the impacts of short- and long-lived pollutants need to be considered together (Johansson et al., 2008; Tanaka et al., 2009; Fuglestvedt et al., 2010) and it has been argued that it is time to consider whether other metrics might be more useful (Shine, 2009). For example, there has been interest

in including the economics of emissions mitigation into a climate metric by applying cost-benefit and cost-effective approaches (e.g., Manne and Richels, 2001). Various alternatives have been presented to overcome some of the GWP limitations, but none has been widely accepted as a suitable replacement to date.

ODP and GWP metrics are often used to evaluate the relative integrated impacts arising from emissions, banks, production, etc., on ozone destruction and climate forcing. If time series of these potential impacts are desired, EESC and radiative forcing are used. These metrics are discussed in Sections 5.2.2 and 5.2.3.

## 5.2.2 Ozone Impacts: ODPs and EESC

### 5.2.2.1 FRACTIONAL RELEASE VALUES AND GLOBAL LIFETIMES

Fractional release values for various halocarbons are used both in the calculation of semi-empirical ODPs and in deriving EESC. The fractional release value at some location in the stratosphere quantifies the fraction of the source gas that has become photochemically degraded and has released its halogen atoms since it entered the stratosphere. The previous Assessment (Daniel and Velders et al., 2007) used fractional release values from earlier assessments, only updating CFC-114 to the value suggested by Schauffler et al. (2003). For this Assessment, we adopt most of the Newman et al. (2007) updated release values; these values are based on National Aeronautics and Space Administration (NASA) ER-2 field campaign observations using an approach similar to Schauffler et al. (2003). Douglass et al. (2008) showed that the lower stratospheric relationships between the fractional release of chlorine from CFC-11 and CFC-12 and the age of air (as discussed in Chapter 1) produced by simulations with realistic age-of-air values are in good agreement with relationships derived from aircraft observations (Schauffler et al., 2003). Another advantage of using the Newman et al. (2007) results is that they provide observationally based relationships between fractional release values and age-of-air values. This allows for more appropriate estimates of EESC that are relevant to various stratospheric locations, and in particular, polar regions. In the derivation of semi-empirical ODPs and of EESC presented in this chapter (see Table 5-1), we use the values of Newman et al. (2007) for all compounds in that study except for HCFC-141b and HCFC-142b. These two compounds were present in small abundances and had large temporal trends when the atmospheric measurements upon which these fractional release values are based were made, leading to large uncertainties. For this reason, we have retained the fractional release

**Table 5-1. Lifetimes, fractional release values, and Ozone Depletion Potentials (ODPs) for long-lived halocarbons.** ODPs recommended in this Assessment and ODPs adopted in the Montreal Protocol are included<sup>a</sup>.

| Halocarbon                       | Lifetime (years) | Fractional Release Value |                              | Semi-Empirical ODP |                              | ODP in Montreal Protocol |
|----------------------------------|------------------|--------------------------|------------------------------|--------------------|------------------------------|--------------------------|
|                                  |                  | WMO (2007) <sup>b</sup>  | This Assessment <sup>c</sup> | WMO (2007)         | This Assessment <sup>d</sup> |                          |
| <b>Annex A-I</b>                 |                  |                          |                              |                    |                              |                          |
| CFC-11                           | 45               | 0.47                     | 0.47                         | 1.0                | 1.0                          | 1.0                      |
| CFC-12                           | 100              | 0.28                     | 0.23                         | 1.0                | 0.82                         | 1.0                      |
| CFC-113                          | 85               | 0.35                     | 0.29                         | 1.0                | 0.85                         | 0.8                      |
| CFC-114                          | 190              | 0.13                     | 0.12                         | 1.0                | 0.58                         | 1.0                      |
| CFC-115                          | 1020             |                          | 0.04                         | 0.44 <sup>e</sup>  | 0.57                         | 0.6                      |
| <b>Annex A-II</b>                |                  |                          |                              |                    |                              |                          |
| Halon-1301                       | 65               | 0.29                     | 0.28                         | 16                 | 15.9                         | 10.0                     |
| Halon-1211                       | 16               | 0.55                     | 0.62                         | 7.1                | 7.9                          | 3.0                      |
| Halon-2402                       | 20               | 0.57                     | 0.65                         | 11.5               | 13.0                         | 6.0                      |
| <b>Annex B-II</b>                |                  |                          |                              |                    |                              |                          |
| CCl <sub>4</sub>                 | 26               | 0.50                     | 0.56                         | 0.73               | 0.82                         | 1.1                      |
| <b>Annex B-III</b>               |                  |                          |                              |                    |                              |                          |
| CH <sub>3</sub> CCl <sub>3</sub> | 5.0              | 0.51                     | 0.67                         | 0.12               | 0.16                         | 0.1                      |
| <b>Annex C-I</b>                 |                  |                          |                              |                    |                              |                          |
| HCFC-22                          | 11.9             | 0.16                     | 0.13                         | 0.05               | 0.04                         | 0.055                    |
| HCFC-123                         | 1.3              |                          |                              | 0.02               | 0.01 <sup>f</sup>            | 0.02                     |
| HCFC-124                         | 5.9              |                          |                              | 0.02               |                              | 0.022                    |
| HCFC-141b                        | 9.2              | 0.34                     | 0.34 <sup>g</sup>            | 0.12               | 0.12                         | 0.11                     |
| HCFC-142b                        | 17.2             | 0.17                     | 0.17 <sup>g</sup>            | 0.07               | 0.06                         | 0.065                    |
| HCFC-225ca                       | 1.9              |                          |                              | 0.02               |                              | 0.025                    |
| HCFC-225cb                       | 5.9              |                          |                              | 0.03               |                              | 0.033                    |
| <b>Annex E</b>                   |                  |                          |                              |                    |                              |                          |
| CH <sub>3</sub> Br               | 0.8              | 0.53                     | 0.60                         | 0.51               | 0.66                         | 0.6                      |
| <b>Others</b>                    |                  |                          |                              |                    |                              |                          |
| Halon-1202                       | 2.9              |                          | 0.62                         | 1.7                |                              |                          |
| CH <sub>3</sub> Cl               | 1.0              | 0.38                     | 0.44                         | 0.02               | 0.02                         |                          |

<sup>a</sup> Ravishankara et al. (2009) have calculated an ODP for N<sub>2</sub>O of 0.017.

<sup>b</sup> In the previous Assessment, fractional release values relative to CFC-11 were used, with CFC-11 assumed to be 0.84. For this table, WMO (2007) values are scaled to a CFC-11 value of 0.47 to allow easy comparison with the current values.

<sup>c</sup> From Newman et al. (2007), values for 3-year-old age of air.

<sup>d</sup> Semi-empirical ODP values are not updated in this Assessment for halocarbons whose fractional release values were not estimated in Newman et al. (2007).

<sup>e</sup> Model-derived value, WMO (2003).

<sup>f</sup> From Wuebbles and Patten (2009) MOZART 3-D model calculation.

<sup>g</sup> Values relative to CFC-11 are retained from WMO (2007) because of large uncertainties associated with the Newman et al. (2007) estimates for these compounds.

values relative to CFC-11 assumed in WMO (2007) for these two HCFCs, and we scale them to the appropriate CFC-11 fractional release value depending on the age of air considered. Additional information regarding the use of fractional release values can be found in Chapter 1. In calculating the 2010 ODP-weighted anthropogenic emissions for the A1 baseline scenario (Section 5.3.1), the most significant fractional release changes are for, in order of decreasing importance, CFC-12, HCFC-22, carbon tetrachloride ( $\text{CCl}_4$ ), and halon-1211. A description of the sensitivity of EESC to fractional release and to other parameters can be found in Newman et al. (2007). We also use absolute fractional release values in this chapter, rather than normalizing all of the values as was done in previous assessments. We do this so the portion of EESC estimates attributable to chlorine and bromine source gases are representative of the actual amount of total inorganic chlorine ( $\text{Cl}_y$ ) and total inorganic bromine ( $\text{Br}_y$ ), respectively, in the regions of the stratosphere considered.

Global lifetimes are also used in the calculation of ODPs and EESC. As discussed in Chapter 1, lifetimes of CFC-114 and CFC-115 have been substantially revised since the previous Assessment. There have also been smaller revisions to several of the HCFCs that are included in Table 5-1. Douglass et al. (2008) also find, based on results from two-dimensional (2-D) and three-dimensional (3-D) models, that the range of atmospheric lifetime estimates for CFC-11 from models that best reproduce the observed relationship between age of air and fractional release is 56–64 years. The lifetime calculated for CFC-12 in this study was consistent with the value from the previous Assessment (100 years). Wuebbles et al. (2009) find consistent lifetimes for CFC-11, 54 years in the Model of Ozone and Related Tracers (MOZART) 3-D model (version 3.1) and 57 years in the current version of the University of Illinois Urbana-Champaign (UIUC) 2-D model, which includes an improved calculation of stratospheric age of air (Youn et al., 2010). In the previous three assessments (WMO, 1999, 2003, 2007), ODP derivations assumed an atmospheric lifetime for CFC-11 of 45 years based on analyses of observations (Cunnold et al., 1997; Volk et al., 1997) and older model results (Prinn and Zander, 1999). Because of the dearth of studies estimating ODS lifetimes with models that accurately calculate age of air, and because the Douglass et al. (2008) study only evaluated the lifetimes of CFC-11 and CFC-12, we continue to use a lifetime of 45 years for CFC-11; however, it should be recognized that in the future this lifetime may be assessed to be too small. The lack of comprehensive studies examining halocarbon lifetimes with models that accurately calculate age of air can be considered a gap in our current understanding. A full discussion of lifetime revisions can be found in Chapter 1.

### 5.2.2.2 OZONE DEPLETION POTENTIALS

An updated list of ODPs is provided in Table 5-1 for a number of long-lived halocarbons. The primary change from the previous Assessment (Daniel and Velders et al., 2007) is to update the semi-empirical ODPs by incorporating revised fractional release values and global lifetimes for some compounds. For ODP estimates in this chapter, fractional release values representative of air that has been in the stratosphere for 3 years are used. In the absence of new evidence, we continue to use a value of 60 for the relative effectiveness of bromine compared to chlorine for destroying ozone ( $\alpha$ ) at midlatitudes. For Antarctic calculations we continue to use a value of 65 (WMO, 2007). The semi-empirical ODP of  $\text{CCl}_4$  is 10% higher than in the previous Assessment owing to a larger fractional release value (see Table 5-1 and Section 5.2.2.1). Although there are still significant gaps in our understanding of the  $\text{CCl}_4$  budget, the recommended lifetime remains 26 years (see Chapter 1).

The ODP for HCFC-123 has been updated based on results from a three-dimensional model (Wuebbles and Patten, 2009). The calculated value of 0.0098 is similar to but smaller than the previous model-derived value of 0.014 based on 2-D model results (WMO, 2003). The ODPs for several short-lived compounds have also been discussed in Chapter 1.

Looking beyond the analyses of ODPs for halocarbons, Ravishankara et al. (2009) have calculated an ODP for nitrous oxide ( $\text{N}_2\text{O}$ ) of 0.017 using a 2-D model. Although  $\text{N}_2\text{O}$  has a relatively small ODP, future changes in emissions and atmospheric concentrations of  $\text{N}_2\text{O}$  could have a significant effect on ozone compared with emissions of controlled ODSs because of the larger magnitude of  $\text{N}_2\text{O}$ 's anthropogenic emissions. The impact of  $\text{N}_2\text{O}$  emissions will be quantified in Section 5.4. The magnitude of past and future  $\text{N}_2\text{O}$  ODP-weighted emissions leads to concerns that include influences on the timing of the recovery of ozone, the “background” ozone level, the distribution of stratospheric ozone depletion, and the possibility of future decreases in ozone due to increasing  $\text{N}_2\text{O}$  (Ravishankara et al., 2009; Wuebbles, 2009).

### 5.2.2.3 EQUIVALENT EFFECTIVE STRATOSPHERIC CHLORINE

EESC has historically been used to relate measured surface mixing ratios of chlorine- and bromine-containing source gases to the stratospheric inorganic chlorine and bromine arising from these gases in key regions of the stratosphere and thus to the amount of ozone they will destroy (Daniel et al., 1995; WMO, 1995, 1999, 2003, 2007). It accounts for the fact that bromine is more

efficient than chlorine (on a per-atom basis) at destroying stratospheric ozone and that different source gases release their chlorine and bromine at different rates and locations. Both integrated EESC changes and the date when EESC returns to 1980 levels have been used in previous assessments to quantify the relative impacts of various hypothetical ODS emission cases. This approach has worked well because all the major anthropogenic sources of stratospheric chlorine and bromine are thought to be known, and they all have reasonably well-understood global lifetimes and stratospheric dissociation rates. Recently, EESC was reformulated so that it accounts for the age-of-air spectrum and the age-of-air dependent fractional release values (Newman et al., 2007). This reformulation allows EESC to represent the total  $Cl_y$  and  $Br_y$  in various regions of the stratosphere.

The concept of EESC does have limitations because of uncertainties in the transport time, uncertainties in the spatial and temporal dependencies of the bromine efficiency for ozone destruction versus chlorine ( $\alpha$ ) (generally considered a constant), the efficiency of stratospheric halogen release from the source gas, and possible temporal changes in transport times and source gas lifetimes (some effects described in Newman et al., 2006, 2007). It should be noted that the EESC concept also does not explicitly account for changing atmospheric emissions and concentration of other relevant constituents that can also affect ozone, such as  $CO_2$  and methane ( $CH_4$ ). Daniel et al. (2010) have recently provided a method to incorporate  $N_2O$  abundances into EESC. We will not adopt this method for the calculation of EESC in this Assessment because its publication was so recent, but we do show the impact of a hypothetical  $N_2O$  emission phase-out on globally averaged total column ozone that can be compared with the impact of other ODS phase-outs on ozone. By comparing 2-D model results with EESC, Daniel et al. (2010) showed that integrated EESC, despite its limitations, is proportional to the calculated integrated total ozone depletion reductions arising from various hypothetical ODS policy actions to within 30%.

The year 1980 is often taken as roughly representative of the time before the major stratospheric ozone losses occurred due to halocarbons. As a result, analyses are often based on the return of EESC to 1980 levels. If stratospheric ozone levels were affected by only halocarbons, the ozone layer would be expected to recover from human activities as anthropogenic ODSs are removed from the atmosphere. However, the actual picture of future levels of stratospheric ozone and the recovery from the past emissions of halocarbons is more complicated, making the use of a single date as a metric for total ozone recovery less meaningful. There are a number of activities and processes that are likely to substantially affect the future distribution and integrated amounts of ozone (see

Section 5.4 and Chapter 3). Some of these potential activities and processes include rocket launches, aviation, climate-related geoengineering actions, and emissions of  $CO_2$ ,  $CH_4$ , and  $N_2O$ . So while the evolution of EESC in this chapter provides important information regarding the impact of certain human activities on stratospheric ozone, ozone is expected to recover at a different rate than this simple metric might imply.

The relative importance of the various future chlorine- and bromine-containing emissions, production, and banks are compared as in previous assessments using EESC in Section 5.4. New in this Assessment is that the impacts of some of these ODS cases are compared in terms of ozone depletion using the results of the Daniel et al. (2010) study (see Section 5.4.2). The intent of this approach is to provide information that can be used for determining which options are available and what their potential effects are on the future ozone layer. It will also allow us to compare the expected impacts of several potential ODS policy options with ozone changes from a broader range of activities, including expected future changes in greenhouse gases such as  $CO_2$ ,  $N_2O$ , and  $CH_4$ .

### 5.2.3 Climate Impacts: GWPs and Radiative Forcing

Direct GWPs are tabulated in this chapter's Appendix 5A. The list of compounds evaluated in Appendix Table 5A-1 is intended to include potential replacements for the Montreal Protocol ODSs, but this list is not exhaustive.  $CO_2$  and  $N_2O$  are also included in the table. Most source gases with atmospheric lifetimes of less than 6 months are not believed to contribute significantly to radiative forcing and are not included in Appendix Table 5A-1 (note that, in contrast to short-lived source gases, short-lived aerosols and tropospheric ozone are thought to contribute significantly to radiative forcing (IPCC, 2007)). Indirect GWPs are discussed later in this section and are also tabulated in Appendix 5A (Appendix Table 5A-4). The uncertainty associated with the direct GWPs listed in Appendix Table 5A-1 is estimated to be  $\pm 35\%$  with 90% confidence (IPCC, 2007) reflecting uncertainties in the radiative efficiencies, lifetimes of the halocarbons, and uncertainties in our understanding of the carbon cycle (IPCC, 2001). It should be noted that because uncertainties in the carbon cycle make an important contribution to the total GWP uncertainty (IPCC, 2007), the relative climatic effects of different halocarbons (e.g., expressed as ratios of their GWPs) are likely accurate to much better than 35%.

We limit further discussion of GWPs to updates since the last Ozone Assessment. There are two reasons that updates have been made: (1) updates to the

atmospheric lifetimes and (2) new radiative efficiency recommendations. Although the atmospheric concentration of CO<sub>2</sub> continues to increase, its AGWPs were chosen to be the same as the IPCC (2007) Assessment so as to reduce confusion when comparing to values from that Assessment. The revisions to the lifetimes and radiative efficiencies discussed below affect GWP calculations and radiative forcing projections.

### 5.2.3.1 LIFETIME UPDATES

The lifetimes of several HCFCs and of most HFCs, including hydrofluoroethers (HFEs), have been updated from the previous Assessment. The lifetime for CH<sub>3</sub>CH<sub>2</sub>OCF<sub>2</sub>CHF<sub>2</sub> (HFE-374pc2) of 5 years given in the previous Assessment was erroneous; the lifetime for this compound is actually rather short (approximately 2 months, see Chapter 1). Accordingly, this compound is now classified as a short-lived species. The lifetimes of CFC-114, CFC-115, and nitrogen trifluoride (NF<sub>3</sub>) were also updated in response to work by Prather and Hsu (2008). A discussion of these lifetime updates and others, and the distinction between short- and long-lived species, can be found in Chapter 1.

### 5.2.3.2 RADIATIVE EFFICIENCY UPDATES

The radiative efficiency values used in the previous Assessment, the currently recommended values, and the values presented in the relevant references for the new and revised compounds are presented in Table 5-2. Since the last Assessment (WMO, 2007), additional radiative efficiency data have become available for HFE-43-10pccc124, HFC-365mfc, HFC-263fb, HFC-245eb,

HFC-245ea, and HFC-329p (all calculated assuming constant vertical profiles). Rajakumar et al. (2006) have provided the first measurements of the lifetimes and the radiative efficiencies for HFC-263fb, HFC-245eb, and HFC-245ea. These radiative efficiencies (Table 5-2) have been adopted in the calculation of the GWPs in the appendix (Appendix Table 5A-1). Inoue et al. (2008) report a radiative efficiency of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> for HFC-365mfc. This value is 10% larger than the value of 0.209 W m<sup>-2</sup> ppb<sup>-1</sup> reported by Barry et al. (1997) that was used in the previous Assessment (WMO, 2007). Inoue et al. (2008) concluded that the approximately 10% difference in the intensity of the infrared (IR) absorption spectrum was the origin of the different radiative efficiencies in the two studies. There being no obvious reason to prefer either study, an average of the results from Barry et al. (1997) and Inoue et al. (2008) was adopted in the current Assessment.

Sulfuryl fluoride (SO<sub>2</sub>F<sub>2</sub>) is being used increasingly as a replacement for methyl bromide (see Chapter 1, Section 1.5.2.2). It has an atmospheric lifetime of about 36 years and a substantial GWP. Papadimitriou et al. (2008a) and Sulbaek Andersen et al. (2009) measured the IR spectrum of SO<sub>2</sub>F<sub>2</sub> and reported radiative efficiencies of 0.222 and 0.196 W m<sup>-2</sup> ppb<sup>-1</sup>, respectively, for this molecule. The integrated absorption cross sections reported by Papadimitriou et al. (2008a) and Sulbaek Andersen et al. (2009) over the range 800–1540 cm<sup>-1</sup> are in excellent agreement (within approximately 1%) and both differ by only about 5% from that reported by Dillon et al. (2008). The approximately 10% difference in radiative efficiencies reported by Papadimitriou et al. (2008a) and Sulbaek Andersen et al. (2009) is probably due to the fact that Sulbaek Andersen et al. (2009) did not consider

**Table 5-2. Radiative efficiency estimates (W m<sup>-2</sup> ppb<sup>-1</sup>) for seven compounds whose recommended values have either changed since, or were not included in, the previous Assessment.**

| Chemical Formula   | Common or Industrial Name     | WMO (2007) | Recent Published Estimates   | This Assessment |
|--|-------------------------------|------------|--|-----------------|
| CHF <sub>2</sub> OCF <sub>2</sub> OC <sub>2</sub> F <sub>4</sub> OCHF <sub>2</sub> | HFE-43-10pccc124 <sup>a</sup> | 1.37       | 1.02 (Wallington et al., 2009)   | 1.02            |
| CH <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>                    | HFC-365mfc                    | 0.21       | 0.23 (Inoue et al., 2008)  | 0.22            |
| CHF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>                   | HFC-329p                      | 0.45       | 0.31 (Young et al., 2009)  | 0.31            |
| CH <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>                                    | HFC-263fb                     |            | 0.13 (Rajakumar et al., 2006)  | 0.13            |
| CH <sub>2</sub> FCHF <sub>2</sub> CF <sub>3</sub>                                  | HFC-245eb                     |            | 0.23 (Rajakumar et al., 2006)  | 0.23            |
| CHF <sub>2</sub> CHFCHF <sub>2</sub>   | HFC-245ea                     |            | 0.18 (Rajakumar et al., 2006)  | 0.18            |
| SO <sub>2</sub> F <sub>2</sub>   | sulfuryl fluoride             |            | 0.222 (Papadimitriou et al., 2008a)<br>0.196 (Sulbaek Andersen et al., 2009) | 0.22            |

<sup>a</sup> Also referred to as H-Galden 1040x.

stratospheric adjustment (allowing the stratospheric temperatures to equilibrate to the greenhouse gas perturbation) in their radiative efficiency calculations. Sulbaek Andersen et al. (2009) used the estimation method described by Pinnock et al. (1995), which agrees to within  $\pm 0.3\%$  with the global annual and annual cloudy-sky instantaneous radiative forcing calculations using the Reading narrowband model (Shine, 1991). Papadimitriou et al. (2008a) applied a line-by-line radiative transfer code, developed at the National Oceanic and Atmospheric Administration (NOAA), to a global-average cloudy-sky profile taking into account stratospheric adjustment. The effect of including stratospheric adjustment for a given gas depends on the position and intensity of its IR absorption features. Forster et al. (2005) have shown that inclusion of stratospheric adjustment increases the instantaneous radiative forcing of HFC-134a by approximately 10%. Pinnock et al. (1995) studied 19 halogenated alkanes and found that inclusion of stratospheric adjustment typically increased the instantaneous radiative efficiency by 5–10% (although in the case of HFC-41 there was actually a 7% decrease, see Table 4 in Pinnock et al. (1995)). Radiative forcing as defined by IPCC is based on the globally and annually averaged net downward irradiance change at the tropopause after allowing for stratospheric temperatures to adjust to radiative equilibrium. Hence, we adopt a value of  $0.22 \text{ W m}^{-2} \text{ ppb}^{-1}$  from Papadimitriou et al. (2008a), which is consistent with the value reported by Sulbaek Andersen et al. (2009).

Wallington et al. (2009) revisited the IR spectrum of HFE-43-10pccc124, previously also referred to as H-Galden 1040x, and argued that the IR spectrum reported by Cavalli et al. (1998) used in previous WMO and IPCC reports is approximately 30% too strong. It was noted that use of the reference spectrum of Cavalli et al. (1998) would lead to carbon balances substantially greater than 100% in laboratory experiments of HFE-43-10pccc124 oxidation. The IR spectrum reported by Wallington et al. (2009) is in good agreement with that measured using the same experimental set-up 12 years earlier by Christidis et al. (1997). As discussed by Young et al. (2008), the radiative efficiency of HFE-43-10pccc124 in WMO (2007) is inconsistent with the expected trends based upon the database for other HFEs. The radiative efficiency reported by Wallington et al. (2009) is adopted here.

Young et al. (2009) reported the first measurements of the lifetime and radiative efficiency for  $\text{CHF}_2\text{CF}_2\text{CF}_2\text{CF}_3$  (HFC-329p); these are used here.

As in all previous assessments, the atmospheric lifetime and radiative efficiency values used in the present Assessment can be traced to experimentally measured rate coefficients and IR spectra. Ab-initio quantum mechanical computational methods are available to calculate rate coefficients and IR spectra. Results from

ab-initio calculations have provided valuable fundamental insight into reaction mechanisms and the underlying processes giving rise to the IR spectra. However, such computational results have generally not been used directly to calculate GWPs. With advances in computational techniques, recent studies (e.g., Blowers and Hollingshead, 2009) suggest that atmospheric lifetimes and radiative efficiencies can now be calculated from first principles with accuracies comparable to those from experimental studies. This suggestion has yet to be fully investigated by the scientific community, and in the present Assessment we do not consider atmospheric lifetimes and radiative efficiencies that have been evaluated only by ab-initio methods.

### 5.2.3.3 UPDATES TO INDIRECT GWPs FROM OZONE DESTRUCTION

In addition to being greenhouse gases themselves, the ODSs play a significant role in the destruction of stratospheric ozone, another radiatively important gas. The distribution of ozone has important implications for Earth's climate system, not only because ozone absorbs solar radiation but also because it is a greenhouse gas that absorbs some of the infrared radiation emitted from Earth's surface and atmosphere. The change in ozone radiative forcing due to the addition of some ODS can be attributed to that ODS as an indirect radiative forcing. Stratospheric ozone losses are generally thought to cause a negative radiative forcing, canceling part of the increased radiative forcing arising from the direct influence of the halocarbons. The magnitude of the indirect effect is strongly dependent on the altitude profile of the halogen-induced ozone loss and will vary depending on the source gas considered. The latest estimate of radiative forcing from changes in stratospheric ozone since preindustrial times is  $-0.05 \pm 0.10 \text{ W/m}^2$  (IPCC, 2007). However, there have not been recent studies that clearly estimate the amount of the ozone forcing attributable to halocarbon changes only.

In spite of the uncertainty associated with the radiative forcing from ozone loss caused by halocarbons, the indirect GWPs for various halocarbons have been included in previous Ozone Assessments using an approach similar to that described in Daniel et al. (1995) (e.g., see WMO, 2003, 2007). This approach is also used here to update indirect GWPs for selected halocarbons (Appendix Table 5A-4) and is based on the assumption of an approximate linear relationship between the change in EESC arising from a particular source gas and radiative forcing arising from stratospheric ozone loss. A complication that is ignored by this approach is that some of the observed ozone depletion, and its associated radiative forcing, is due to processes not related to ODSs. The previously published

indirect GWPs have primarily changed over time as a response to updates in the EESC scenarios, changes in the estimated efficiency of bromine relative to chlorine for destroying ozone, and changes in the estimates of the overall stratospheric ozone radiative forcing owing to halocarbon changes. These factors continue to represent important uncertainties in estimating the indirect GWPs using the EESC approach. This approach also cannot capture the source gas-dependent variations in the ozone loss profile and its resulting impact on radiative forcing. In past estimates of these indirect GWPs, the 1980 level of EESC has been assumed to represent a value below which no additional ozone loss occurs. This implied that the presence of an ODS after EESC fell below this level would lead to no additional ozone loss or negative radiative forcing due to that loss. No such threshold is adopted here, leading to slightly more negative indirect GWPs for the longer-lived ODSs in the absence of other changes. However, the change in stratospheric ozone from 1979 to 1998 is now estimated to be responsible for  $-0.05 \text{ W/m}^2$  forcing (IPCC, 2007). The adoption of this lower revised IPCC radiative forcing due to stratospheric ozone, compared with  $-0.15 \pm 0.10 \text{ W/m}^2$  in WMO (2007), dominates the changes compared to the previous Assessment and makes the indirect effects less negative. The current calculations also incorporate the updated fractional release values for midlatitudes and polar regions (Newman et al., 2007). We continue to assume that radiative forcing due to polar

ozone loss is responsible for 40% of the  $-0.05 \text{ W/m}^2$  and that the polar depletion saturates at 1990 EESC levels (Daniel et al., 1995).

As a step toward obtaining indirect GWPs through a more fundamental approach, Youn et al. (2009) have explicitly evaluated the indirect radiative forcing for two of the halons, halon-1211 and halon-1301, using 2-D and 3-D atmospheric models. In Table 5-3, these values are compared with the direct and indirect GWPs found in WMO, 2007 (Daniel and Velders et al., 2007) and those updated for this Assessment using the approach discussed in the previous paragraph. The indirect GWP for halon-1211 derived by Youn et al. (2009) is much smaller (about 60%) than the WMO (2007) value, but does fall within a single standard deviation of it. The Youn et al. (2009) indirect GWP is larger in magnitude by about a factor of ten compared to its direct effect. The indirect effect of halon-1301 is about 25% smaller than previously reported but also agrees with the WMO (2007) value to within a single standard deviation. The updated indirect GWPs reported here for halon-1211 calculated using the EESC scaling approach is in much better agreement with the Youn et al. (2009) values than the WMO (2007) central estimate was. While the Youn et al. (2009) work represents a single study, these analyses suggest that more comprehensive atmospheric models have the potential to reduce our uncertainties in the halocarbon indirect GWPs.

**Table 5-3. Direct and indirect Global Warming Potentials (mass basis) of halons.** Youn et al. (2009) lifetimes are e-folding times based on an exponential curve fitted to the simulated atmospheric decay.

|   | Lifetimes (years) |            | Global Warming Potentials<br>for 100-years Time Horizon |                |                     |                     |                      |            |
|---|-------------------|------------|---|----------------|---------------------|---------------------|----------------------|------------|
|   |                   |            | Direct GWP  |                | Indirect GWP        |                     | Net GWP <sup>a</sup> |            |
|   | Halon-1211        | Halon-1301 | Halon-1211  | Halon-1301     | Halon-1211          | Halon-1301          | Halon-1211           | Halon-1301 |
| <b>This Assessment</b>                  | 16                | 65         | 1890<br>± 660   | 7140<br>± 2500 | -11,720<br>± 23,430 | -27,060<br>± 54,130 |                      |            |
| <b>WMO (2007)</b>                       | 16                | 65         | 1890<br>± 660   | 7140<br>± 2500 | -40,280<br>± 27,120 | -49,090<br>± 34,280 |                      |            |
| <b>Youn et al. (2009)<br/>2-D Model</b> | 14.4              | 72.4       | 1796  | 7122           | -16,294             | -36,247             | -14,498              | -29,127    |
| <b>Youn et al. (2009)<br/>3-D Model</b> | 10.9              | 70.1       | 1699  | 6903           | -17,050             | -37,252             | -15,351              | -30,349    |

<sup>a</sup> Concerns remain about the quantitative accuracy of adding the indirect forcing due to ozone changes to the direct forcing for the well-mixed halons. This addition was not performed in WMO (2007) or in this chapter, except for the results taken from Youn et al. (2009).

## 5.3 FUTURE BASELINE SCENARIOS

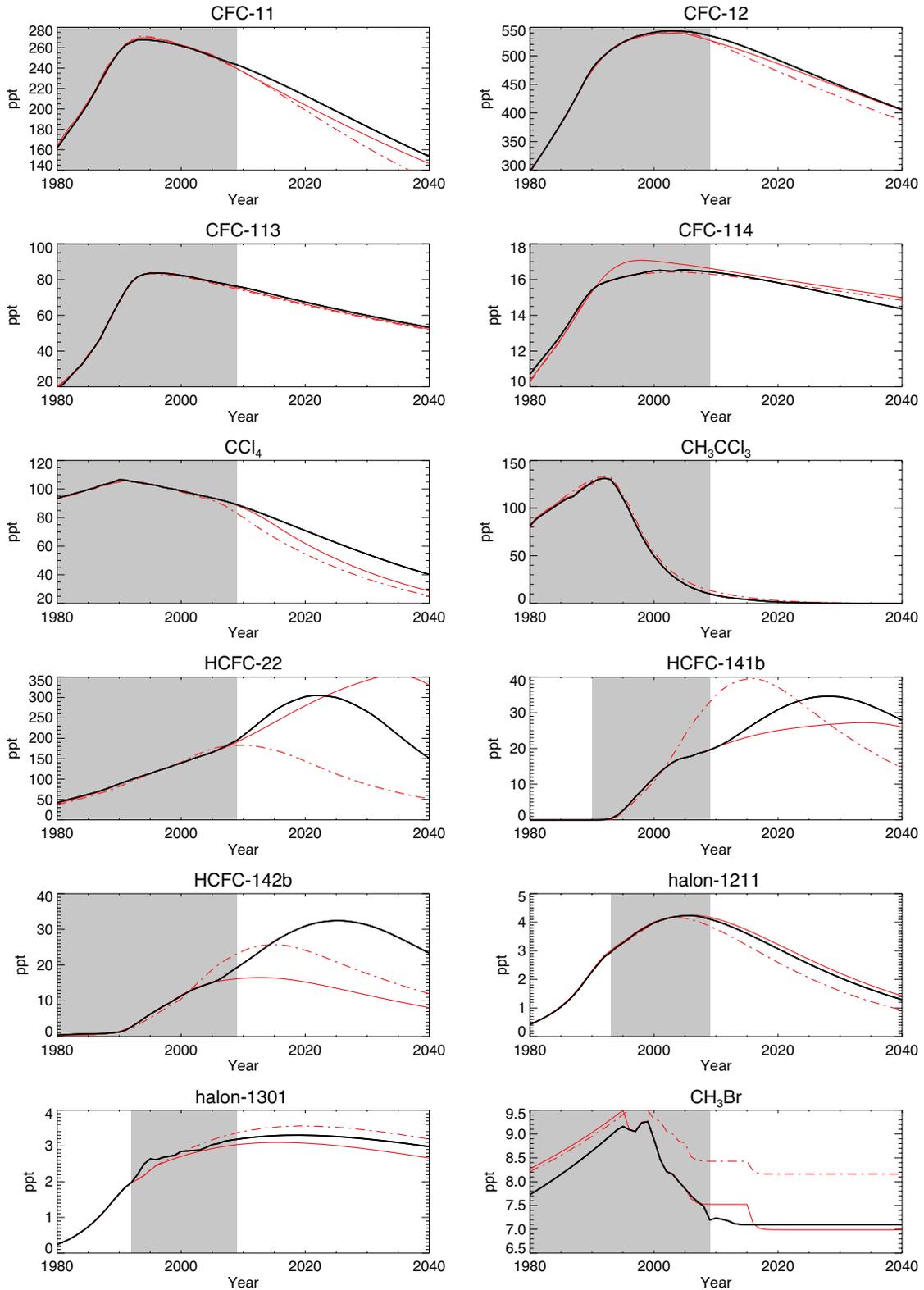
### 5.3.1 Chlorine- and Bromine-Containing Ozone-Depleting Substances

A new baseline scenario for the period 1950–2100 is developed for all ODSs along the same lines as in the previous Assessment (WMO, 2007), with future projections consistent with current controls imposed by the Montreal Protocol. Observed global average mixing ratios through the beginning of 2009 are used as a starting point for the projections, together with the production of ODSs through 2008 reported by the countries to the United Nations Environment Programme (UNEP, 2009), estimates of the bank sizes of ODSs for 2008 from the Technology and Economic Assessment Panel (TEAP, 2009), approved essential use exemptions for CFCs, critical-use exemptions for methyl bromide for 2008–2010, and production estimates of methyl bromide for quarantine and pre-shipment (QPS) use. Details of the baseline scenario are given in Appendix Table 5A-2. Calculated mixing ratios are tabulated in Appendix Table 5A-3 for each of the considered halocarbons from 1955 through 2100 (See also Figure 5-1). The years when observations are used are indicated in the table by the shaded regions. For those years, scenario mixing ratios are equal to the observations.

The mixing ratios in the new baseline scenario are similar to those in the previous Assessment (WMO, 2007) for most species. The larger future mixing ratios (2010–2050) for CFC-11 (+5 to 9 parts per trillion (ppt)) and CFC-12 (up to +9 ppt) are the result of slightly larger fractions of the bank emitted annually, based on 1999–2008 averages. The new baseline scenario has significantly larger future mixing ratios for  $\text{CCl}_4$  (up to +12 ppt) than in WMO (2007) because of a different assumption regarding the decrease in future emissions (see Section 5.4.2.1). Emissions of each of the three considered HCFCs begin to decline at some time in the next decade in the baseline scenario due to existing Montreal Protocol controls. The projected future mixing ratios of HCFC-22 after about 2025 are lower than projected in the previous Assessment as a direct result of the accelerated HCFC phase-out (Montreal Protocol Adjustment of 2007, see Section 5.4.5). The initially larger mixing ratios in the period 2010–2020 are the result of an increase in reported production and a larger fraction of the bank emitted annually. The mixing ratios of HCFC-141b and HCFC-142b are larger than in the previous Assessment, by up to 8 ppt and 20 ppt, respectively, because of an increase in reported production and a different assumption regarding the future distribution of the total HCFC consumption over the three main HCFCs (see Appendix Table 5A-2). The mixing ratios of halon-1301 in the new baseline scenario

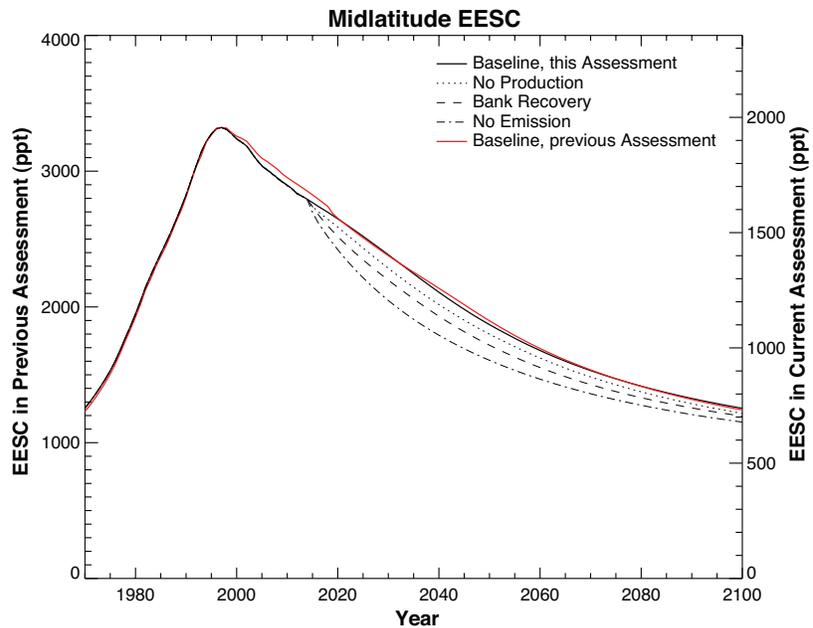
are somewhat different from those in the previous Assessment's baseline scenario. The older ones were based on a bank release calculation after 1995 because of large differences in observational records that existed at that time for the 1995–2005 period. Revised calibrations and measurements with new instruments using mass spectrometry (at NOAA) have led to an improved consistency between the labs (NOAA and Advanced Global Atmospheric Gases Experiment (AGAGE)) for the global mean mixing ratios and the rates of change in recent years (see Figure 1-1 of Chapter 1). Therefore, the mixing ratios here are taken as an average of the observations from those two networks in recent years and are derived using a consistent scaling to the NOAA data in years before AGAGE measured halon-1301 (before 2004).

The EESC corresponding to the baseline scenario is shown in Figure 5-2. The absolute values of EESC (right-hand axis) are substantially lower than presented in the previous Assessment because different fractional release values have been adopted and they are no longer scaled so the fractional release value of CFC-11 is 0.84. As stated in Section 5.2.2.1, this approach is taken because it allows the values now to provide meaningful estimates of  $\text{Cl}_y$  and  $\text{Br}_y$  abundances for 3-year-old air, a benefit that would be lost if the former scaling method were applied. Furthermore, since EESC is used in this chapter only as a relative measure, the absolute values are not important. If current EESC values are scaled so the peak value is the same as in the previous Assessment, the figure shows that the time series are quite similar. Differences appear because of the revised relative fractional release values and because of slightly revised emissions. In previous assessments, the year 1980 was taken as a benchmark year, representing a time before the major stratospheric ozone losses occurred due to halocarbons. Some ozone losses caused by human activities likely had already occurred due to, for example, halocarbon and  $\text{N}_2\text{O}$  emissions (see Chapter 3). Nevertheless, the year EESC returns to 1980 levels has been used as a measure for some degree of ozone layer recovery and to compare scenarios. Although we continue to recognize the limitations of this metric (see Section 5.2.2) it is used here to compare the new baseline scenario with the one in the previous Assessment and to compare the effects of hypothetical ODS emission reductions of chlorine- and bromine-containing ODSs (Table 5-4). In the new baseline scenario, including only Montreal Protocol-controlled ODSs, EESC returns to its 1980 levels in 2046 for mid-latitude conditions. This is 2–3 years earlier than in the previous Assessment (WMO, 2007) and is the result of two partially offsetting changes. First, future emissions of ODSs give a delay of 2–3 years, mainly as the net result of larger future emissions of  $\text{CCl}_4$ , smaller future emissions of HCFCs owing to the accelerated HCFC phase-out (2007 Adjustment of the Montreal Protocol, see Section 5.4.5),



**Figure 5-1.** Historical and projected mixing ratios (in parts per trillion, ppt) of selected ODSs for the new baseline (A1) scenario (black) compared with the baseline scenarios of the previous Assessment (WMO, 2007) (solid red) and for WMO (2003) (dashed red). Shaded regions indicate years when mixing ratios are taken directly from observations (see Chapter 1).

**Figure 5-2.** Midlatitude EESC projections (in parts per trillion, ppt) calculated for the current baseline (A1) scenario (solid black) and three test cases: zero future production (dotted), full recovery and destruction of the 2010 bank (dashed), and zero future emission (dot-dashed) (all right-hand axis). EESC values for the baseline scenario of the previous Assessment are also shown (red, left-hand axis). For ease of comparison, the two ordinate axes are relatively scaled so the EESC peak of the current baseline scenario falls on top of the previous baseline scenario peak. Absolute EESC values are different in the two Assessments because in the previous Assessment, different relative halogen fractional release values were used, and the values were scaled so the CFC-11 absolute fractional release value was 0.84. No scaling was performed here so that EESC is more directly representative of  $Cl_y$  and  $Br_y$ .



and a smaller 1980 mixing ratio of  $CH_3Br$  (see Chapter 1, Section 1.2.1.6). Second, the use of revised fractional release values based on recent measurements brings forward the return to 1980 levels by 5–6 years. For Antarctic conditions EESC returns to its 1980 levels in the baseline in 2073. This is 7–8 years later than in the previous Assessment (WMO, 2007), mainly due to the use of fractional release values representative for Antarctic conditions (age of air = 5.5 years) and of a smaller 1980 mixing ratio of  $CH_3Br$  (Chapter 1, Section 1.2.1.6), with smaller contributions from the revisions in  $CCl_4$  and HCFCs emissions.

**5.3.2  $CO_2$ ,  $CH_4$ , and  $N_2O$**

The importance of non-ODS greenhouse gases to future ozone levels has been quantified in several published articles and is discussed in Chapter 3. In this chapter, IPCC Special Report on Emissions Scenarios (SRES)

(IPCC, 2000) scenario A1B is used to prescribe the future evolution of these three gases in the two 2-D model runs described in Daniel et al. (2010). The results of that study are used here to evaluate the impact of hypothetical future controls involving  $N_2O$  and the ODSs on globally averaged total column ozone against a backdrop of  $CO_2$  and  $CH_4$  changes and their associated impacts on ozone.

### 5.3.3 ODP- and GWP-Weighted Emissions, EESC, and Radiative Forcing

The contributions of ODSs to metrics relevant to ozone depletion and to climate change are shown in Figures 5-3 and 5-6. The panels of Figure 5-3 show the ODP-weighted emissions, GWP-weighted (100-year) emissions, EESC, and radiative forcing (RF) for the A1 baseline scenario from 1980–2100. In terms of EESC

**Table 5-4 (at right).** Comparison of scenarios and cases <sup>a</sup>: the year when EESC drops below the 1980 value for both midlatitude and Antarctic vortex cases, and integrated EESC differences (midlatitude case) relative to the baseline (A1) scenario <sup>b</sup>. Also shown are changes in integrated ODP- and GWP-weighted emissions and, for selected cases, changes in integrated ozone depletion from 2011–2050. Future projected changes in  $CH_4$  and  $CO_2$  are also expected to significantly alter ozone levels, perhaps by amounts larger than any of the cases considered in this table. However, their effects are not included here because changes in  $CH_4$  and  $CO_2$  that would decrease globally averaged ozone depletion would increase climate forcing. Values cited in chapter text calculated as differences between table entries may appear slightly inconsistent with table entries because of rounding.

| Scenario and Cases <sup>a</sup>                                 | Percent Difference in Integrated EESC Relative to Baseline Scenario for the Midlatitude Case |                         | Year (x) When EESC is Expected to Drop Below 1980 Value <sup>b</sup> | Antarctic Vortex <sup>c</sup> | Change in ODP-Weighted Emission: 2011–2050 | Change in GWP-Weighted Emission: 2011–2050 | Percent Difference in Integrated O <sub>3</sub> Depletion <sup>f</sup> : 2011–2050 |
|---|--|-------------------------|--|-------------------------------|--|--|--|
|   | Midlatitude <sup>c</sup>   |                         |  |                               | (Million tons CFC-11-eq)                   | (Billion tons CO <sub>2</sub> -eq)         |  |
|   | $\int_{1980}^x EESC dt$  | $\int_{2011}^x EESC dt$ |  |                               |  |  |  |
| <b>Scenarios</b>  |  |                         |  |                               |  |  |  |
| A1: Baseline scenario   | -  | -                       | 2046.5   | 2072.7                        | -  | -  | -  |
| <b>Cases of zero production from 2011 onward of:</b>            |  |                         |  |                               |  |  |  |
| P0: All ODSs  | -5.4   | -15                     | 2043.0   | 2069.7                        | -0.70                                      | -13.2                                      |  |
| CFCs  | 0.0  | 0.0                     | 2043.0   | 2069.7                        | 0  | 0  |  |
| Halons  | 0.0  | 0.0                     | 2043.0   | 2069.7                        | 0  | 0  |  |
| HCFCs   | -3.2   | -8.8                    | 2044.5   | 2071.8                        | -0.45                                      | -13.2                                      | -0.15  |
| CH <sub>3</sub> Br for QPS                                      | -2.4   | -6.7                    | 2044.9   | 2070.8                        | -0.26                                      | -0.002                                     |  |
| <b>Cases of zero emissions from 2011 onward of:</b>             |  |                         |  |                               |  |  |  |
| E0: All ODSs (does not include N <sub>2</sub> O)                | -16  | -43                     | 2033.5   | 2059.4                        | -3.82                                      | -27.2                                      | -0.67  |
| CFCs  | -3.9   | -11                     | 2043.3   | 2068.5                        | -1.27                                      | -7.9                                       |  |
| Halons  | -5.0   | -14                     | 2043.3   | 2069.4                        | -1.09                                      | -0.4                                       |  |
| HCFCs   | -4.9   | -13                     | 2043.8   | 2071.4                        | -0.66                                      | -18.1                                      |  |
| CCl <sub>4</sub> <sup>g</sup>                                   | -2.8   | -7.6                    | 2044.6   | 2071.6                        | -0.54                                      | -0.9                                       |  |
| CH <sub>3</sub> CCl <sub>3</sub>                                | 0  | -0.1                    | 2046.5   | 2072.7                        | -0.004                                     | -0.004                                     |  |
| CH <sub>3</sub> Br for QPS                                      | -2.4   | -6.7                    | 2044.9   | 2070.8                        | -0.26                                      | -0.002                                     | -0.09  |
| Anthropogenic N <sub>2</sub> O <sup>h</sup>                     |  |                         |  |                               | -6.0                                       | -103                                       | -0.35  |
| <b>Cases of full recovery of the 2011 banks of:</b>             |  |                         |  |                               |  |  |  |
| B0: All ODSs  | -10  | -27                     | 2039.3   | 2064.6                        | -2.57                                      | -13.1                                      |  |
| CFCs  | -3.9   | -11                     | 2043.3   | 2068.5                        | -1.27                                      | -7.9                                       | -0.13  |
| Halons  | -5.0   | -14                     | 2043.3   | 2069.4                        | -1.09                                      | -0.4                                       | -0.15  |
| HCFCs   | -1.8   | -4.8                    | 2045.8   | 2072.4                        | -0.22                                      | -4.9                                       | -0.07  |
| <b>Cases of full recovery of the 2015 banks of:</b>             |  |                         |  |                               |  |  |  |
| B0: All ODSs  | -7.1   | 20                      | 2040.3   | 2065.7                        | -2.03                                      | -11.3                                      |  |
| CFCs  | -2.6   | -7.0                    | 2044.0   | 2069.4                        | -0.95                                      | -5.5                                       |  |
| Halons  | -3.3   | -9.1                    | 2043.8   | 2069.8                        | -0.83                                      | -0.3                                       |  |
| HCFCs   | -1.9   | -5.3                    | 2045.5   | 2072.2                        | -0.26                                      | -5.5                                       |  |
| <b>CH<sub>3</sub>Br sensitivity:</b>                            |  |                         |  |                               |  |  |  |
| Same as A1, but critical-use exemptions continue at 2011 levels | +0.3   | +0.8                    | 2046.6   | 2073.0                        | +0.03                                      | +0.0003                                    |  |

<sup>a</sup> Significance of ozone-depleting substances for future EESC were calculated in the hypothetical “cases” by setting production or emission to zero in 2011 and subsequent years or the bank of the ODSs to zero in the year 2011 or 2015.

<sup>b</sup> When comparing to WMO (2007), revised fractional halogen release values have contributed to an earlier EESC recovery year for midlatitudes and a later one for the Antarctic vortex.

<sup>c</sup> For midlatitude conditions, an age-of-air value of 3 years, corresponding fractional release values, and a value for  $\alpha$  of 60 are used. For Antarctic vortex conditions, an age-of-air value of 5.5 years with corresponding fractional release values and a value for  $\alpha$  of 65 are used.

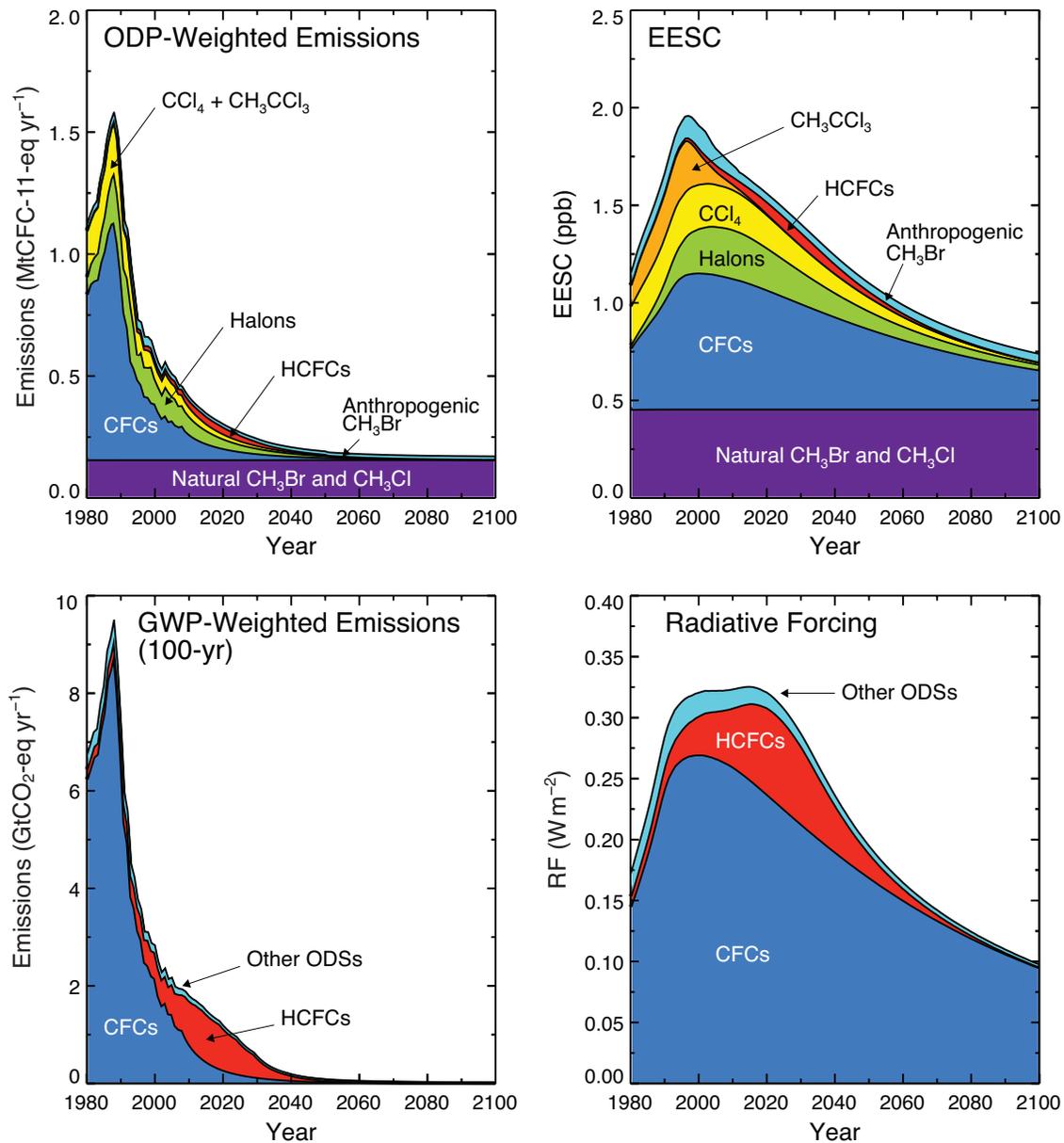
<sup>d</sup> Using semi-empirical ODPs from Table 5-1.

<sup>e</sup> Using direct GWPs with 100-year time horizon (see Appendix Table 5A-1).

<sup>f</sup> Integrated globally averaged total column ozone changes are taken from Daniel et al. (2010).

<sup>g</sup> Banks are assumed to be zero. Emissions include uncertain sources such as possible fugitive emissions and unintended by-product emissions.

<sup>h</sup> The integrated ODP- and GWP-weighted emissions correspond to the elimination of all anthropogenic N<sub>2</sub>O emissions from 2011 onward in the A1B SRES scenario.



**Figure 5-3.** ODP- and GWP-weighted emissions, EESC, and radiative forcing of the chlorine- and bromine-containing ODSs of the baseline (A1) scenario. Only the direct GWP-weighted emissions and radiative forcing are considered here. Semi-empirical steady-state ODPs (Table 5-1) and 100-year GWPs (Appendix Table 5A-1) are used to weight emissions. The emissions and radiative forcing of the HFCs are not included in these graphs because of the large range in HFC scenarios. They are shown in Figure 5-5.

**Figure 5-4 (at right).** Banks of CFCs, HCFCs, and halons in 1995, 2008, and 2020 in megatonnes (Mt) and weighted by their ODPs and 100-year GWPs (direct term only). The 2008 bank is from TEAP (2009) for almost all compounds. The 1995 bank is derived by a backwards calculation using the historic emissions, UNEP production data, and the 2008 bank. The 2020 bank is calculated in the baseline scenario from estimates of future production and bank release rates. The pie slices show the sizes relative to those of the maximum values (1995 for the ODP- and GWP-weighted banks and 2008 for the bank in Mt) and therefore don't fill a full circle. The total bank size is given below each pie chart. For comparison, the HFC bank size has been estimated to have been 1.1 GtCO<sub>2</sub>-eq in 2002 and 2.4 GtCO<sub>2</sub>-eq in 2008, and has been projected to be 4.6 GtCO<sub>2</sub>-eq in 2015 in a business-as-usual scenario (Velders et al., 2009).

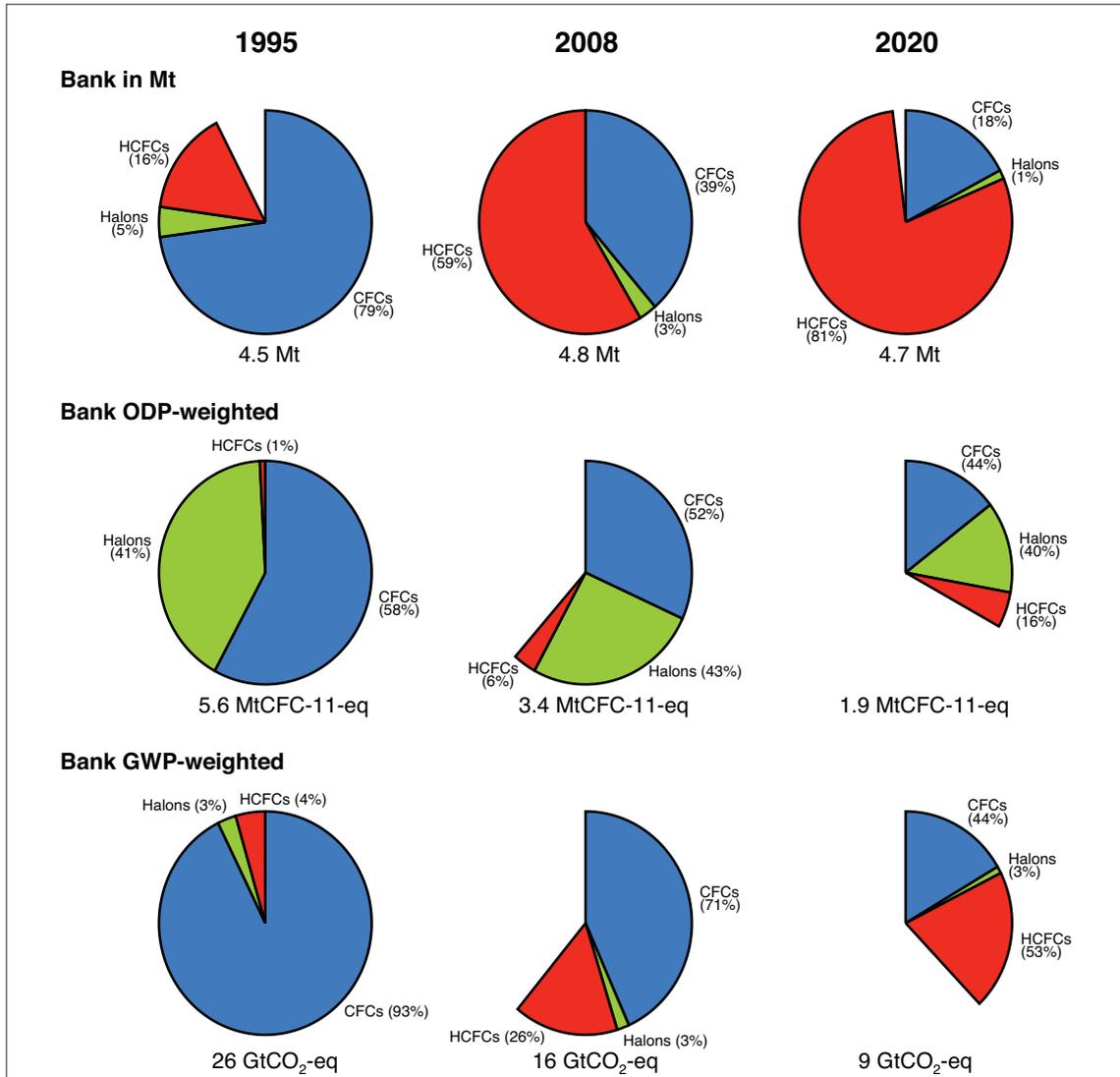
contribution, the largest contribution in the past and future comes from the CFCs and natural CH<sub>3</sub>Cl and CH<sub>3</sub>Br emissions. In terms of radiative forcing the CFCs are also the most important ODSs, but the HCFCs are projected to contribute more than 0.05 W/m<sup>2</sup> at their peak.

CFC, HCFC, and halon bank size estimates for 1995 and 2008 and projections for 2020 are shown in Figure 5-4. The contributions of the ODSs to the bank are compared by mass and when weighted by their ODPs and GWPs (100-year). The total size of the bank by mass remains more or less constant over time, but decreases significantly when considering their potential effect on depletion of the ozone layer (ODP-weighted) and on climate forcing (GWP-weighted). The decreasing contribution of the CFCs and increasing contribution of the HCFCs is particularly apparent when examining the banks by mass and when weighted by GWPs. The relative contributions of both the CFCs and halons remain the largest when considering the ODP-weighted banks.

## 5.4 IMPACTS OF HUMAN ACTIVITIES RELEVANT TO OZONE POLICY

### 5.4.1 Background

In this section, we assess the importance of various human activities that are relevant to ozone policy formulation. The focus is primarily on the extent to which future ozone depletion may be affected. We also discuss the potential effect of HFCs on climate forcing because the widespread use of HFCs has occurred directly as a result of ODS controls of the Montreal Protocol. We discuss geoengineering using atmospheric sulfur injections, and CO<sub>2</sub> and CH<sub>4</sub> emissions not because they necessarily have relevance for ozone policy decisions, but to assess their potential for inadvertent ozone impacts as a result of climate change policies or the absence of such policies.



## 5.4.2 Ozone Impacts

The Montreal Protocol and its Amendments and Adjustments have effectively controlled the emission of the most important ozone-depletion gases containing chlorine and bromine. It is a testament to the success of the Montreal Protocol that current potential policy options and activities that do not involve chlorine- or bromine-containing compounds are expected to have some of the greatest effects on future ozone levels. However, to maintain consistency with past reports and to address the relative importance of continued emissions of halogenated source gases, we provide in Section 5.4.2.1 an analysis of various hypothetical test cases using EESC as the comparison metric.

Chapter 8 of the previous Assessment (Daniel and Velders et al., 2007) focused strictly on the EESC index to quantify the potential effects of additional ODS controls on stratospheric ozone depletion. Here, results from 2-D model calculations in Daniel et al. (2010) are presented to augment the historical reliance on EESC and as a way to assess the ozone impact of several different assumptions of future emissions of halocarbons (e.g., CFCs, HCFCs, halons, CH<sub>3</sub>Br) and N<sub>2</sub>O (Section 5.4.2.2 and Chapter 3) (see Table 5-4). The phase-out and baseline scenarios assumed in Daniel et al. (2010) were similar to those in this chapter. However, that paper should be consulted for a consistent comparison of ozone changes with EESC changes. Estimates of ozone impacts from ODSs and N<sub>2</sub>O future emission changes also allow for comparison with other activities and emissions, such as CO<sub>2</sub> and CH<sub>4</sub>. The computational efficiency of 2-D models makes it possible now to perform multiple long-term simulations in a reasonable amount of time to examine the effects of various scenarios. The residual circulation framework used in 2-D models has been shown to provide realistic simulations of atmospheric transport on long timescales (>30 days). Recent studies have demonstrated good overall model agreement with a variety of observations in reproducing transport-sensitive features in the meridional plane (e.g., Fleming et al., 2007). These capabilities make these models useful tools for studying long-term ozone changes.

### 5.4.2.1 CHLORINE- AND BROMINE-CONTAINING ODSs

Alternative test cases, based on the baseline scenario of ODSs (Section 5.3.1), are constructed and used to examine the relative effects of reducing future emissions of groups of halocarbons on EESC and stratospheric ozone levels. These alternative cases fall into four categories: (1) “No future emission” cases; (2) “No future production” cases; (3) cases assuming the full capture and destruction of the 2011 bank; and (4) cases assuming full capture and destruction of the 2015 bank. For the bank

cases, the entire bank is considered, not just the portion that is estimated to be “accessible.” The 2015 bank recovery cases are run to quantify the impact of the implementation date of hypothetical bank emission controls; it should be recognized, however, that we do not have an estimate of the uncertainty in the future bank projections, on which these calculations are based. Full elimination of emissions, production, and banks are considered rather than some smaller fractional reduction because the intent is to provide policy-neutral cases that can be used to determine the impacts of other specific policy options. The impact of any option that involves a smaller reduction can be determined by simply scaling the results of Table 5-4. For example, if the “accessible” bank is estimated to be 30% of the total bank, the results in the table for that compound can be simply multiplied by 0.3 to determine the impact of capture and destruction of the accessible bank. The elimination of all future emissions represents the greatest possible reduction in future abundances that can be imparted by direct controls. The elimination of future production allows the ODSs currently residing in banks to continue to be released to the atmosphere as they would in the baseline scenario. The projections that consider the full capture and destruction of the 2011 bank complement the “No Production” scenarios in that the full 2011 bank is destroyed in a manner that releases no ODSs to the atmosphere; future production and the resulting future buildup of banks is allowed to continue, however. The expected future production is virtually zero for the CFCs and halons, but still significant for the HCFCs and possibly for CCl<sub>4</sub>. The “No production” and “Full capture and destruction of the 2011 bank” cases are complementary in the sense that they may be combined to approximately estimate the “No emission” cases.

The effects of the alternative test cases are presented in Table 5-4 using metrics similar to those of previous assessments, i.e., the year EESC returns to its 1980 level for midlatitude and Antarctic vortex conditions, and the change in integrated EESC relative to the baseline scenario. These integrated values are dependent on the choice of the 1980 level. If a lower level were chosen, for example the 1975 level, the tendency is for the CFC options to gain in importance relative to the other ODS policy options. This results from the longer atmospheric lifetimes of the CFCs. Also in this table is the change in cumulative ODP- and GWP-weighted (direct contribution only) emissions. The latter gives an indication of the potential effects of the cases for climate forcing. In general, the various cases presented here lead to smaller integrated EESC differences (when integrated from 1980) and return year differences from the baseline scenario than the same test cases from WMO (2007). This is expected, as banks of most ODSs are smaller due to continued emission for 4 more years, and there are now fewer years to continue

to produce the various ODSs before the mandated phase-out.  $\text{CCl}_4$  represents an exception to this. The increasing apparent importance of a  $\text{CCl}_4$  production or consumption phase-out arises from projected  $\text{CCl}_4$  emissions being larger in the current baseline scenario than in WMO (2007). The increased future emissions are based on an extrapolation of declining global emissions over the last 5 years (6%/year). This decline in  $\text{CCl}_4$  emissions has not mirrored the strong decrease in reported production of CFC-11 and CFC-12 as it did in the 1980s and 1990s. This revised projection is thus not based on an improved understanding of the budget of  $\text{CCl}_4$ , which still cannot be balanced nor can the interannual variability be explained with our current knowledge of  $\text{CCl}_4$  sources and sinks (see Chapter 1). The incomplete understanding of the  $\text{CCl}_4$  budget represents a significant gap.

Emissions of CFCs and halons from the banks are the largest sources of current ODP-weighted emissions of ODSs. An immediate phase-out of halon bank emission sources reduces future integrated EESC more than the elimination of emissions of any other compound or compound group, with slightly more of an impact than the elimination of future HCFC emissions. A delay of four years, from 2011 to 2015, in the capture and destruction of the estimated banks of CFCs and halons is currently thought to reduce the potential ozone and climate benefits by about 30% since ODSs continue to be emitted from these banks and production is thought to have essentially ceased.

A phase-out of methyl bromide emissions from quarantine and pre-shipment (QPS) applications beginning in 2011 would shift the year midlatitude EESC reaches the 1980 level earlier by 1.5 years compared to continued use at current levels. Continuing critical-use exemptions (CUE) at the approved 2011 level would delay the return of EESC to 1980 levels by 0.2 years.

The elimination of all emissions of chlorine- and bromine-containing ODSs after 2010 would shift the year midlatitude EESC reaches the 1980 level by about 13 years, from 2046 to 2033. In terms relevant to climate, this would reduce emissions of these compounds by about 0.7 gigatonnes (Gt) of  $\text{CO}_2$ -equivalent ( $\text{GtCO}_2\text{-eq}$ ) per year averaged over 2011 through 2050. Future production of HCFCs and the sum of the current banks of CFCs plus HCFCs contribute about equally to this number. In comparison, global anthropogenic emissions of  $\text{CO}_2$  were greater than 30 Gt per year in 2008.

In past assessments, the potential impact of chlorine-containing VSLS has been neglected in the evaluation of hypothetical ODS emissions phase-outs. However, it is likely that their contribution is not negligible. As discussed in Chapter 1, anthropogenic VSLS are currently expected to contribute about 39 ppt chlorine to the

stratosphere with fairly large uncertainty. Because these likely release their chlorine quickly, this amount could contribute directly to EESC with a unit fractional release value. If included in EESC in this way, at midlatitudes, a phase-out of these compounds is expected to advance the return of EESC to 1980 levels by almost 3 years. The magnitude of this effect is significant compared to the long-lived ODS cases presented in Table 5-4. This impact depends strongly on the region of the stratosphere considered, with greater impacts in regions where less chlorine has been liberated from long-lived source gases, but where chemical ozone loss is still important. It is also unclear how VSLS emission reductions in specific locations and during different times of the year would quantitatively affect the abundance of stratospheric chlorine.

The uncertainties of the effects of the test cases presented in Table 5-4 have been estimated by varying several model parameters for each class of compounds (CFC, HCFCs, etc.) in the calculation: the size of the banks in 2008, the annual emission rate from the banks, the fractional release values, and the lifetimes of the compounds (Douglass et al., 2008; Martinerie et al., 2009). The lifetimes and annual emission rate from the banks are only varied for 2009–2100, since the data through 2008 is constrained by observations. A variation of 20% in the size of the 2008 banks of CFCs, HCFCs, and halons results in a variation of about 20% in the change in integrated EESC, for each class of compounds, in the case of a full recovery of the banks. The year EESC returns to the 1980 level varies by less than a year. Doubling the annual emission rate from the banks increases the change in integrated EESC by up to 15%, while reducing the annual emission rate by 50% decreases the changes in integrated EESC by up to 30%. Again, for most cases, the year EESC returns to the 1980 level varies by less than a year. Variations of 20% in the fractional release values per class of compound gives similar variations. Variations of up to  $\pm 3$  years occur in the year EESC returns to the 1980 level when varying the lifetimes of the CFCs by  $\pm 20\%$ . The effects of such a variation on the change in integrated EESC is less than  $\pm 20\%$  for each compound group. These uncertainties have been applied to entire groups of compounds. These uncertainties are likely independent across compound groups for the size of the banks and annual emission rates from the banks, but perhaps not for the fractional release values and lifetimes.

The benefits of the Montreal Protocol that are calculated to have already been achieved are highlighted in Section 5.5. The cases considered here show that the options for limiting future halogenated ODS emissions are expected to have a much smaller impact on future ozone depletion and climate than what has already been accomplished by the Montreal Protocol.

### 5.4.2.2 CO<sub>2</sub>, CH<sub>4</sub>, AND N<sub>2</sub>O

The increasing concentration of carbon dioxide (CO<sub>2</sub>) in Earth's atmosphere warms the troposphere but cools the stratosphere. This cooling leads to slower gas-phase ozone loss reactions (Haigh and Pyle, 1979; Rosenfield et al., 2002), and thus to an increase in stratospheric ozone. Cooling of the polar lower stratosphere can also lead to enhanced polar stratospheric cloud (PSC) formation and more ozone destruction via more efficient heterogeneous chemistry (Chapter 3, Section 3.2.3). Increasing concentrations of methane and its effects on hydrogen oxides can enhance the destruction of ozone in the upper stratosphere. Increases in methane (CH<sub>4</sub>) can also reduce the ozone loss in the stratosphere by converting chlorine from active species to the reservoir HCl, and can lead to NO<sub>x</sub>-induced ozone production in the troposphere and lower stratosphere via the CH<sub>4</sub> oxidation cycle. Increases in methane and the subsequent oxidation to water vapor will also lead to weak stratospheric cooling. Future levels of CO<sub>2</sub> and CH<sub>4</sub> may be higher for some period of time compared with today. If they are, they would be expected to lead to higher levels of column ozone at midlatitudes (e.g., Li et al., 2009; Waugh et al., 2009; Hsu and Prather, 2010). Thus, there is the possibility of a "super-recovery," where the total amount of atmospheric ozone exceeds 1960 levels. Both 2-D (Rosenfield et al., 2002; Chipperfield and Feng, 2003; Portmann and Solomon, 2007; Daniel et al., 2010), and 3-D model (SPARC CCMVal, 2010) calculations suggest that increases in CO<sub>2</sub> and CH<sub>4</sub> will lead to total column ozone increases that are larger than what can be caused by decreases in future ODS or nitrous oxide (N<sub>2</sub>O) emissions. Because increasing levels of CO<sub>2</sub> and CH<sub>4</sub> are expected to continue to lead to increased total ozone, but also increased climate forcing, we present this information as relevant for inadvertent ozone impacts due to climate policy choices. Further complicating the matter is that, for ozone, changes in circulation due to greenhouse gases are expected to be the dominant factor in the tropics, and this will lead to lower column ozone levels there. Additional discussion of the impacts of CO<sub>2</sub> and CH<sub>4</sub> on ozone can be found in Chapter 3.

N<sub>2</sub>O emissions reductions, in contrast, would reduce climate forcing, and the resulting decrease in stratospheric nitrogen oxides would lead to higher ozone levels. Ravishankara et al. (2009) have shown that when ODS emissions are weighted by their steady-state ODPs, N<sub>2</sub>O emissions represent the single most important anthropogenic emissions today for ozone depletion. Unmitigated, these emissions are also expected to remain the most significant throughout the 21<sup>st</sup> century. In the current atmosphere, CFCs lead to much more ozone depletion than does N<sub>2</sub>O because of the large historic emissions and long lifetimes of the CFCs. The 2-D models used in Daniel et

al. (2010) suggest that N<sub>2</sub>O causes an ozone depletion in the current atmosphere of about 3 Dobson units (DU) compared with the ODSs depleting about 18 DU. However, when the impact of phase-outs of future emissions are considered, an immediate phase-out of all anthropogenic N<sub>2</sub>O emissions leads to a greater reduction in ozone depletion integrated through 2100 than the integrated ozone depletion reduction arising from an elimination of all future ODS emissions (Daniel et al., 2010). The climate forcing and ozone impacts of a hypothetical emissions phase-out beginning in 2011 of several ODSs and anthropogenic N<sub>2</sub>O are compared in the final three columns of Table 5-4. These comparisons show the relative significance of these policy options using cumulative ODP- and GWP-weighted emissions and ozone integrated from 2011–2050. The significance of N<sub>2</sub>O compared to the ODSs is not surprising given the higher current ODP-weighted emissions compared to the controlled ODSs. We emphasize that all the phase-outs considered are purely hypothetical with no consideration given to the economic or technological feasibility of implementing them.

### 5.4.2.3 N<sub>2</sub>O FROM AUTOMOTIVE BIOFUELS

Anthropogenic emissions of N<sub>2</sub>O total approximately 6.7 TgN yr<sup>-1</sup> (IPCC, 2007). Agriculture is responsible for 2.8 TgN yr<sup>-1</sup> and related emissions from rivers, estuaries and coastal zones add a further 1.7 TgN yr<sup>-1</sup>. Emissions associated with fossil fuel combustion and industrial activities, biomass burning, atmospheric deposition, and human excreta combined account for the remaining 2.2 TgN yr<sup>-1</sup>. The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model provides a life cycle assessment of biofuel production and uses, and includes allocation and differentiation of biofuels based on different agricultural practices (Wang, 2010). The GREET model provides N<sub>2</sub>O emission factors for corn ethanol, sugarcane ethanol, and soy biodiesel in the United States of America (USA) of approximately 45, 25, and 17 g/MMBtu of fuel produced (MMBtu = million British thermal units, 1 MMBtu = 1.055 gigajoules (GJ)). The USA is the largest biofuel producer, and corn ethanol is the dominant biofuel produced in the USA and has the highest N<sub>2</sub>O emissions per megajoule (MJ) of fuel produced. Combining 40 g N<sub>2</sub>O/MMBtu with a production of 17.5 million tonnes of oil equivalent in 2008 (British Petroleum, 2009; 1 tonne of oil equivalent = 42 GJ) we estimate an emission of 0.018 TgN yr<sup>-1</sup> associated with production of corn ethanol in the USA. This is approximately 0.2% of the total anthropogenic emission of 6.7 TgN yr<sup>-1</sup> (IPCC, 2007). Crutzen et al. (2008) have argued that depending on N fertilizer uptake efficiency by plants, the formation of N<sub>2</sub>O during the production of commonly used automotive biofuels, such as biodiesel from rapeseed

and bioethanol from corn (maize), can negate the CO<sub>2</sub> mitigation from fossil fuel savings. However, the analysis by Crutzen et al. (2008) does not consider allocation of emissions to the coproducts in the process (e.g., animal feed produced during corn ethanol production).

The contribution of automotive biofuels to global N<sub>2</sub>O emissions is currently significantly below 1% and expected to remain so in the future. While global agricultural activities emit substantial amounts of N<sub>2</sub>O, biofuel production itself is currently not a major contributor to N<sub>2</sub>O emissions. Although current biofuel production represents a small fraction of total crude oil production, and increases in biofuel production appear likely, second generation biofuels (e.g., lignocellulosic ethanol) are anticipated to have substantially lower environmental impacts. Historical changes in the atmospheric concentrations of N<sub>2</sub>O and emissions sources are discussed in Section 1.5.1.2 of Chapter 1.

#### **5.4.2.4 GEOENGINEERING: ENHANCING EARTH'S ALBEDO BY STRATOSPHERIC INJECTION OF SULFUR**

There is increasing concern that efforts to reduce global greenhouse gas emissions will not be sufficient to prevent Earth's climate from warming to levels that have never been experienced by modern societies. This has intensified the discussion about deliberate atmospheric modification schemes ("geoengineering") to counteract enhanced greenhouse warming due to industrial emissions (for example, see the review panel report on geoengineering (Royal Society, 2009)). Although fraught with uncertainties and side effects that have yet to be studied in detail (Keith et al., 2010), the notion of enhancing Earth's albedo by increasing particulate scattering of visible light in the stratosphere dates back many decades (e.g., Budyko, 1977; Dyson and Marland, 1979). It has been estimated that injection of particles designed for optimum scattering of shortwave radiation (e.g., sulfate or aluminum oxide) might be economically viable and would likely be the most cost-effective method of a class of geoengineering options called "solar radiation management" (Teller et al., 1997; Lenton et al., 2009; Royal Society, 2009). These studies also point out that the proposed solar radiation management techniques likely have the largest side effects of the geoengineering options considered. For example, changes in shortwave radiation would likely result in local temperature and precipitation changes, including increased prevalence of droughts (Hegerl and Solomon, 2009). Various possible side effects of geoengineering (e.g., Robock, 2008) besides the impact on ozone are not further discussed in this Assessment. Other methods that have been suggested for managing solar radiation

or taking up carbon dioxide (e.g., launching mirrors into space to harvest or block radiation; fertilizing the ocean to promote uptake of CO<sub>2</sub> by phytoplankton) could also impact stratospheric ozone, but are not considered here due to a lack of scientific investigations that would allow for an assessment of the impacts of these approaches.

Part of the reason injection of sulfate into the stratosphere has received considerable attention in recent years from the scientific community as an option for solar radiation management (Crutzen, 2006) is due to observations of modest cooling of the globe following major volcanic eruptions, which may be viewed a natural analog to this particular approach to manage Earth's radiation budget. The 1991 eruption of Mt. Pinatubo, for example, resulted in a decrease of global mean temperatures by 0.5°C for a few years (Soden et al., 2002). Observations from recent volcanic eruptions have shown that stratospheric ozone in middle and high latitudes is strongly influenced by the enhanced burden of liquid sulfate aerosols (e.g., Tabazadeh et al., 2002; Solomon et al., 1996; Portmann et al., 1996; Tilmes et al., 2008a). Recent model calculations have estimated a global temperature decrease of about one degree at Earth's surface could be achieved within about five years after the start of a hypothetical sulfate aerosol injection experiment (Robock et al., 2008; Tilmes et al., 2009). However, Heckendorn et al. (2009) have shown that the size distribution of aerosol particles is not fixed as assumed in earlier studies but strongly depends on different injection assumptions. The ability to achieve some amount of cooling that might be required to offset enhanced greenhouse-gas warming may be limited due to the coagulating and settling of aerosols. This process would also warm the tropical tropopause, perhaps resulting in enhanced abundances of stratospheric water vapor, which could accelerate ozone loss especially in the tropics and midlatitudes (Heckendorn et al., 2009). However, a significant increase of stratospheric water vapor was not observed after large volcanic eruptions.

Tilmes et al. (2008b, 2009) estimated the impact of an enhanced burden of stratospheric sulfur on the ozone layer during the period of time when stratospheric halogen loading is projected to slowly decline (Newman et al., 2007). Assuming an injection into the tropical stratosphere of a mass of volcanic-sized (submicron) sulfate aerosols large enough to counteract a doubling of CO<sub>2</sub> with respect to preindustrial values (Rasch et al., 2008a), ozone depletion in the Arctic polar vortex might be expected to double or triple (Tilmes et al., 2009). In addition, the expected recovery of the Antarctic ozone hole from the reduction in atmospheric halogen loading brought about by the Montreal Protocol might be delayed by between 30 and 70 years, depending on the assumed particle sizes (Tilmes et al., 2008b) (see Chapter 3). The

estimated impact on stratospheric ozone at low latitudes is expected to be smaller (about  $\pm 3\%$ ) for 2050 chlorine conditions (Tilmes et al., 2009).

Studies to quantify the impact of geoengineering on ozone have so far assumed basic scenarios and idealized conditions, and they have focused entirely on sulfate aerosols. Particle size distributions are usually described in simple terms, with large uncertainties in the evolution of those distributions (Rasch et al., 2008b). More comprehensive microphysical models, such as the one described in Heckendorn et al. (2009), are necessary to describe the complete size-distributions for geoengineering experiments. Dynamical and chemical changes in the stratosphere as a result of geoengineering are still uncertain given our current modeling capabilities (Chapter 3).

Uncertainties also exist in the amount of sulfur necessary to counteract global warming, which in turn depends on the amount of aerosol deposition (e.g., Heckendorn et al., 2009) and on the strength of the stratospheric circulation in the models, whether assumed for present-day conditions, or for a future accelerated stratospheric circulation (Rasch et al., 2008a). To date there have been no investigations of the impact on ozone caused by a gradual ramp-up of the amount of  $\text{SO}_2$  injected, with the purpose of keeping global average temperature nearly constant (Wigley, 2006). The amount of ozone that might be destroyed by deliberately increasing the aerosol loading of the stratosphere might also differ following a large volcanic eruption that further increases the amount of sulfur in the stratosphere (Tilmes et al., 2008b). Finally, there has been little study of an engineered stratospheric reflecting layer that uses materials other than sulfate (e.g., particles manufactured for maximum scattering of shortwave radiation and extended stratospheric lifetimes, as proposed by Teller et al., 1997).

These and other remaining gaps in our understanding of the full impacts of geoengineering on stratospheric ozone (and other aspects of the environment) are significant. The potential for significant risks to the ozone layer and the climate system, both known and unknown, from solar radiation management, as well as the fact that these approaches do not address other problems like ocean acidification as a result of increasing  $\text{CO}_2$  levels, have been acknowledged (Royal Society, 2009).

#### 5.4.2.5 EMISSIONS FROM AVIATION AND ROCKETS

##### *Aviation*

The importance of current aircraft emissions for ozone is well recognized (IPCC, 1999; WMO, 2003; Wuebbles et al., 2006; Maurice and Lee, 2009; Lee et al., 2009). Aircraft emissions, overall, are thought to increase globally averaged ozone columns by less than

0.5%, primarily due to photochemical production of ozone catalyzed by nitrogen oxides ( $\text{NO}_x$ ), odd hydrogen ( $\text{HO}_x$ ) (from  $\text{H}_2\text{O}$ ), and hydrocarbon (HC) emissions. The production of ozone by emissions of  $\text{NO}_x$  and HCs is offset by the destruction of ozone that occurs when emissions of aerosols and water vapor enhance abundances of ozone-destroying active halogens. As a consequence, little or no impact on stratospheric ozone column abundances is expected from aircraft emissions transported into the lower stratosphere from the troposphere (WMO, 2003; Brasseur, 2008; Lee et al., 2009). New studies reinforce that there is a dual nature of aircraft emissions directly within the stratosphere or near the tropopause, with ozone production in some regions, and losses in others, and a strong dependence of the sign of net ozone changes on the latitude and altitude of those assumed emissions (Meilinger et al., 2005; Søvde et al., 2007; Pitari et al., 2008; Köhler et al., 2008; Cariolle et al., 2009).

Aviation-perturbed ozone can also affect the tropospheric oxidizing capacity, and thus levels of methane, a species that influences ozone chemistry in both the troposphere and stratosphere. Köhler et al. (2008) estimate that the increase in the oxidizing capacity of the troposphere due to aircraft emissions has reduced the lifetime of methane by 3.0%. Given that increases in methane are expected to increase stratospheric ozone (e.g., Section 5.4.2.2), this indirect change due to aircraft would be expected to have an offsetting effect on the increase in ozone columns.

Given that a large shift of worldwide aviation from subsonic to supersonic travel is unlikely in the foreseeable future, this Assessment assumes that aircraft emissions will be predominantly tropospheric. In this case, the net impact of those emissions will be ozone production, with some regional variation such as larger enhancements in heavily traveled flight corridors (e.g., Northern Hemisphere middle latitudes in summer). Ozone changes are expected to be smaller in the Southern Hemisphere, where there are fewer flights and emissions.

##### *Rockets*

A summary of the important processes that can contribute to ozone loss from rocket launches is found in Chapter 1. In the context of scientific and regulatory frameworks for protecting stratospheric ozone, the treatment of combustion emissions from rockets is somewhat complicated because ODP calculations involve some poorly understood processes, may be only regionally appropriate (not globally), and depend on many factors (e.g., propellant type, trajectory, latitude of launch site, etc.). In addition, the atmospheric lifetimes of rocket emissions (except for  $\text{CO}_2$ ) are less than a few years, which are short compared to the lifetimes of most halocarbon source

gases. As is the case for aircraft, the impacts from rockets are due to primary and secondary products of combustion (e.g., H<sub>2</sub>O, NO<sub>x</sub>, hydrogen chloride (HCl), alumina, soot, and sulfate), and not to the fuels themselves. As with other processes presented in this chapter, the impact of rocket emissions on ozone may attract more attention in the coming decades if the space launch market grows (Ross et al., 2009).

Several new classes of rocket propellant are of particular concern even though they do not contain chlorine, because they could still have significant effects on ozone. The first, composed of aluminum and H<sub>2</sub>O, has been proposed recently as an “environmentally friendly” solid rocket motor replacement. Because the emission from an Al/H<sub>2</sub>O rocket is mainly composed of alumina particles (compared to 30% for conventional solid rocket motors), ozone losses from such a rocket could exceed those from conventional solid rocket motors for equal emission rates if there is an ample reservoir of chlorine in the stratosphere, which will be the case for at least a few decades. The second, a “hybrid” that uses N<sub>2</sub>O and solid hydrocarbon as propellants, is being developed for widespread commercial spaceflight and could account for about one-third of all rocket emissions by 2020 (Seedhouse, 2008). Very little is known about the nature and magnitude of the emissions from this new hybrid rocket engine, though initial concerns for stratospheric ozone will focus on uncombusted N<sub>2</sub>O and soot.

Given these uncertainties and the long lead times in space launch hardware engineering and development, the lack of metrics for addressing the global impacts of rocket emissions can be particularly problematic (Ross et al., 2009). Improved understanding of the processes involved in ozone depletion and development of suitable metrics can provide an important framework for launch industries to identify the factors responsible for the environmental impacts of rockets. This could allow, for example, for choice of propellant that best minimizes the environmental impacts.

#### 5.4.2.6 SUMMARY

The ozone impacts of the processes discussed in Section 5.4.2 are qualitatively compared in Table 5-5. Our understanding of the ozone impact of activities directly relating to production and emissions of halocarbons and CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O is fairly advanced, while important gaps remain in our understanding of the impacts of other activities like aviation, space transport, and geoeengineering. Chlorine- and bromine-containing ODSs play the largest role in current ozone depletion while the enhancement of CO<sub>2</sub> and CH<sub>4</sub> above background levels has likely led to higher globally averaged ozone levels than otherwise would have occurred. However, because of the controls

already imposed by the Montreal Protocol on production and consumption of ODSs and the long atmospheric lifetimes of these compounds, the ability to further reduce future atmospheric ODS concentrations and thus ozone depletion through additional controls is more limited than before. Future ozone evolution is expected to be largely affected by activities and emissions not currently regulated by the Montreal Protocol, particularly by changes in CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O. Some of these activities and emissions will likely increase ozone and some will decrease it. Our ability to project future stratospheric ozone is becoming more complicated, in that activities controlled by the Montreal Protocol are likely no longer the most important ones for the future evolution of stratospheric ozone.

### 5.4.3 Climate Impacts

#### 5.4.3.1 MAJOR HFCs USED AS REPLACEMENTS FOR ODSs

Global production and use of CFCs and halons have decreased significantly because of the phase-outs under the Montreal Protocol and its subsequent Amendments and Adjustments. As a direct result, the use of HCFCs and HFCs as replacements has increased in Article 5 and non-Article 5 countries (see Chapter 1). The HCFC increases occurred earlier and have been confirmed by long-term growth in observed atmospheric mixing ratios (Montzka et al., 2009; Stohl et al., 2009) (Chapter 1). Recent changes in northern-latitude mixing ratio observations are consistent with reduced use of HCFCs in non-Article 5 countries and increased use in Article 5 countries (Montzka et al., 2009). HCFCs have been used as low-ODP substitutes in many applications for high-ODP substances and were classified under the Protocol as “transitional substitutes” to be used during the time it took to commercialize new ozone-safe alternatives and replacements. In 2007 the Parties to the Montreal Protocol decided to accelerate the HCFC phase-out, in part to protect future climate. HCFC production and consumption in Article 5 countries will be frozen in 2013 and stepwise reduced, with a virtually complete phase-out in 2030. Non-Article 5 countries have agreed to a virtually complete phase-out in 2020. In adopting the accelerated HCFC phase-out, the Parties agreed to promote the use of HCFC alternatives that minimize the impact on climate.

With the global phase-out of HCFCs, much of the future application demand for refrigeration and air conditioning and heating is likely to met by HFCs, while the demand for thermal-insulating foam production is likely to be met by HFCs as well as hydrocarbons and not-in-kind thermal insulation such as fiberglass and mineral wool (IPCC/TEAP, 2005; Velders et al., 2009). HFCs

**Table 5-5. Qualitative summary of anthropogenic processes affecting stratospheric ozone.**

| Activity   | Mechanism  | Effect on Ozone Layer                          |                            |   |
|--|--|--|----------------------------|---|
|  |  | Ozone Column Increase or Decrease <sup>a</sup> | Understanding <sup>b</sup> | Approximate Maximum Impact <sup>c</sup>           |
| Destruction of CFC banks                             | Ozone destruction by chlorine chemistry                                  | +  | High                       | Medium  |
| Destruction of HCFC banks                            | Ozone destruction by chlorine chemistry                                  | +  | High                       | Small   |
| Destruction of halon banks                           | Ozone destruction by chlorine and bromine chemistry                      | +  | High                       | Medium  |
| Eliminate HCFC production                            | Ozone destruction by chlorine chemistry                                  | +  | High                       | Medium  |
| Eliminate CH <sub>3</sub> Br production              | Ozone destruction by bromine chemistry                                   | +  | Medium                     | Medium  |
| Eliminate CCl <sub>4</sub> production                | Ozone destruction by chlorine chemistry                                  | +  | Medium-Low                 | Medium  |
| Reduction in N <sub>2</sub> O emissions <sup>d</sup> | Ozone destruction by NO <sub>x</sub>                                     | +  | High                       | Medium  |
|  | Mitigation of ozone destruction by chlorine/bromine chemistry            | -  | Medium                     | Small   |
| Reduction in CH <sub>4</sub> emissions <sup>d</sup>  | Ozone production   | -  | Medium                     | Large   |
|  | Ozone destruction by HO <sub>x</sub>                                     | +  | Medium                     | Small   |
|  | Mitigation of ozone destruction by chlorine chemistry                    | -  | Medium                     | Small   |
| Reduction in CO <sub>2</sub> emissions <sup>d</sup>  | Middle- and upper-stratospheric temperature changes                      | -  | High                       | Large   |
|  | Formation of PSCs  | +  | Medium                     | Large   |
|  | Circulation changes <sup>e</sup>   | + & -  | Low                        | Large   |
| Increased aviation emissions                         | Aerosols: heterogeneous ozone destruction by halogens                    | -  | Medium                     | Depends on # of flights, altitudes, and locations |
|  | Production of ozone by HC/HO <sub>x</sub> /NO <sub>x</sub> chemistry     | +  | Medium                     | "   |
|  | Contrail frequency   | ?  | Low                        | "   |
|  | Activation of halogens   | -  | Low                        | "   |
| Increased rocket / space-transport emissions         | SRM <sup>f</sup> – ozone destruction by chlorine chemistry               | -  | High                       | Small at present launch rate                      |
|  | SRM <sup>f</sup> – aerosols: Heterogeneous ozone destruction by halogens | -  | Medium                     | "   |
|  | Water vapor  | -  | Low                        | "   |
|  | Soot   | ?  | Low                        | "   |
|  | Ozone destruction by NO <sub>x</sub>                                     | -  | Low                        | "   |
| Geoengineering by sulfur injection                   | Heterogeneous ozone destruction by halogens                              | -  | Medium-Low                 | Potentially large                                 |

**Table 5-5, continued (notes).**

Notes:

- <sup>a</sup> The “+” sign indicates more column ozone (i.e., less depletion) for the indicated policy option or activity; the “-” sign indicates less column ozone.
- <sup>b</sup> Understanding: “Low” indicates an inability to accurately quantify due to unknown or unquantifiable processes or emissions; “Medium” indicates remaining gaps in our understanding; “High” indicates that processes and values are believed to be well modeled and understood.
- <sup>c</sup> Approximate maximum impact: a relative scale that relates the various activities. This column is somewhat subjective and some of the entries depend strongly on the amount of future activity. Rocket emissions and aviation emissions have the potential to be important, given our current understanding, but specific information regarding flight altitude, number of flights, type of fuel, aerosol emissions, etc., needs to be specified before they can be usefully compared to the other ozone impacts.
- <sup>d</sup> The impacts of a reduction in N<sub>2</sub>O, CH<sub>4</sub>, and/or CO<sub>2</sub> emissions will depend on the sizes of the reductions. Therefore, the “Approximate maximum impact” is somewhat more subjective than for the ODS phase-outs.
- <sup>e</sup> Circulation changes are expected to decrease (increase) total column ozone in the tropics (extratropics). See discussion in Chapter 3.
- <sup>f</sup> SRM stands for solid rocket motor.

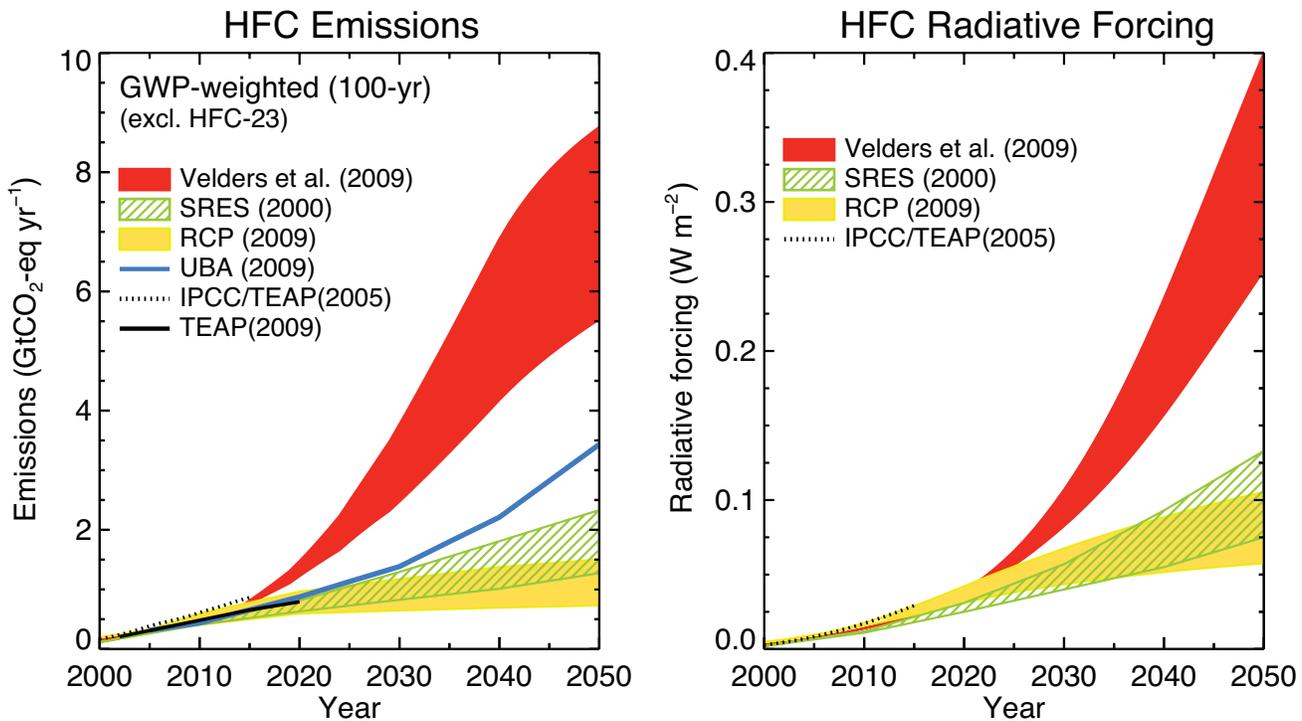
do not deplete the ozone layer but, along with CFCs and HCFCs, are greenhouse gases, which contribute to the radiative forcing of climate (IPCC/TEAP, 2005; Velders et al., 2009). Thus, the current transition away from CFCs in Article 5 countries and HCFCs in Article 5 and non-Article 5 countries has implications not only for the ozone layer, but also for future climate. HFCs are not controlled by the Montreal Protocol, but they are included in the basket of gases of the Kyoto Protocol.

The HFC emissions scenarios discussed here can be divided in two classes:

- One class consists of non-intervention scenarios based on growth rates in gross domestic product and population (IPCC, 2000) for the period up to the middle or end of the 21<sup>st</sup> century. In these scenarios, historical and current technological developments are extrapolated without intervention from political processes. Such scenarios were first developed for the IPCC–Special Report on Emissions Scenarios (SRES) (IPCC, 2000) during the time when HFCs had still very limited usage and when the transition from CFCs and HCFCs had just begun. New non-intervention HFC scenarios have been formulated by Velders et al. (2009) and by the German Federal Environment Agency (UBA, 2009). The scenarios in Velders et al. (2009) are based on assumptions similar to those of IPCC-SRES with respect to growth rates in gross domestic product and population, but have incorporated new current information on (1) reported recent increases in consumption of HCFCs in Article 5 countries of about 20% yr<sup>-1</sup> (through 2007), (2) replacement patterns of HCFCs by HFCs as reported in non-Article 5 countries, and (3) accelerated phase-out schedules of HCFCs in Article 5 and non-Article 5 countries (2007 Adjustment of the Montreal Protocol). The scenarios of UBA (2009) are based on more fundamental sector-specific growth rates and emissions factors for all relevant sectors in Article 5 and non-Article 5 countries and take into account the accelerated HCFC phase-out schedules.
- The other class of scenarios is based on projections of technological developments affected by policy incentives and can therefore be seen as intervention scenarios. The discussions by the Parties of the Montreal Protocol to promote the use of HCFC alternatives that minimize the impact on climate can also be considered an intervention. An intervention scenario was developed for IPCC/TEAP (2005) and recently updated (TEAP, 2009), covering short time periods up to 2015 and 2020, respectively. Others (Rao and Riahi, 2006; Ottinger Schaefer et al., 2006; van Vuuren et al., 2006) have reported HFC scenarios similar to those of SRES. Many of these latter scenarios have performed a relatively simple analysis to project future HFC emissions. Ottinger Schaefer et al. (2006) estimated HFC emissions through 2020 using a detailed sector analysis, but their analysis was performed before the 2007 accelerated HCFC phase-out was adopted, and their 2008 HFC emissions do not agree with the emissions derived from observations.

The new scenarios constructed for IPCC, the Representative Concentration Pathways (RCPs), also contain HFC emissions, but use relatively simple or older analyses for the HFCs (Riahi and Nakicenovic, 2007; Clarke et al., 2007; Smith and Wigley, 2006; Wise et al., 2009; van Vuuren et al., 2006, 2007).

In Figure 5-5 global HFC emissions and radiative forcing are shown for six of the scenarios described above. The scenarios do not contain emissions from HFC-23, which is a by-product from the production of HCFC-22 and is not significantly used as a replacement for ODSs. HFC-23 emissions are estimated to be  $0.20 \pm 0.03$  GtCO<sub>2</sub>-eq yr<sup>-1</sup> for 2006–2008 (Montzka et al., 2010), but are likely to decrease in the coming decade as a result of mitigation efforts for climate protection and because of projected decreases in HCFC-22 production. However, if mitigation is not successful, and unregulated production of HCFC-22 for use as a feedstock increases substantially, it is possible for HFC-23 emissions to increase in the future. The GWP-weighted HFC emissions are similar

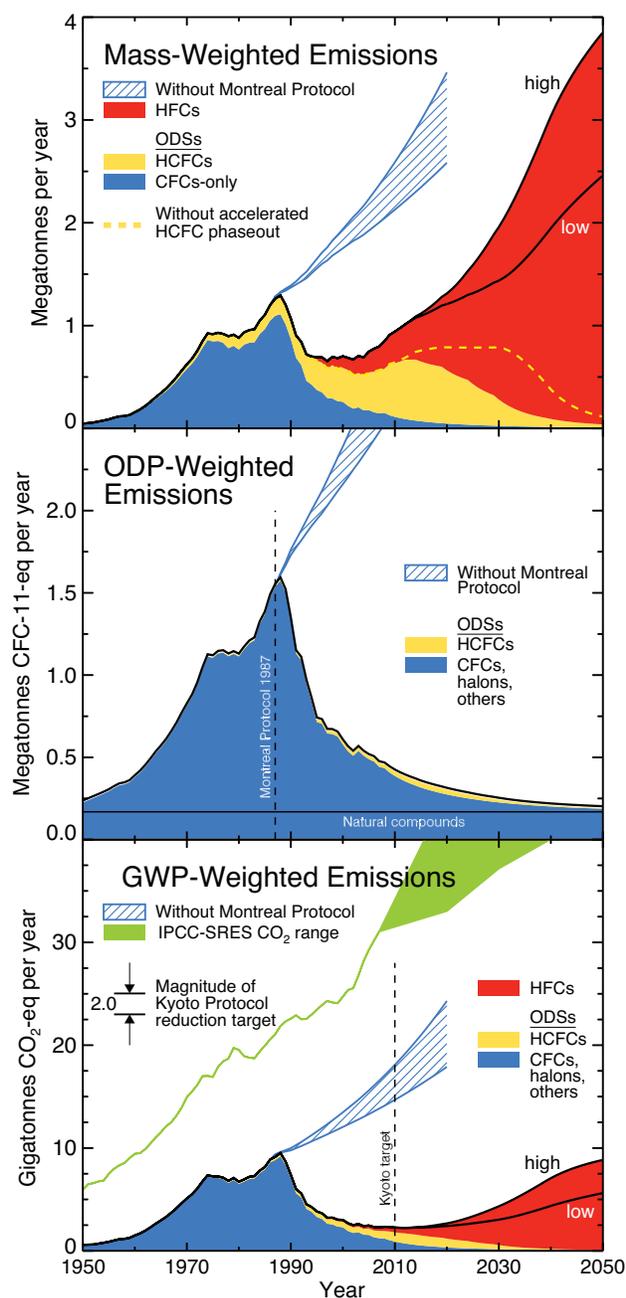


**Figure 5-5.** Global HFC emissions (left) and radiative forcing (right) in four long-term and two short-term scenarios. The long-term scenarios for the period 2000–2050 include the RCP scenarios and the non-intervention scenarios from Velders et al. (2009), UBA (2009), and SRES (IPCC, 2001). The short-term scenarios for the period 2000–2015/2020 include the IPCC-TEAP (2005) and TEAP (2009) scenarios. The RCP scenarios and the short-term scenarios assume intervention to mitigate climate forcing. Emissions of HFC-23, which is a by-product from the production of HCFC-22, are not included. HFC-23 emissions are estimated to be  $0.20 \pm 0.03$  GtCO<sub>2</sub>-eq yr<sup>-1</sup> for 2006–2008 (Montzka et al., 2010). The emission values are multiplied by their GWPs (100-year time horizon) to obtain annual equivalent GtCO<sub>2</sub> emissions. A GtCO<sub>2</sub>-eq equals 1000 million metric tons carbon dioxide equivalent (MMTCO<sub>2</sub>e). The color-shaded regions bound the upper and lower limits of the respective scenarios. Adapted from Velders et al. (2009).

through about 2015 for all six scenarios. However, while the emissions of TEAP (2009) increase linearly through 2020, the emissions of Velders et al. (2009) and UBA (2009) increase faster as a consequence of the growth rates in gross domestic product and the limits on consumption of HCFCs in Article 5 countries. By 2050, the total GWP-weighted HFC emissions are 5.5–8.8 GtCO<sub>2</sub>-eq yr<sup>-1</sup> in Velders et al. (2009) and 3.5 GtCO<sub>2</sub>-eq yr<sup>-1</sup> in UBA (2009); both are significantly larger than those of SRES (1.3–2.3 GtCO<sub>2</sub>-eq yr<sup>-1</sup>) (IPCC, 2000). The HFC emissions in Velders et al. (2009) are about four times larger than those of SRES in 2050 for two principal reasons. First, the starting points (2008) for consumption of HFCs by Velders et al. (2009) are substantially higher than assumed in SRES, based on higher reported consumption of HCFCs from 2000 to 2007 (UNEP, 2009) than was assumed in SRES. Second, in the Velders et al. (2009) study, the HFCs assumed to meet future demand (HFC-125 and HFC-143a) have larger GWPs than the HFCs

assumed in SRES (mostly HFC-134a). This follows from assuming that the future use of HFCs in applications in developing countries will follow the same trends already observed in developed countries. The current consumption values for HFC-125 and HFC-143a are supported by their emissions as estimated from observed atmospheric mixing ratios and account for approximately 80% of the CO<sub>2</sub>-eq emission of HFCs in the year 2050. The lower emissions in the UBA (2009) scenarios compared with Velders et al. (2009) are the result of lower growth rates during 2020–2050 for the major HFC-consuming sectors and different replacement patterns for ODSs by HFCs and not-in-kind alternatives.

The current and expected future increased use of HFCs is largely the result of the phase-out of CFCs and HCFCs by the provisions of the Montreal Protocol, in combination with economic growth and an increase in living standards. As shown in Figure 5-6, total direct GWP-weighted emissions of ODSs peaked in 1988 at

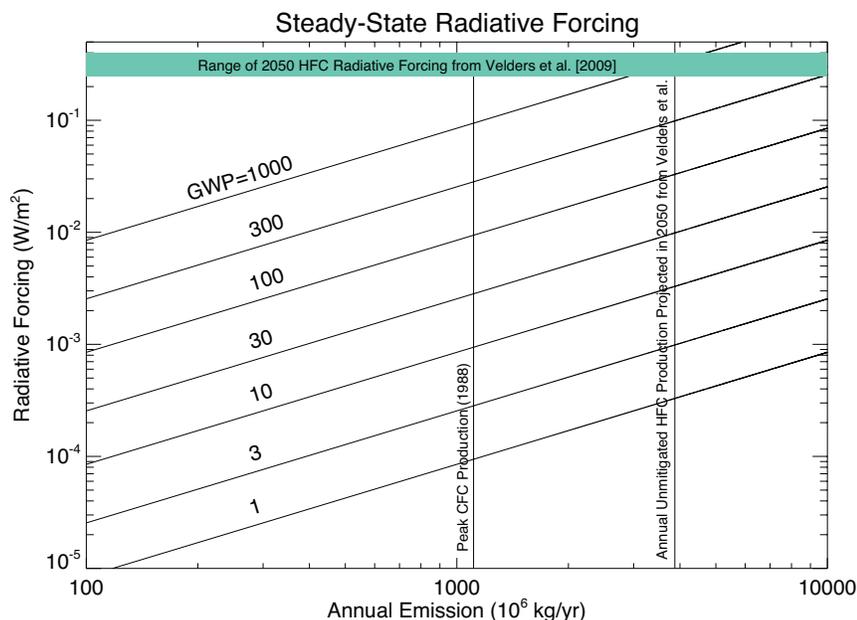


9.4 GtCO<sub>2</sub>-eq yr<sup>-1</sup> and decreased after that, whereas HFC emissions are projected to monotonically increase, primarily in Article 5 countries, exceeding those of ODSs after about 2020 in both Velders et al. (2009) and UBA (2009). In a business-as-usual scenario, starting in 1987, without Montreal Protocol regulations the GWP-weighted emissions of ODSs reach 15–18 GtCO<sub>2</sub>-eq yr<sup>-1</sup> by 2010 (Velders et al., 2007). So, growth in HFC use and emissions would offset at least part of the climate benefits calculated to have been achieved by the Montreal Protocol.

**Figure 5-6.** Emissions of ODSs (CFCs, halons, HCFCs, and others) and their non-ozone-depleting substitutes (HFCs) from 1950 to 2050 (adapted from Velders et al., 2007, 2009). Emissions are the total from developing and developed countries. The legends identify the specific compound classes included in each panel. The high and low HFC labels identify the upper and lower limits, respectively, in global baseline scenarios from Velders et al. (2009). The blue hatched regions indicate the emissions that would have occurred, in the absence of the Montreal Protocol, with 2–3% annual production increases in ODSs. *Top panel:* Global mass-weighted emissions expressed in megatonnes per year. The yellow dashed line shows HCFC emissions calculated without the provisions of the accelerated HCFC phaseout under the 2007 Adjustment of the Montreal Protocol. *Middle panel:* Global ODP-weighted emissions expressed in megatonnes of CFC-11-equivalent per year. The emissions of individual gases are multiplied by their respective ODPs (CFC-11 = 1) to obtain aggregate, equivalent CFC-11 emissions. The dashed line marks 1987, the year of the Montreal Protocol signing. *Bottom panel:* Global GWP-weighted emissions expressed in gigatonnes of CO<sub>2</sub>-equivalent per year. The emissions of individual gases are multiplied by their respective GWPs (direct, 100-year time horizon; CO<sub>2</sub> = 1) to obtain aggregate, equivalent CO<sub>2</sub> emissions. Shown for reference are emissions for the range of IPCC-SRES CO<sub>2</sub> scenarios (IPCC, 2000). The CO<sub>2</sub> emissions for 1950–2007 are from global fossil fuel and cement production. Beyond 2007, the shaded region for CO<sub>2</sub> reflects the range bracketed by the A1B and B2 SRES scenarios. The dashed line denotes 2010, the middle year of the first commitment period of the Kyoto Protocol. Also shown is the magnitude of the reduction target of the first commitment period of the Kyoto Protocol, which is based on a 1990–2010 projection of global greenhouse gas emission increases and the reduction target for participating countries.

The HFC scenario results are further put into context by comparing to projected global CO<sub>2</sub> emissions. Global annual HFC emissions in 2050 as projected by UBA (2009) and Velders et al. (2009) are equivalent (CO<sub>2</sub>-eq basis) to 6–8% and 9–19%, respectively, of projected global CO<sub>2</sub> emissions in IPCC/SRES business-as-usual scenarios (A1B, A2, B1, and B2) (Figure 5-6).

In these HFC scenarios, only the direct contribution to climate forcing due to ODS and HFC emissions is considered. Indirect climate forcings associated with



**Figure 5-7.** Relationship between annual emission rates and steady-state radiative forcing for compounds having seven different GWPs. Relationships are valid for compounds having lifetimes less than 20 years or so. For example, if 1 Tg/yr ( $10^9$  kg/yr) were emitted of a gas with a GWP of 1, the steady-state radiative forcing would be slightly less than  $10^{-4}$  W/m<sup>2</sup>. For comparison, the 2008 estimated radiative forcing from CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O was 1.74, 0.5, and 0.17 W/m<sup>2</sup>, respectively (<http://www.esrl.noaa.gov/gmd/aggi/>).

halocarbon usage arise from the energy used or saved during the application or product lifetime and energy required to manufacture the product, including the halocarbon used. For example, thermal insulating products in buildings and appliances reduce energy consumption, and refrigeration and AC systems consume energy over their lifetimes. A full evaluation of the total climate forcing resulting from the global transition away from CFCs and HCFCs toward HFCs requires consideration of both direct and indirect impacts over all associated halocarbon, non-halocarbon, and not-in-kind application lifecycles.

Three primary options are available to reduce the future climate impact of HFCs as demand continues to increase for products currently using HCFCs and HFCs: first is an increasing implementation of not-in-kind technologies (non-fluorocarbon based); second, use of HFCs that result in less energy used, because many products have significantly higher indirect climate impacts due to the energy used over the lifetime of the product than they do from emissions of the chemicals contained in the product; and third, lower-GWP HFC or other replacement chemicals could be used to satisfy demand. Figure 5-7 shows steady-state radiative forcing resulting from a given annual emission rate for seven representative GWP limits on replacements. If the total 2050 HFC production projected in Velders et al. (2009) were to be met, for example, by HFCs with an average GWP less than 10 or 100, and emissions are assumed to equal production, the steady-state globally averaged radiative forcing would be less than 0.003 or 0.03 W/m<sup>2</sup>, respectively. These values are substantially smaller than the 0.25–0.4 W/m<sup>2</sup> range estimated in the unmitigated case in Velders et al. (2009). This analysis assumes that even very short-lived HFCs

can be considered to be well mixed. In reality, the global-mean lifetimes and radiative efficiencies of substances that are not well mixed will depend on the location of emission. There is currently not sufficient discussion of impacts of such short-lived substances on radiative forcing and climate in the literature to assess the significance of their inhomogeneous abundances on this type of analysis.

#### 5.4.3.2 OTHER REPLACEMENTS FOR ODSs

Unsaturated HFCs (also known as hydrofluoroolefins, HFOs), hydrofluoroketones and perfluoroketones, hydrofluoroethers (HFEs), perfluoropolyethers, ammonia, hydrocarbons and CO<sub>2</sub> are either under consideration or in use as replacements for ODSs. The potential for these compounds to contribute to radiative forcing of climate is considered in this section (other potential environmental impacts are discussed in Section 5.4.4). Most of these compounds are short-lived, which limits their radiative forcing. See Chapter 1 for additional discussion of these compounds, and Tables 1-10 and 1-11 for a list of alternatives for ozone-depleting substances.

The reaction of hydroxyl radicals (OH) with unsaturated HFCs proceeds rapidly, and as a consequence, these unsaturated HFCs have atmospheric lifetimes that are in the range of 1–20 days. With such short lifetimes the contribution of unsaturated HFCs to radiative forcing will be small. For example, HFC-1234yf (CF<sub>3</sub>CF=CH<sub>2</sub>) has a GWP of approximately 4 (Nielsen et al., 2007; Papadimitriou et al., 2008b). HFC emissions are projected to be dominated by HFC-125 and HFC-143a and reach 3.5–8.8 GtCO<sub>2</sub>-eq yr<sup>-1</sup> in 2050 (see Section 5.4.3.1). While substitution by unsaturated HFCs would reduce the

contribution of HFCs to radiative forcing, a full life cycle analysis (including emissions associated with the energy usage by appliances using the different compounds and including an analysis of the production of trifluoroacetic acid (TFA) and tropospheric ozone) would be needed to assess the total systemic environmental impact.

The atmospheric removal mechanism for HFEs is reaction with OH radicals. These rate coefficients decrease with increasing degree of fluorination of the ether. As seen from Appendix Table 5A-1, highly fluorinated HFEs (e.g.,  $\text{CHF}_2\text{OCF}_3$ ) can have substantial atmospheric lifetimes and large GWPs. Also, as evident from Appendix Table 5A-1 and discussed in Chapter 1, HFEs bearing several hydrogen atoms (e.g.,  $\text{C}_2\text{H}_5\text{OC}_4\text{F}_9$ ) have short atmospheric lifetimes and small GWPs. The GWPs for HFEs thus span a large range, and it is not possible to make any general statement regarding the benefit of the substitution of HFCs by HFEs. The benefits need to be assessed on a case-by-case basis. Perfluoropolyethers are not reactive toward OH radicals, or any other oxidant species in the atmosphere, have atmospheric lifetimes probably in excess of 800 years (Young et al., 2006), and will have large GWPs. The volatility and magnitude of possible emissions need to be considered when assessing the potential environmental impact of perfluoropolyethers. Finally, we note that the atmospheric oxidation products of unsaturated HFCs (HFOs), HFEs, hydrofluoroketones, perfluoroketones, and perfluoropolyethers are  $\text{COF}_2$ ,  $\text{HC(O)F}$ , HF, and fluorinated carboxylic acids (Calvert et al., 2008; D'Anna et al., 2005; Good and Francisco, 2003; Taniguchi et al., 2003; Wallington et al., 1994). These products have short atmospheric lifetimes and are not expected to contribute to radiative forcing.

As for the HFCs (Section 5.4.3.1), a full evaluation of the total environmental effects resulting from the global transition away from CFCs and HCFCs toward the compounds discussed in this section or other compounds requires consideration of both direct and indirect environmental impacts over all associated halocarbon, non-halocarbon, and not-in-kind application lifecycles.

#### 5.4.4 Other Environmental Impacts

The potential exists for certain HCFCs, HFCs, HFEs, and unsaturated HFCs (HFOs) to contribute to tropospheric ozone formation, and degrade to give toxic compounds. The atmospheric degradation of HCFCs, HFCs, HFEs, and unsaturated HFCs is initiated by reaction with OH radicals leading to the formation of halogenated carbonyl compounds, which undergo further oxidation to HF, HCl,  $\text{CO}_2$ , and, in some cases, trifluoroacetic acid (TFA) (see for example, IPCC/TEAP 2005; Calvert et al., 2008; Hurley et al., 2008; Nielsen et al., 2007; Papadimitriou et al., 2008b).

Hayman and Derwent (1997) assessed the potential contribution of HCFCs and HFCs to the formation of tropospheric ozone and concluded that these compounds do not have a large potential to contribute to ground-level ozone formation. As indicated from the lifetimes of the compounds listed in Appendix Table 5A-1, the reactivity of HFEs toward OH radicals is comparable to those of analogous HCFCs and HFCs. As with HCFCs and HFCs, HFEs are not expected to make a significant contribution to ground-level ozone formation. OH radicals react rapidly with  $>\text{C}=\text{C}<$  double bonds, and unsaturated HFCs are typically much more reactive than HCFCs, saturated HFCs, and HFEs. The photochemical ozone creation potential (POCP) concept is a well-established method of ranking compounds by their ability to form ozone in the troposphere. POCP values are determined along an idealized straight-line trajectory using a photochemical trajectory model. Using the approach outlined by Derwent et al. (1998) and Jenkin (1998), Wallington et al. (2010) have estimated POCPs for representative unsaturated HFCs. The results are presented in Table 5-6 together with values for selected alkanes, alkenes, and HFCs. As seen from this table, the POCPs for unsaturated HFCs (HFOs) are much larger than those for longer-lived HFCs, much smaller than those for the parent alkenes, and for many compounds (including the commercially significant HFC-1234yf) lie between those of methane and ethane. Methane and ethane are oxidized sufficiently slowly that they do not contribute to any appreciable degree to local air quality issues and are generally exempt from air quality regulations. Luecken et al. (2010) conducted an atmospheric modeling study of the impact of replacing all HFC-134a currently used in vehicle air conditioning systems in the USA with HFC-1234yf. They concluded that such large-scale use of HFC-1234yf would result in a less than 0.01% increase in total ozone formed. Thus, this study provides further support for the expectation that unsaturated HFCs from mobile air conditioning will not make a significant contribution to tropospheric ozone formation in the near future.

The formation of hydrogen fluoride (HF) and hydrogen chloride (HCl) from the degradation of these source gases also should be addressed. Assuming that the combined global emissions of HCFCs, HFCs, HFEs, and unsaturated HFCs (HFOs) are of the order of 100 kilotonnes (Kt) per year, that they are uniformly distributed in the atmosphere, and an annual global precipitation of  $4.9 \times 10^{17}$  liters (Erchel, 1975), the concentrations of HF and HCl in precipitation from degradation of HCFCs, HFCs, HFEs, and HFOs will be of the order of  $3 \times 10^{-9}$  molar. Although HF and HCl are strong acids, the concentration of fluoride and chloride and the additional acidity in precipitation resulting from the atmospheric oxidation of HCFCs, HFCs (saturated and unsaturated), and HFEs would be minor.

**Table 5-6. Photochemical ozone creation potentials (POCPs) for selected hydrofluoro-olefins and related alkanes, alkenes, and hydrofluoro-carbons.**

| Compound   | Industrial or Common Name          | POCP              |
|--|------------------------------------|-------------------|
| CH <sub>2</sub> =CH <sub>2</sub>                   | ethylene; ethene                   | 100 <sup>a</sup>  |
| CH <sub>2</sub> =CF <sub>2</sub>                   | 1,1 difluoroethylene;<br>HFO-1132a | 18.0 <sup>b</sup> |
| CF <sub>2</sub> =CF <sub>2</sub>                   | Perfluoroethylene;<br>HFO-1114     | 12.5 <sup>b</sup> |
| CH <sub>3</sub> CH=CH <sub>2</sub>                 | propylene; propene                 | 117 <sup>c</sup>  |
| CH <sub>2</sub> =CHCF <sub>3</sub>                 | HFO-1243zf                         | 10.7 <sup>b</sup> |
| CH <sub>2</sub> =CFCF <sub>3</sub>                 | HFO-1234yf                         | 7.0 <sup>b</sup>  |
| (Z)-CHF=CFCF <sub>3</sub>                          | HFO-1225ye(Z)                      | 5.6 <sup>b</sup>  |
| CF <sub>2</sub> =CFCF <sub>3</sub>                 | Perfluoropropylene;<br>HFO-1216    | 5.4 <sup>b</sup>  |
| CH <sub>3</sub> CH <sub>2</sub> CH=CH <sub>2</sub> | 1-butene                           | 104 <sup>c</sup>  |
| CH <sub>2</sub> =CHCF <sub>2</sub> CF <sub>3</sub> | HFO-1345czf                        | 6.6 <sup>b</sup>  |
| CH <sub>4</sub>                                    | methane                            | 0.6 <sup>d</sup>  |
| CH <sub>2</sub> F <sub>2</sub>                     | HFC-32                             | 0.2 <sup>e</sup>  |
| C <sub>2</sub> H <sub>6</sub>                      | ethane                             | 8 <sup>c</sup>    |
| CH <sub>3</sub> CHF <sub>2</sub>                   | HFC-152a                           | 1.0 <sup>e</sup>  |
| CH <sub>3</sub> CF <sub>3</sub>                    | HFC-143a                           | 0.0 <sup>e</sup>  |
| CH <sub>2</sub> FCF <sub>3</sub>                   | HFC-134a                           | 0.1 <sup>e</sup>  |
| C <sub>3</sub> H <sub>8</sub>                      | propane                            | 14 <sup>c</sup>   |
| CH <sub>2</sub> FCHF <sub>2</sub> CF <sub>3</sub>  | HFC-245eb                          | 0.2 <sup>b</sup>  |
| CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>   | HFC-236ea                          | 0.0 <sup>b</sup>  |
| CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>    | HFC-227ea                          | 0.0 <sup>e</sup>  |
| <i>n</i> -C <sub>4</sub> H <sub>10</sub>           | butane                             | 31 <sup>c</sup>   |

<sup>a</sup> By definition.  
<sup>b</sup> Wallington et al. (2010).  
<sup>c</sup> Derwent et al. (2007).  
<sup>d</sup> Derwent et al. (1998).  
<sup>e</sup> Hayman and Derwent (1997).

TFA is a persistent, potentially toxic degradation product of some HCFCs (e.g., HCFC-123, -124), HFCs (e.g., HFC-134a, -227ea), and unsaturated HFCs (e.g., -1234yf, -1225ye (CF<sub>3</sub>CF=CHF)). Its sources (natural and anthropogenic), sinks, and potential environmental effects have been reviewed by Tang et al. (1998), Solomon et al. (2003), and IPCC/TEAP (2005). In WMO (2007) it was concluded that “TFA from the degradation of HCFCs and HFCs will not result in environmental concentrations capable of significant ecosystem damage.” The available data suggest that the same conclusion is applicable to unsaturated HFCs and HFES. It has been shown that TFA is

ubiquitous in precipitation and ocean water even in remote areas (Berg et al., 2000; Frank et al., 2002; Scott et al., 2005; Scott et al., 2006; Von Sydow et al., 2000). Frank et al. (2002) estimated that the oceans contain 268 million tonnes of TFA. At a global level, the natural environmental loading of TFA greatly exceeds that expected from the atmospheric degradation of HCFCs, HFCs, and unsaturated HFCs (Kotamarthi et al., 1998). While Tromp et al. (1995) have argued that TFA will accumulate to high levels in seasonal wetlands, Boutonnet et al. (1999) showed that the assumptions made by Tromp et al. were highly improbable. Benesch et al. (2002) showed that TFA does not adversely affect the development of soil microbial communities and pool plant species in vernal ponds. Luecken et al. (2010) assessed the TFA concentrations following replacement of all HFC-134a currently used in vehicle air conditioning systems in the USA with HFC-1234yf. Their model predicted peak concentrations in rainfall of 1264 nanograms per liter. This level is similar to peak concentrations currently observed (Scott et al., 2006) and is approximately two orders of magnitude lower than the level considered safe for the most sensitive aquatic organisms (Luecken et al., 2010). See also Section 1.3.6.3 of Chapter 1 for a discussion on HFC-1234yf. Chapter 1 also discusses our current understanding of the sources of TFA. A current gap in our understanding is the lack of information concerning the natural sources and loss processes of TFA. This gap limits our ability to provide a precise assessment of the role of human activities in affecting local or regional abundances of TFA.

In summary, HCFCs, HFCs, HFES, and HFOs are not expected to contribute significantly to the formation of tropospheric ozone. In the concentrations expected in the environment in the near future, the degradation products of HCFCs, HFCs (saturated and unsaturated), and HFES are not expected to be toxic. However, for thorough understanding of the environmental impacts of replacements for CFCs, HCFCs, and long-lived HFCs, an evaluation of the ODPs, GWPs, atmospheric fate, safety, and toxicity is required for each replacement.

#### 5.4.5 Impact of 2007 Accelerated HCFC Phase-Out

In 2007 the Parties to the Montreal Protocol adjusted the Protocol by accelerating the HCFC phase-out to protect the ozone layer and, in part, to further protect future climate. HCFC consumption in Article 5 countries will be frozen in 2013 and stepwise reduced, with a virtually complete phase-out in 2030. Before the 2007 Adjustment, a freeze in consumption was in place for Article 5 countries starting in 2016 with a complete phase-out in 2040. Non-Article 5 countries have agreed to a virtually

complete phase-out in 2020. The Adjustment also slightly changed the phase-out schedule for non-Article 5 countries, increasing the interim reduction during 2010 through 2014 from 65% to 75% below the baseline level.

The accelerated HCFC phase-out has beneficial implications for the ozone layer and does have the potential to reduce climate forcing. It is expected to cause a reduction in cumulative HCFC emissions, relative to the current baseline scenario of this chapter, of 11–14 megatonnes (Mt) for the period 2011–2050, or an ODP-weighted equivalence of 0.6–0.8 MtCFC-11-eq (Figure 5-6). Following the same methods of calculating mixing ratios and EESC as described in Section 5.2, this emission reduction accelerates the projected return of EESC to 1980 levels by 4–5 years. The resulting percentage reduction in EESC, integrated from 2011 until the 1980 level is reattained, is 10–12%, which is larger than any of the hypothetical zero-production cases discussed in Section 5.4.3.1.

In adopting the accelerated HCFC phase-out, the Parties agreed to promote the use of HCFC alternatives that minimize the impact on climate and other environmental effects. The evaluation of the impact of a replacement of HCFCs with HFCs and other compounds requires consideration of both direct and indirect impacts, such as due to changes in energy usage associated with a particular replacement, over all associated halocarbon and not-in-kind application lifecycles. However, estimating all indirect impacts is extremely difficult. If only direct contributions are considered, the HCFC cumulative emissions reduction attributable to the accelerated phase-out is, in terms of climate forcing and relative to the current baseline, estimated to be 0.4–0.6 GtCO<sub>2</sub>-eq yr<sup>-1</sup> averaged over 2011 through 2050. In comparison, global anthropogenic emissions of CO<sub>2</sub> were greater than 30 Gt per year in 2008. Not-in-kind alternative technologies (such as Stirling cycles, mineral wool, thermoacoustic refrigeration) are expected to only play a minor replacement role for the HCFCs. Therefore, to realize most of this forcing reduction, the avoided HCFC consumption and emissions must be replaced by alternative compounds with small GWPs (e.g., ammonia, hydrocarbons, CO<sub>2</sub>, low-GWP HFCs).

In addition to these potential benefits of the accelerated HCFC phase-out, there is also a climate benefit from the reduction in HFC-23 by-product emissions resulting from reduced HCFC-22 production.

## 5.5 THE WORLD AVOIDED BY OZONE POLICY

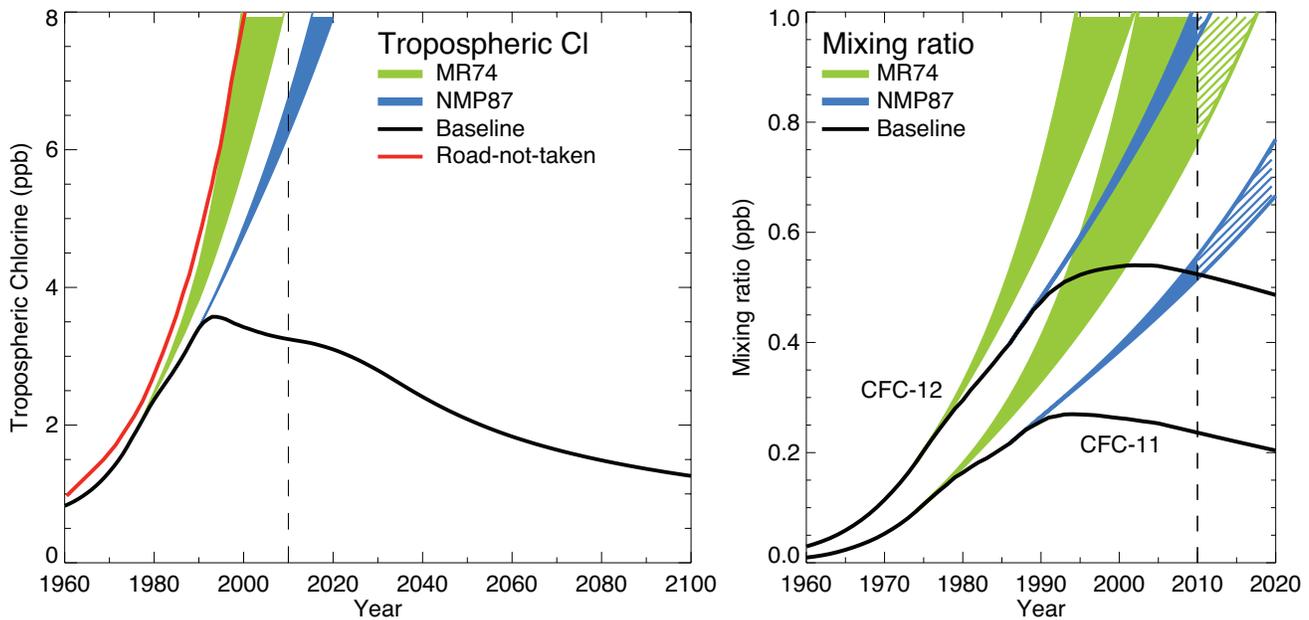
The success of the Montreal Protocol and its subsequent Amendments and Adjustments (Andersen and Sarma, 2002; UNEP, 2009) is evident from the large decreases in the production of ODSs since their peak at the end of the 1980s, from the large decreases in emissions, and from decreases in midlatitude EESC since the middle of

the 1990s that are expected to continue throughout the 21<sup>st</sup> century. The success becomes even more striking when comparing current projections of production, emissions, and mixing ratios of ODSs and of the ozone layer with what might have happened without the Montreal Protocol. Scenarios generated to explore what might have occurred in the absence of ozone mitigation policies have been sometimes referred to as the “road not taken” or “world avoided” scenarios. The studies discussed in Section 5.5.3, made possible by the recent progress in chemistry-climate modeling (CCM), demonstrate the considerable damage mankind could have inflicted upon the Earth System in the space of just a few decades, and the benefit of the Montreal Protocol for both the ozone layer and climate.

ODSs affect the climate system both as greenhouse gases and indirectly through their effect on ozone. Both mechanisms are discussed below, starting with a discussion of ODS emission scenarios in a “World Avoided” by the Montreal Protocol.

### 5.5.1 ODS Production

An assessment of how ODS mitigation policies have affected climate and the ozone layer first requires establishing alternative scenarios of ODS production and emission. These scenarios are based on various reasonable assumptions about what might have happened in the absence of a policy response to scientific advances regarding the environmental impact of halocarbons, and about rates of emissions growth in such non-intervention scenarios. For example, two of the different scenarios that have been considered follow from the assumptions that (1) early warnings of dangers posed by CFCs to the ozone layer (Molina and Rowland, 1974) would have been ignored or would not have existed (referred to here as the MR74 scenario), and (2) that the Montreal Protocol was not implemented (NMP87 scenario) (Velders et al., 2007). Although negotiations about limiting the emissions of ODSs had started prior to the discovery of the ozone hole (Farman et al., 1985; Chubachi and Kajiwara, 1986), a failure to detect polar ozone depletion or to link it to CFCs would likely have led to the adoption of weaker controls, particularly in subsequent negotiations that tightened the initial measures following dissemination of the results attributing the Antarctic losses to halocarbons (Parson, 2003). Prather et al. (1996) developed a scenario similar to MR74 assuming business-as-usual market-driven growth of CFC production after 1974. Under that scenario, although the ozone hole would have been detected, ozone science would have been delayed by around a decade. The mechanism of ozone depletion would have been established later, and emissions would have kept rising at 6% per year, with new uses for CFCs being introduced, until with a delay of 10 years ODS mitigation



**Figure 5-8.** *Left panel:* Total chlorine from the baseline scenario (black) compared with three “World Avoided” scenarios. The “Road-not-taken” scenario is from Prather et al. (1996) and includes only the portion of the “Free Market” curve (described in that study) before controls were implemented. The MR74 and NMP87 scenarios are derived from Velders et al. (2007). *Right panel:* Tropospheric mixing ratios of the most significant CFCs under the MR74 (green) (no identification of the link between CFCs and ozone in 1974 by Molina and Rowland (1974)) and the NMP87 (blue) (no Montreal Protocol restrictions) scenarios; and as observed and assuming compliance with the fully amended and adjusted Montreal Protocol (black). (From Velders et al., 2007).

policies would have been introduced. In this scenario, the tropospheric abundance of total chlorine would rise to 9 parts per billion (ppb) by 2002 before mitigation policies took effect to reduce atmospheric abundances of chlorine. The Velders et al. (2007) MR74 scenario does not include mitigation. The second scenario from Velders et al. (2007), NMP87, is more conservative than MR74 and assumes CFC production would grow in proportion to the economy after 1987 (a characteristic of mature markets), with growth rates of 2–3%/year. Figure 5-8 summarizes the various World Avoided scenarios. Before 1987, NMP87 follows the observed chlorine abundance. Figure 5-6 shows the global emissions of ODSs and HFCs from 1950 to 2050 weighted by mass, ODPs, and GWPs for the baseline scenario and for the NMP87 scenario (Velders et al., 2007, 2009). Each of these scenarios results in a greatly enhanced stratospheric halogen loading compared to what has actually occurred.

### 5.5.2 Radiative Forcing

The radiative forcing (RF) potential of CFCs is well established, as was highlighted in WMO (1986). Velders et al. (2007) calculated the radiative forcing for the MR74 and NMP87 scenarios introduced above, and for the actual

and projected emissions of all ODSs (Table 5-7). For present-day abundances, the RF associated with halocarbons is around  $0.3 \text{ W/m}^2$  or approximately 18% of that of  $\text{CO}_2$  (IPCC, 2007). Under the MR74 scenario, by 2010 the radiative forcing due to all ODS would contribute 44% to 89% as much to global warming as  $\text{CO}_2$ . Under NMP87, in 2010 the RF associated with ODSs would amount to about one-third of that of  $\text{CO}_2$ . Even under this more conservative scenario, the RF increase due to ODSs between 1988 and 2010 would be at least  $0.34 \text{ W/m}^2$ , which is substantial compared to the increase in RF due to  $\text{CO}_2$  of  $0.55 \text{ W/m}^2$  that has been experienced over that period.

The ODS forcing results should be adjusted for (a) the likely negative radiative forcings associated with ozone depletion caused by the ODS emissions (IPCC, 2007), and (b) the reduced emissions of replacement products that would not be needed without the mandated ODS reductions. HFCs are examples of replacement compounds; their usage is projected to grow sharply as a side effect of the Montreal Protocol (Figure 5-6), with potentially large increases in associated RF of up to  $0.4 \text{ W/m}^2$  in non-intervention scenarios by 2050 (Velders et al., 2009). Although the ODS emissions under a no-Montreal Protocol scenario (NMP87) would have a considerably larger radiative forcing, continuing unmitigated emissions of high-GWP HFCs could

**Table 5-7. Direct radiative forcing ( $W/m^2$ ) of controlled ODSs and  $CO_2$  (Velders et al., 2007; IPCC, 2001; IPCC, 2007).** For comparison: in 2008,  $CH_4$  and  $N_2O$  were responsible for a direct radiative forcing of 0.50, and 0.17  $W/m^2$ , respectively ([www.esrl.noaa.gov/gmd/aggi/](http://www.esrl.noaa.gov/gmd/aggi/)).

| Scenario               | 1975 | 1988      | 2010      |
|------------------------|------|-----------|-----------|
| ODS Baseline           | 0.12 | 0.26      | 0.32      |
| ODS MR74 <sup>a</sup>  | 0.12 | 0.30–0.34 | 0.8–1.6   |
| ODS NMP87 <sup>b</sup> | 0.12 | 0.26      | 0.60–0.65 |
| $CO_2$                 | 0.94 | 1.25      | 1.78–1.82 |

<sup>a</sup> Scenario in which the early warnings of dangers posed by CFCs to the ozone layer (Molina and Rowland, 1974) were ignored or did not exist.

<sup>b</sup> Scenario in which the Montreal Protocol was not implemented (“no Montreal Protocol”).

nonetheless substantially offset the effects of other greenhouse gas mitigation efforts. See Section 5.4.2.1 for more details regarding future HFC emissions. The combined effects of ozone depletion and enhanced HFC emissions are estimated to offset about 30% of the radiative forcing avoided by the ODSs phased out under the Montreal Protocol by 2010 (Velders et al., 2007).

In comparing the benefits of the Montreal and Kyoto Protocols for climate, one also needs to assume that if the Montreal Protocol did not exist, the ODSs would almost certainly have been included in the Kyoto Protocol because of the ODSs’ considerable GWPs. However, this would have likely resulted in a delay in implementing controls similar to the one described by Prather et al. (1996), and could have led to unmitigated growth of CFCs lasting longer than what actually occurred.

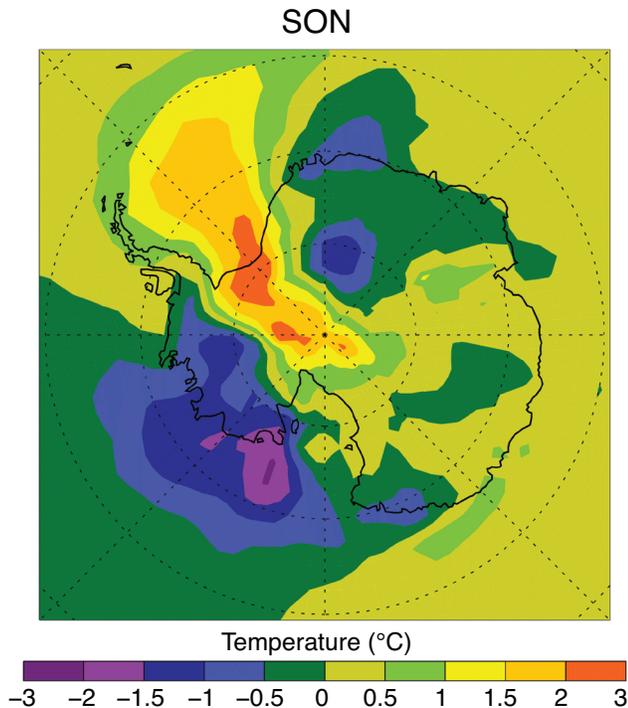
Even allowing for these offsetting effects, Velders et al. (2007) note that actions taken under the Montreal Protocol have been of considerably greater benefit to climate than the reduction target of the first commitment period (2008–2012) of the Kyoto Protocol (Figure 5-6). The annual ODS emission reduction resulting from the Montreal Protocol is estimated to be 10 to 12  $GtCO_2$ -eq  $yr^{-1}$  by 2010, or 5 to 6 times the Kyoto Protocol reduction target. In making this comparison, it is acknowledged that the Kyoto Protocol does not include anthropogenic halocarbons because these substances had previously been regulated by the Montreal Protocol. Also unlike the Kyoto Protocol, the Montreal Protocol has gone through a series of Amendments and Adjustments that have led to further emission reductions. The Kyoto Protocol has not yet gone through this process. The first commitment period aims for an overall reduction, relative to 1990 levels, of 5.2% of  $CO_2$ -equivalent greenhouse gas emissions in Annex 1 countries. A proposed target for 2050 aims for 80% emission reductions, relative to 1990. Even compared to this

much more ambitious target, the climate benefit of the Montreal Protocol calculated to date is significant.

### 5.5.3 Climate and Ozone Impacts Avoided by the Montreal Protocol

Prather et al. (1996) also estimated the consequences to ozone of unmitigated halocarbon emissions growth. Using a 2-D model, they calculated a 10% loss of extrapolar, annual-mean ozone by 1998, relative to 1980. More recently, Morgenstern et al. (2008) and Newman et al. (2009) assessed the impact of a continuing increase of chlorine in the atmosphere on both ozone depletion and climate. By using comprehensive CCMs, these are the first studies to examine the atmospheric structural and dynamical response to highly elevated chlorine. Both studies demonstrate the substantial changes that would likely have occurred if it were not for the Montreal Protocol.

Morgenstern et al. (2008) compare climate under a 9 ppb total chlorine loading—the peak chlorine abundance projected in the Prather et al. (1996) scenario in about 2002—to the actual peak chlorine loading of around 3.5 ppb, which occurred in the late 1990s. In designing their calculations, they deliberately exclude the direct radiative effect of the CFC increases (the main topic of Velders et al., 2007) to focus exclusively on ozone changes and their climate impacts. The additional chlorine leads to a reduction of total ozone everywhere in their model (Morgenstern et al., 2009), with losses ranging from about 5% in the tropics to 20–30% in Arctic and over 50% in Antarctic spring; the average ozone loss between 60°S and 60°N in their model amounts to 8.3%. This is slightly less than estimated by Prather et al. (1996) for a somewhat lower chlorine abundance. The losses peak in three regions, namely in the chlorine layer around 40 km associated with gas-phase catalytic ozone destruction (Molina and Rowland, 1974), and at both high-latitude regions around 20 km, associated with heterogeneous polar processes. The ozone loss has a considerable impact on stratospheric temperatures, with the upper stratosphere cooling by up to 6 K, and a few degrees cooling in the lower stratosphere with warming above it associated with a change in upwelling of 9.6  $\mu m$  radiation due to the ozone loss. Morgenstern et al. (2008) also find substantial extratropical near-surface regional climate change. At southern high latitudes, they find a surface warming of up to 3 K in spring in the lee of the Antarctic Peninsula, and cooling in parts of Western and Eastern Antarctica (Figure 5-9); these calculations are qualitatively consistent with observations in recent decades (leading for example to the collapse of the Larsen B ice shelf; MacAyeal et al., 2003). Morgenstern et al. (2008) associate the climate change found in their model simulations with a further strengthening of the Southern Annular



**Figure 5-9.** Difference between the 9 and 3.5 ppb total chlorine cases in Antarctic spring (September–November) temperature (°C) 20 m above the surface. (From Morgenstern et al., 2008).

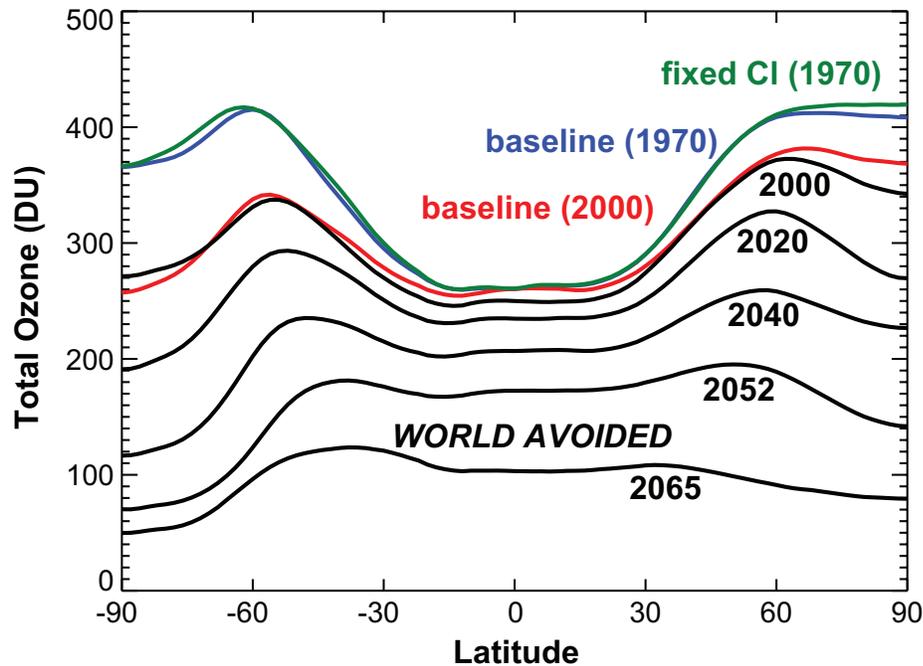
Mode (SAM), the leading mode of variability of the southern extratropics, as has been observed during the period of historic ozone depletion (Thompson and Solomon, 2002; Fogt et al., 2009). For the Northern Hemisphere, their model produces substantial cooling in winter over Northern Asia and Western Europe, and warming over Northern North America and Greenland. Morgenstern et al. (2008) calculate a radiative forcing associated with the ozone depletion of  $-0.05 \text{ W/m}^2$ , which, in absolute terms, is at least an order of magnitude less than the direct radiative forcing associated with the increased ODSs (Velders et al., 2007). However, they note that regional climate change due to the additional ozone depletion, over Antarctica and the northern continents, is large compared to recent observed climate changes.

In assessing these regional climate impacts, one needs to consider that the skill of climate models in representing regional climate trends on decadal timescales is often low, particularly in the Northern Hemisphere (e.g., Figure TS.24 of IPCC, 2007). In the Northern Hemisphere, atmosphere-ocean global circulation models (AOGCMs) typically disagree on basic patterns of climate change, both among each other and compared with observations (e.g., Gillett, 2005). At southern high latitudes, climate models are somewhat more successful in representing patterns of climate change (e.g., Gillett and Thompson, 2003). The

projection by Morgenstern et al. (2008) appears plausible when comparing the patterns of the results to past climate changes in the Antarctic region. For the Northern Hemisphere, it is likely that ozone depletion would have led to substantial regional climate change, but the geographical pattern of change remains poorly understood.

Newman et al. (2009) perform and evaluate a transient simulation using the Goddard Earth Observing System Chemistry Climate Model (GEOSCCM) model (Pawson et al., 2008) in which EESC follows the MR74 scenario of Velders et al. (2007) with an assumed growth rate of 3% per year, leading to 9 ppb in 2019. They terminate their simulation in 2065 when EESC reaches 45 ppb. Other greenhouse gases follow the IPCC (2000) A1B scenario. In their simulation, such drastic increases of ODSs completely alter the structure of the stratosphere. Total global ozone drops by two-thirds during the course of the simulation; the loss is approximately linear in EESC. The ozone loss produced by Newman et al. (2009) is similar to that of Prather et al. (1996) for similar chlorine loading, although a strict comparison is complicated by Newman et al. (2009) displaying ozone loss as a function of equivalent effective chlorine and Prather et al. (1996) using actual chlorine. The changes found by Newman et al. (2009) are initially largely driven by high-latitude ozone loss (Figure 5-10). In around 2020 in the simulation, Arctic ozone in April drops below 220 Dobson units (DU) and would thus satisfy a common definition of an Arctic ozone hole. By 2060, Arctic ozone in the simulation drops below 100 DU in spring. There is a progressive deepening and lengthening of the lifetime of the Antarctic polar vortex in the simulation, eventually leading to a year-round ozone hole with westerlies in the southern mid- and high-latitude stratosphere. Newman et al. (2009) refer to this as the “perpetual winter.” At the end of the simulation, minimum ozone columns reach about 50 DU over Antarctica. After about 2045 in the simulation, enhanced upwelling cools the tropical lower stratosphere and triggers heterogeneous chemical processes similar to those currently observed in the Antarctic ozone hole. In the simulation, this leads to precipitous ozone depletion and nearly complete ozone loss in the tropical lower stratosphere by 2058. Newman et al. (2009) compare their results to complementary simulations assuming ODS abundances fixed at 1960 levels or following the A1 scenario (WMO, 2007) to demonstrate the effect of mitigating ODS emissions when the reference scenario has such dramatic chlorine increases.

Both Morgenstern et al. (2008) and Newman et al. (2009) exclude certain feedbacks that would have otherwise affected their results. In both studies, climate change due to ozone loss is not allowed to affect ocean conditions, which can have impacts that extend into the middle atmosphere (Kodama et al., 2007). In Newman et al. (2009), the direct RF due to the increasing ODSs (Velders et al., 2007)



**Figure 5-10.** Zonal-mean total ozone in the World Avoided simulation (black), in 1970 for chlorine fixed at 1960 levels (green), and for a baseline scenario simulation in 1970 (blue) and 2000 (red). (Adapted from Newman et al., 2009).

is also not reflected in the ocean conditions; Morgenstern et al. (2008) exclude this effect by keeping the ODSs the same for radiation as in their reference simulation. Newman et al. (2009) prescribe tropospheric ozone and thus suppress feedback effects on tropospheric chemistry (e.g., tropospheric ozone production or loss caused by the increasing ultraviolet (UV) radiation). Morgenstern et al. (2008) use photolysis rates in the troposphere that do not reflect changes to the ozone column, thus also not allowing for such feedbacks. However, substantial decreases of tropospheric ozone do occur in Morgenstern et al. (2008) due to a decreased influx of stratospheric ozone. Further feedbacks not correctly treated in the simulations relate to a shortening of lifetimes of ODSs and long-lived greenhouse gases in the World Avoided simulations. Such shortening could occur from increased actinic fluxes and an acceleration of the Brewer-Dobson circulation, and would cause increasing emissions of ODSs to lead to less-than-proportional increases in their atmospheric abundances.

#### 5.5.4 UV Impacts of the Avoided Ozone Depletion

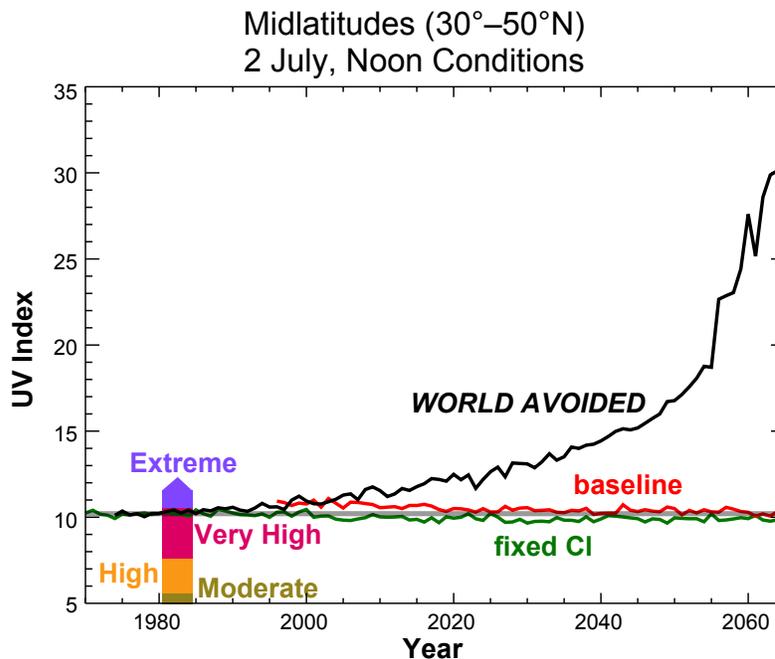
The decreases in ozone abundances in the World Avoided simulations (Prather et al., 1996; Morgenstern et al., 2008; Newman et al., 2009) would have led to an increase in solar ultraviolet radiation at Earth's surface. The magnitude of these increases varies with wavelength, depending on the absorption cross section of ozone, and with latitude, according to the latitudinal distribution

of ozone depletion. Newman et al. (2009) calculate the spectral changes in UV occurring in their simulation. At the shortest UV-B wavelengths, in relative terms, the calculated changes are extremely large; however, in absolute terms the surface irradiance at these wavelengths is weak. Regarding biologically relevant radiation, they show that decreases in stratospheric ozone due to increasing CFCs would have led to marked increases in erythemally weighted irradiance (which is proportional to the UV Index; Chapter 2), up to three times more in the summer of northern midlatitudes by 2065 (Figure 5-11), and with UV Index values in excess of 30 at midlatitudes of both hemispheres. The excess radiation would have had large impacts on the biosphere and on human health; for example, Northern Hemisphere midlatitude ozone losses would have led to a reduction of the sunburn time, at local noon for clear-sky midsummer conditions, from 15 to 5 minutes, and would increase DNA-damaging UV by approximately 550% between 1980 and 2065 (Newman et al., 2009).

#### 5.5.5 Summary

“Road not taken” or “World Avoided” studies indicate that the Montreal Protocol has had considerable benefits for both the ozone layer and climate change. Total chlorine would have increased much beyond the observed peak of around 3.5 ppb. Consequences of uncontrolled growth in ODSs would have resulted both directly from the radiative forcing of the halocarbons, and indirectly from the ensuing ozone depletion. In 2010, the

**Figure 5-11.** Erythemally weighted UV radiation (expressed in terms of the UV Index) for noon conditions on 2 July at northern midlatitudes. Black: World Avoided. Red: A1 baseline scenario (WMO, 2007) for ODSs. Green: CI fixed at 1960 levels. Gray: 1975–1985 average of the fixed-CI simulation. The conventional color scale used in reporting the UV Index to the public is superimposed for reference showing the highest four divisions. (Adapted from Newman et al., 2009).



RF associated with unmitigated emissions of halocarbons could have reached 2 to 5 times what has actually occurred. The chemical consequences could have included a thinned ozone layer everywhere on the globe, the occurrence of an Arctic ozone hole, regional climate change in middle and high latitudes of both hemispheres, increased UV with associated biological and medical consequences, and changes in stratospheric circulation including, in an extreme case, year-round westerlies in the Southern-Hemisphere stratosphere (the “perpetual winter”). While many details associated with these calculated World Avoided impacts may have large uncertainties associated with them, there is no doubt that the Montreal Protocol and its Amendments and Adjustments have avoided additional profound changes to stratospheric ozone and climate.

## REFERENCES

- Andersen, S.O., and K.M. Sarma, *Protecting the Ozone Layer — the Official UN History*, Earthscan, ISBN 1-85383-905-1, London, 2002.
- Barry, J., G. Locke, D. Scollard, H. Sidebottom, J. Treacy, C. Clerbaux, R. Colin, and J. Franklin, 1,1,1,3,3,-Pentafluorobutane (HFC-365mfc): Atmospheric degradation and contribution to radiative forcing, *Int. J. Chem. Kinet.*, 29 (8), 607-617, doi: 10.1002/(SICI)1097-4601(1997)29:8<607::AID-KIN6>3.0.CO;2-Y, 1997.
- Benesch, J.A., M.S. Gustin, G.R. Cramer, and T.M. Cahill, Investigation of effects of trifluoroacetate on vernal pool ecosystems, *Environ. Toxicol. Chem.*, 21 (3), 640-647, doi: 10.1002/etc.5620210325, 2002.
- Berg, M., S.R. Müller, J. Mühlemann, A. Wiedmer, and R.P. Schwarzenbach, Concentrations and mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in Switzerland, *Environ. Sci. Technol.*, 34, 2675-2683, doi: 10.1021/es990855f, 2000.
- Berntsen, T.K., J.S. Fuglestedt, M.M. Joshi, K.P. Shine, N. Stuber, M. Ponater, R. Sausen, D.A. Hauglustaine, and L. Li, Response of climate to regional emissions of ozone precursors: Sensitivities and warming potentials, *Tellus*, 57B (4), 283-304, 2005.
- Blowers, P., and K. Hollingshead, Estimations of global warming potentials from computational chemistry calculations for CH<sub>2</sub>F<sub>2</sub> and other fluorinated methyl species verified by comparison to experiment, *J. Phys. Chem. A*, 113 (20), 5942-5950, doi: 10.1021/jp8114918, 2009.
- Boutonnet, J.C., P. Bingham, D. Calamari, C. de Rooij, J. Franklin, T. Kawano, J.-M. Libre, A. McCulloch, G. Malinverno, J.M. Odom, G.M. Rusch, K. Smythe, I. Sobolev, R. Thompson, and J.M. Tiedje, Environmental risk assessment of trifluoroacetic acid, *Hum. Ecol. Risk Assess.*, 5 (1), 59-124, 1999.
- Brasseur, G.P., *A Report on the Way Forward Based on the Review of Research Gaps and Priorities*, Aviation Climate Change Research Initiative, Federal Aviation Administration, 53 pp., available: [http://www.faa.gov/about/office\\_org/headquarters\\_offices/aep/aviation\\_climate/media/ACCRI\\_Report\\_final.pdf](http://www.faa.gov/about/office_org/headquarters_offices/aep/aviation_climate/media/ACCRI_Report_final.pdf),

- 2008.
- British Petroleum, *BP Statistical Review of World Energy June 2009*, Beacon Press, available: [http://www.bp.com/liveassets/bp\\_internet/globalbp/globalbp\\_uk\\_english/reports\\_and\\_publications/statistical\\_energy\\_review\\_2008/STAGING/local\\_assets/2009\\_downloads/statistical\\_review\\_of\\_world\\_energy\\_full\\_report\\_2009.pdf](http://www.bp.com/liveassets/bp_internet/globalbp/globalbp_uk_english/reports_and_publications/statistical_energy_review_2008/STAGING/local_assets/2009_downloads/statistical_review_of_world_energy_full_report_2009.pdf), 2009.
- Budyko, M.I., Present-day climatic changes, *Tellus*, 29 (3), 193-204, doi: 10.1111/j.2153-3490.1977.tb00725.x, 1977.
- Calvert, J.G., R.G. Derwent, J.J. Orlando, G.S. Tyndall, and T.J. Wallington, *Mechanisms of Atmospheric Oxidation of the Alkanes*, 1008 pp., Oxford University Press, New York, NY, U.S.A., 2008.
- Cariolle D., D. Caro, R. Paoli, D.A. Hauglustaine, B. Cuénot, A. Cozic, and R. Paugam, Parameterization of plume chemistry into large-scale atmospheric models: Application to aircraft NO<sub>x</sub> emissions, *J. Geophys. Res.*, 114, D19302, doi: 10.1029/2009JD011873, 2009.
- Cavalli, F., M. Glasius, J. Hjorth, B. Rindone, and N.R. Jensen, Atmospheric lifetimes, infrared spectra and degradation products of a series of hydrofluoroethers, *Atmos. Environ.*, 32 (21), 3767-3773, doi: 10.1016/S1352-2310(98)00106-X, 1998.
- Chipperfield, M.P., and W. Feng, Comment on: Stratospheric ozone depletion at northern mid-latitudes in the 21<sup>st</sup> century: The importance of future concentrations of greenhouse gases nitrous oxide and methane, *Geophys. Res. Lett.*, 30 (7), 1389, doi: 10.1029/2002GL016353, 2003.
- Christidis, N., M.D. Hurley, S. Pinnock, K.P. Shine, and T.J. Wallington, Radiative forcing of climate change by CFC-11 and possible CFC-replacements, *J. Geophys. Res.*, 102 (D16), 19597-19609, doi: 10.1029/97JD01137, 1997.
- Chubachi, S., and R. Kajiwara, Total ozone variations at Syowa, Antarctica, *Geophys. Res. Lett.*, 13 (12), 1197-1198, doi: 10.1029/GL013i012p01197, 1986.
- Clarke, L.E., J.A. Edmonds, H.D. Jacoby, H.M. Pitcher, J.M. Reilly, and R.G. Richels, *Scenarios of Greenhouse Gas Emissions and Atmospheric Concentrations*, Sub-report 2.1a of Synthesis and Assessment Product 2.1 by the U.S. Climate Change Science Program and the Subcommittee on Global Change Research, Department of Energy, Office of Biological & Environmental Research, Washington, D.C., U.S., 154 pp., 2007.
- Crutzen, P.J., Albedo enhancement by stratospheric sulfur injections: A contribution to resolve a policy dilemma?, *Clim. Change*, 77 (3-4), 211-220, doi: 10.1007/s10584-006-9101-y, 2006.
- Crutzen, P.J., A.R. Mosier, K.A. Smith, and W. Winiwarter, N<sub>2</sub>O release from agro-biofuel production negates global warming reduction by replacing fossil fuels, *Atmos. Chem. Phys.*, 8 (2), 389-395, doi: 10.5194/acp-8-389-2008, 2008.
- Cunnold, D.M., R.F. Weiss, R.G. Prinn, D. Hartley, P.G. Simmonds, P.J. Fraser, B. Miller, F.N. Alyea, and L. Porter, GAGE/AGAGE measurements indicating reductions in global emissions of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> in 1992-1994, *J. Geophys. Res.*, 102 (D1), 1259-1269, 1997.
- Daniel, J.S, and G.J.M. Velders (Lead Authors), A.R. Douglass, P.M.D. Forster, D.A. Hauglustaine, I.S.A. Isaksen, L.J.M. Kuijpers, A. McCulloch, and T.J. Wallington, Halocarbon scenarios, ozone depletion potentials, and global warming potentials, Chapter 8 in *Scientific Assessment of Ozone Depletion: 2006*, Global Ozone Research and Monitoring Project—Report No. 50, World Meteorological Organization, Geneva, Switzerland, 2007.
- Daniel, J.S., S. Solomon, and D.L. Albritton, On the evaluation of halocarbon radiative forcing and global warming potentials, *J. Geophys. Res.*, 100 (D1), 1271-1285, 1995.
- Daniel, J.S., E.L. Fleming, R.W. Portmann, G.J.M. Velders, C.H. Jackman, and A.R. Ravishankara, Options to accelerate ozone recovery: Ozone and climate benefits, *Atmos. Chem. Phys.*, 10 (16), 7697-7707, doi: 10.5194/acp-10-7697-2010, 2010.
- D'Anna, B., S.R. Sellevåg, K. Wirtz, and C.J. Nielsen, Photolysis study of perfluoro-2-methyl-3-pentanone under natural sunlight conditions, *Environ. Sci. Technol.*, 39 (22), 8708-8711, doi: 10.1021/es048088u, 2005.
- Derwent, R.G., M.E. Jenkin, S.M. Saunders, and M.J. Pilling, Photochemical ozone creation potentials for organic compounds in Northwest Europe calculated with a master chemical mechanism, *Atmos. Environ.*, 32 (14-15), 2429-2441, 1998.
- Derwent, R.G., M.E. Jenkin, N.R. Passant, and M.J. Pilling, Reactivity-based strategies for photochemical ozone control in Europe, *Environ. Sci. Policy*, 10 (5), 445-453, doi: 10.1016/j.envsci.2007.01.005, 2007.
- Dillon, T.J., A. Horowitz, and J.N. Crowley, The atmospheric chemistry of sulphuryl fluoride, SO<sub>2</sub>F<sub>2</sub>, *Atmos. Chem. Phys.*, 8 (6), 1547-1557, doi: 10.5194/acp-8-1547-2008, 2008.
- Douglass, A.R., R.S. Stolarski, M.R. Schoeberl, C.H. Jackman, M.L. Gupta, P.A. Newman, J.E. Nielsen, and E.L. Fleming, Relationship of loss, mean age of air and the distribution of CFCs to stratospheric circulation and implications for atmospheric lifetimes, *J. Geophys. Res.*, 113, D14309, doi: 10.1029/2007JD009575, 2008.

- Dyson, F.J., and G. Marland, Technical fixes for the climate effects of CO<sub>2</sub>, in *Workshop on the Global Effects of Carbon Dioxide from Fossil Fuels*, edited by W.P. Elliott and L. Machta, CONF-770385, U.S. Department of Energy, Washington, D.C., U.S., pp. 111-118, 1979.
- Erchel, E., *World Water Balance*, Elsevier, New York, NY, U.S.A., 1975.
- Farman, J.C., B.G. Gardiner, and J.D. Shanklin, Large losses of total ozone in Antarctica reveal seasonal ClO<sub>x</sub>/NO<sub>x</sub> interaction, *Nature*, *315*, 207-210, doi: 10.1038/315207a0, 1985.
- Fisher, D.A., C.H. Hales, D.L. Filkin, M.K.W. Ko, N.D. Sze, P.S. Connell, D.J. Wuebbles, I.S.A. Isaksen, and F. Stordal, Model calculations of the relative effects of CFCs and their replacements on stratospheric ozone, *Nature*, *344*, 508-512, doi: 10.1038/344508a0, 1990.
- Fleming, E.L., C.H. Jackman, D.K. Weisenstein, and M.K.W. Ko, The impact of interannual variability on multidecadal total ozone simulations, *J. Geophys. Res.*, *112*, D10310, doi: 10.1029/2006JD007953, 2007.
- Fogt, R.L., J. Perlwitz, S. Pawson, and M.A. Olsen, Inter-annual relationships between polar ozone and the SAM, *Geophys. Res. Lett.*, *36*, L04707, doi: 10.1029/2008GL036627, 2009.
- Forster, P.M. de F., J.B. Burkholder, C. Clerbaux, P.F. Coheur, M. Dutta, L.K. Gohar, M.D. Hurley, G. Myhre, R.W. Portmann, A. Ravishankara, K.P. Shine, T.J. Wallington, and D. Wuebbles, Resolution of the uncertainties in the radiative forcing of HFC-134a, *J. Quant. Spectrosc. Radiat. Transfer*, *93* (4), 447-460, doi: 10.1016/j.jqsrt.2004.08.038, 2005.
- Frank, H., E.H. Christoph, O. Holm-Hansen, and J.L. Bullister, Trifluoroacetate in ocean waters, *Environ. Sci. Technol.*, *36*, 12-15, doi: 10.1021/es0101532, 2002.
- Fuglestedt, J.S., K.P. Shine, T. Berntsen, J. Cook, D.S. Lee, A. Stenke, R.B. Skeie, G.J.M. Velders, and I.A. Waitz, Transport impacts on atmosphere and climate: Metrics, *Atmos. Environ.*, *44* (37), 4648-4677, doi: 10.1016/j.atmosenv.2009.04.044, 2010.
- Gillett, N.P., Northern Hemisphere circulation, *Nature*, *437* (7058), 496, doi: 10.1038/437496a, 2005.
- Gillett, N.P., and D.W.J. Thompson, Simulation of recent Southern Hemisphere climate change, *Science*, *302* (5643), 273-275, 2003.
- Good, D.A., and J.S. Francisco, Atmospheric chemistry of alternative fuels and alternative chlorofluorocarbons, *Chem. Rev.*, *103* (12), 4999-5024, doi: 10.1021/cr020654l, 2003.
- Haigh, J.D., and J.A. Pyle, A two-dimensional calculation including atmospheric carbon dioxide and stratospheric ozone, *Nature*, *279*, 222-224, doi: 10.1038/279222a0, 1979.
- Hayman, G.D., and R.G. Derwent, Atmospheric chemical reactivity and ozone-forming potentials of potential CFC replacements, *Environ. Sci. Technol.*, *31* (2), 327-336, 1997.
- Heckendorn, P., D. Weisenstein, S. Fueglistaler, B.P. Luo, E. Rozanov, M. Schraner, L.W. Thomason, and T. Peter, The impact of geoengineering aerosols on stratospheric temperature and ozone, *Env. Res. Lett.*, *4* (4), doi: 10.1088/1748-9326/4/4/045108, 2009.
- Hegerl, G.C., and S. Solomon, Risks of climate engineering, *Science*, *325* (5943), 955-956, doi: 10.1126/science.1178530, 2009.
- Hsu, J., and M.J. Prather, Global long-lived chemical modes excited in a 3-D chemistry transport model: Stratospheric N<sub>2</sub>O, NO<sub>y</sub>, O<sub>3</sub>, and CH<sub>4</sub> chemistry, *Geophys. Res. Lett.*, *37*, L07805, doi: 10.1029/2009GL042243, 2010.
- Hurley, M.D., T.J. Wallington, M.S. Javadi, and O.J. Nielsen, Atmospheric chemistry of CF<sub>3</sub>CF=CH<sub>2</sub>: Products and mechanisms of Cl atom and OH radical initiated oxidation, *Chem. Phys. Lett.*, *450*, 263-267, doi: 10.1016/j.cplett.2007.11.051, 2008.
- Inoue, Y., M. Kawasaki, T.J. Wallington, and M.D. Hurley, Atmospheric chemistry of CF<sub>3</sub>CH<sub>2</sub>CF<sub>2</sub>CH<sub>3</sub> (HFC-365mfc): Kinetics and mechanism of chlorine atom initiated oxidation, infrared spectrum, and global warming potential, *Chem. Phys. Lett.*, *462*, 164-168, doi: 10.1016/j.cplett.2008.07.054, 2008.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change: The IPCC Scientific Assessment*, edited by J.T. Houghton, G.J. Jenkins, and J.J. Ephraums, 364 pp., Cambridge University Press, Cambridge, U.K., 1990.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change, 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios*, edited by J.T. Houghton, L.G. Meira Filho, J. Bruce, H. Lee, B.A. Callander, E. Haites, N. Harris, and K. Maskell, 339 pp., Cambridge University Press, Cambridge, U.K., 1995.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change 1995: The Science of Climate Change*, edited by J.T. Houghton, L.G. Meira Filho, B.A. Callander, N. Harris, A. Kattenberg, and K. Maskell, 572 pp., Cambridge University Press, Cambridge, U.K., 1996.
- IPCC (Intergovernmental Panel on Climate Change), *Aviation and the Global Atmosphere, A Special Report of the Intergovernmental Panel on Climate Change*, edited by J.E. Penner, D. Lister, D.J. Griggs, D.J. Dokken, and M. McFarland, 373 pp.,

- Cambridge University Press, Cambridge, U.K., doi: 10.2277/0521664047, 1999.
- IPCC (Intergovernmental Panel on Climate Change), *Special Report on Emissions Scenarios*, Special Report of Working Group III of the Intergovernmental Panel on Climate Change, edited by N. Nakicenovic and R. Swart, 570 pp., Cambridge University Press, Cambridge, U.K. and New York, NY, U.S.A., 2000.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, and C.A. Johnson, 881 pp., Cambridge University Press, Cambridge, U.K., 2001.
- IPCC (Intergovernmental Panel on Climate Change), *Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor, and H.L. Miller, 996 pp., Cambridge University Press, Cambridge, U.K., and New York, NY, U.S.A., 2007.
- IPCC (Intergovernmental Panel on Climate Change), *Summary Report of the IPCC Expert Meeting on the Science of Alternative Metrics*, 18–20 March 2009, Oslo, Norway. IPCC-XXX/Doc.13 (31.III.2009), available: [www.ipcc.ch/meetings/session30/doc13.pdf](http://www.ipcc.ch/meetings/session30/doc13.pdf), 2009.
- IPCC/TEAP (Intergovernmental Panel on Climate Change/Technology and Economic Assessment Panel), *IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons*, prepared by Working Groups I and III of the Intergovernmental Panel on Climate Change, and the Technical and Economic Assessment Panel, Cambridge University Press, Cambridge, U.K., and New York, NY, U.S.A., 2005.
- Jenkin, M.E., Photochemical ozone and PAN creation potentials: Rationalisation and methods of estimation, *AEA Technology plc*, Report AEAT-4182/20150/003, 1998.
- Johansson, D.J.A., U.M. Persson, and C. Azar, Uncertainty and learning: Implications for the trade-off between short-lived and long-lived greenhouse gases, *Clim. Change*, 88 (3-4), 293-308, doi: 10.1007/s10584-007-9381-x, 2008.
- Johnson, C.E., and R.G. Derwent, Relative radiative forcing consequences of global emissions of hydrocarbons, carbon monoxide and NO<sub>x</sub> from human activities estimated with a zonally-averaged two-dimensional model, *Clim. Change*, 34 (3-4), 439-462, doi: 10.1007/BF00139301, 1996.
- Keith, D.W., E. Parson, and M.G. Morgan, Research on global sun block needed now, *Nature*, 463, 426-427, doi: 10.1038/463426a, 2010.
- Kodama, C., T. Iwasaki, K. Shibata, and S. Yukimoto, Changes in the stratospheric mean meridional circulation due to increased CO<sub>2</sub>: Radiation- and sea surface temperature-induced effects, *J. Geophys. Res.*, 112, D16103, doi: 10.1029/2006JD008219, 2007.
- Köhler, M.O., G. Rädcl, O. Dessens, K.P. Shine, H.L. Rogers, O. Wild, and J.A. Pyle, Impact of perturbations to nitrogen oxide emissions from global aviation, *J. Geophys. Res.*, 113, D11305, doi: 10.1029/2007JD009140, 2008.
- Kotamarthi, V.R., J.M. Rodriguez, M.K.W. Ko, T.K. Tromp, N.D. Sze, and M.J. Prather, Trifluoroacetic acid from the degradation of HCFCs and HFCs: A three-dimensional modeling study, *J. Geophys. Res.*, 103 (D5), 5747-5758, 1998.
- Lee, D.S., G. Pitari, V. Grewe, K. Gierens, J.E. Penner, A. Petzold, M.J. Prather, U. Schumann, A. Bais, T. Berntsen, D. Iachetti, L.L. Lim, and R. Sausen, Transport impacts on atmosphere and climate: Aviation, *Atmos. Environ.*, 44 (37), doi: 10.1016/j.atmosenv.2009.06.005, 2009.
- Lenton, T.M., and N.E. Vaughan, The radiative forcing potential of different climate geoengineering options, *Atmos. Chem. Phys.*, 9 (15), 5539-5561, doi: 10.5194/acp-9-5539-2009, 2009.
- Li, F., R.S. Stolarski, and P.A. Newman, Stratospheric ozone in the post-CFC era, *Atmos. Chem. Phys.*, 9 (6), 2207-2213, doi: 10.5194/acp-9-2207-2009, 2009.
- Luecken, D.J., R.L. Waterland, S. Papasavva, K. Tadonno, W.T. Hutzell, J.P. Rugh, and S.O. Andersen, Ozone and TFA impacts in North America from degradation of 2,3,3,3-tetrafluoropropene (HFO-1234yf), a potential greenhouse gas replacement, *Environ. Sci. Technol.*, 44 (1), 343-348, doi: 10.1021/es902481f, 2010.
- MacAyeal, D.R., T.A. Scambos, C.L. Hulbe, and M.A. Fahnestock, Catastrophic ice-shelf break-up by an ice-shelf-fragment-capsize mechanism, *J. Glaciol.*, 49 (164), 22-36, 2003.
- Manne, A.S., and R.G. Richels, An alternative approach to establishing trade-offs among greenhouse gases, *Nature*, 410, 675-677, doi: 10.1038/35070541, 2001.
- Martinerie, P., E. Nourtier-Mazauric, J.-M. Barnola, W.T. Sturges, D.R. Worton, E. Atlas, L.K. Gohar, K.P. Shine, and G.P. Brasseur, Long-lived halocarbon

- trends and budgets from atmospheric chemistry modelling constrained with measurements in polar firm, *Atmos. Chem. Phys.*, 9 (12), 3911-3934, doi: 10.5194/acp-9-3911-2009, 2009.
- Maurice, L.Q., and D.S. Lee (eds.), *Assessing Current Scientific Knowledge, Uncertainties and Gaps in Quantifying Climate Change, Noise and Air Quality Aviation Impacts*, L.Q. Maurice, D.S. Lee, D.J. Wuebbles, I. Isaksen, L. Finegold, M. Vallet, M. Pilling, and J. Spengler, Final Report of the International Civil Aviation Organization (ICAO) Committee on Aviation and Environmental Protection (CAEP) Workshop, U.S. Federal Aviation Administration and Manchester Metropolitan University, Washington D.C. and Manchester, available: <http://web.mit.edu/aeroastro/partner/reports/caepimpac-treport.pdf>, 2009.
- Meilinger, S.K., B. Kärcher, and Th. Peter, Microphysics and heterogeneous chemistry in aircraft plumes – high sensitivity on local meteorology and atmospheric composition, *Atmos. Chem. Phys.*, 5 (2), 533-545, doi: 10.5194/acp-5-533-2005, 2005.
- Molina, M.J., and F.S. Rowland, Stratospheric sink for chlorofluoromethanes: Chlorine atom-catalysed destruction of ozone, *Nature*, 249, 5460, 810-812, doi: 10.1038/249810a0, 1974.
- Montzka, S.A., J.H. Butler, B.D. Hall, D.J. Mondeel, and J.W. Elkins, A decline in tropospheric organic bromine, *Geophys. Res. Lett.*, 30 (15), doi: 10.1029/2003GL017745, 2003.
- Montzka, S.A., B.D. Hall, and J.W. Elkins, Accelerated increases observed for hydrochlorofluorocarbons since 2004 in the global atmosphere, *Geophys. Res. Lett.*, 36, L03804, doi: 10.1029/2008GL036475, 2009.
- Montzka, S.A., L. Kuijpers, M.O. Battle, M. Aydin, K.R. Verhulst, E.S. Saltzman, and D.W. Fahey, Recent increase in global HFC-23 emissions, *Geophys. Res. Lett.*, 37, L02808, doi: 10.1029/2009GL041195, 2010.
- Morgenstern, O., P. Braesicke, M.M. Hurwitz, F.M. O'Connor, A.C. Bushell, C.E. Johnson, and J.A. Pyle, The world avoided by the Montreal Protocol, *Geophys. Res. Lett.*, 35, L16811, doi: 10.1029/2008GL034590, 2008.
- Morgenstern, O., P. Braesicke, F.M. O'Connor, A.C. Bushell, C.E. Johnson, S.M. Osprey, and J.A. Pyle, Evaluation of the new UKCA climate-composition model – part 1: The stratosphere, *Geosci. Model Dev.*, 2 (1), 43-57, doi: 10.5194/gmd-2-43-2009, 2009.
- Newman, P.A., E.R. Nash, S.R. Kawa, S.A. Montzka, and S.M. Schauffler, When will the Antarctic ozone hole recover?, *Geophys. Res. Lett.*, 33, L12814, doi: 10.1029/2005GL025232, 2006.
- Newman, P.A., J.S. Daniel, D.W. Waugh, and E.R. Nash, A new formulation of equivalent effective stratospheric chlorine (EESC), *Atmos. Chem. Phys.*, 7 (17), 4537-4552, doi: 10.5194/acp-7-4537-2007, 2007.
- Newman, P.A., L.D. Oman, A.R. Douglass, E.L. Fleming, S.M. Frith, M.M. Hurwitz, S.R. Kawa, C.H. Jackman, N.A. Krotkov, E.R. Nash, J.E. Nielsen, S. Pawson, R.S. Stolarski, and G.J.M. Velders, What would have happened to the ozone layer if chlorofluorocarbons (CFCs) had not been regulated?, *Atmos. Chem. Phys.*, 9 (6), 2113-2128, doi: 10.5194/acp-9-2113-2009, 2009.
- Nielsen, O.J., M.S. Javadi, M.P. Sulbaek Andersen, M.D. Hurley, T.J. Wallington, and R. Singh, Atmospheric chemistry of  $\text{CF}_3\text{CF}=\text{CH}_2$ : Kinetics and mechanisms of gas-phase reactions with Cl atoms, OH radicals, and  $\text{O}_3$ , *Chem. Phys. Lett.*, 439, 18-22, doi: 10.1016/j.cplett.2007.03.053, 2007.
- Ottinger Schaefer, D., D. Godwin, and J. Harnisch, Estimating future emissions and potential reductions of HFCs, PFCs, and  $\text{SF}_6$ , *Energy J. Special Issue 3*, 27, 63-68, in *Multi-Greenhouse Gas Mitigation and Climate Policy*, edited by F.C. de la Chesnaye and J.P. Weyant, International Association for Energy Economics, 2006.
- Papadimitriou, V.C., R.W. Portmann, D.W. Fahey, J. Mühle, R.F. Weiss, and J.B. Burkholder, Experimental and theoretical study of the atmospheric chemistry and global warming potential of  $\text{SO}_2\text{F}_2$ , *J. Phys. Chem. A*, 112, 12657-12666, doi: 10.1021/jp806368u, 2008a.
- Papadimitriou, V.C., R.K. Talukdar, R.W. Portmann, A.R. Ravishankara, and J.B. Burkholder,  $\text{CF}_3\text{CF}=\text{CH}_2$  and (Z)- $\text{CF}_3\text{CF}=\text{CHF}$ : Temperature dependent OH rate coefficients and global warming potentials, *Phys. Chem. Chem. Phys.*, 10, 808-820, doi: 10.1039/b714382f, 2008b.
- Parson, E.A., *Protecting the Ozone Layer: Science and Strategy*, 396 pp., Oxford University Press, New York, NY, U.S.A., 2003.
- Pawson, S., R.S. Stolarski, A.R. Douglass, P.A. Newman, J.E. Nielsen, S.M. Frith, and M.L. Gupta, Goddard Earth Observing System chemistry-climate model simulations of stratospheric ozone-temperature coupling between 1950 and 2005, *J. Geophys. Res.*, 113, D12103, doi: 10.1029/2007JD009511, 2008.
- Pinnock, S., M.D. Hurley, K.P. Shine, T.J. Wallington, and T.J. Smyth, Radiative forcing of climate by hydrochlorofluorocarbons and hydrofluorocarbons, *J. Geophys. Res.*, 100 (D1), 23227-23238, doi: 10.1029/95JD02323, 1995.
- Pitari, G., D. Iachetti, E. Mancini, V. Montanaro, N. De

- Luca, C. Marizy, O. Dessens, H. Rogers, J. Pyle, V. Grewe, A. Stenke, and O.A. Søvde, Radiative forcing from particle emissions by future supersonic aircraft, *Atmos. Chem. Phys.*, 8 (14), 4069-4084, doi: 10.5194/acp-8-4069-2008, 2008.
- Portmann, R.W., and S. Solomon, Indirect radiative forcing of the ozone layer during the 21<sup>st</sup> century, *Geophys. Res. Lett.*, 34, L02813, doi: 10.1029/2006GL028252, 2007.
- Portmann, R.W., S. Solomon, R.R. Garcia, L.W. Thomason, L.R. Poole, and M.P. McCormick, Role of aerosol variations in anthropogenic ozone depletion in the polar regions, *J. Geophys. Res.*, 101 (D17), 22991-23006, 1996.
- Prather, M.J., Time scales in atmospheric chemistry: Theory, GWPs for CH<sub>4</sub> and CO, and runaway growth, *Geophys. Res. Lett.*, 23 (19), 2597-2600, 1996.
- Prather, M.J., Lifetimes of atmospheric species: Integrating environmental impacts, *Geophys. Res. Lett.*, 29 (22), 2063, doi: 10.1029/2002GL016299, 2002.
- Prather, M.J., and J. Hsu, NF<sub>3</sub>, the greenhouse gas missing from Kyoto, *Geophys. Res. Lett.*, 35, L12810, doi: 10.1029/2008GL034542, 2008.
- Prather, M., P. Midgley, F. Sherwood Rowland, and R. Stolarski, The ozone layer: The road not taken, *Nature*, 381, 551-554, doi: 10.1038/381551a0, 1996.
- Prinn, R.G. and R. Zander (Lead Authors), D.M. Cunnold, J.W. Elkins, A. Engel, P.J. Fraser, M.R. Gunson, M.K.W. Ko, E. Mahieu, P.M. Midgley, J.M. Russell III, C.M. Volk, and R.F. Weiss, Long-lived ozone-related compounds, Chapter 1 in *Scientific Assessment of Ozone Depletion: 1998*, Global Ozone Research and Monitoring Project—Report No. 44, World Meteorological Organization, Geneva, Switzerland, 1999.
- Rajakumar, B., R.W. Portmann, J.B. Burkholder, and A.R. Ravishankara, Rate coefficients for the reactions of OH with CF<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> (HFC-263fb), CF<sub>3</sub>CHFCH<sub>2</sub>F (HFC-245eb), and CHF<sub>2</sub>CHFCHF<sub>2</sub> (HFC-245ea) between 238 and 375 K, *J. Phys. Chem. A*, 110, 6724-6731, doi: 10.1021/jp056248y, 2006.
- Rao, S., and K. Riahi, The role of non-CO<sub>2</sub> greenhouse gases in climate change mitigation: Long-term scenarios for the 21<sup>st</sup> century, *Energy J. Special Issue 3*, 27, 177-200, in *Multi-Greenhouse Gas Mitigation and Climate Policy*, edited by F.C. de la Chesnaye, and J.P. Weyant, International Association for Energy Economics, 2006.
- Rasch, P.J., P.J. Crutzen, and D.B. Coleman, Exploring the geoengineering of climate using stratospheric sulfate aerosols: The role of particle size, *Geophys. Res. Lett.*, 35, L02809, doi: 10.1029/2007GL032179, 2008a.
- Rasch, P.J., S. Tilmes, R.P. Turco, A. Robock, L. Oman, C.-C. Chen, G.L. Stenchikov, and R.R. Garcia, An overview of geoengineering of climate using stratospheric sulphate aerosols, *Phil. Trans. Royal Soc. A*, 366 (1882), 4007-4037, doi: 10.1098/rsta.2008.0131, 2008b.
- Ravishankara, A.R., A.A. Turnipseed, N.R. Jensen, S. Barone, M. Mills, C.J. Howard, and S. Solomon, Do hydrofluorocarbons destroy stratospheric ozone?, *Science*, 263, 71-75, 1994.
- Ravishankara, A.R., J.S. Daniel, and R.W. Portmann, Nitrous oxide (N<sub>2</sub>O): The dominant ozone-depleting substance emitted in the 21<sup>st</sup> century, *Science*, 326 (5949), 123-125, doi: 10.1126/science.1176985, 2009.
- Riahi, K., and N. Nakicenovic (eds.), Greenhouse Gases—Integrated Assessment, *Technol. Forecast. Soc. Change*, Special Issue, 74 (7), September 2007, 234 pp., ISSN 0040-1625, doi: 10.1016/S0040-1625(07)00140-0, 2007.
- Robock, A., 20 reasons why geoengineering may be a bad idea, *Bull. Atom. Sci.*, 64 (2), 14-18, doi: 10.2968/064002006, 2008.
- Robock, A., L. Oman, and G. Stenchikov, Regional climate responses to geoengineering with tropical and Arctic SO<sub>2</sub> injections, *J. Geophys. Res.*, 113, D16101, doi: 10.1029/2008JD010050, 2008.
- Rosenfield, J.E., A.R. Douglass, and D.B. Considine, The impact of increasing carbon dioxide on ozone recovery, *J. Geophys. Res.*, 107 (D6), 4049, doi: 10.1029/2001JD000824, 2002.
- Ross, M., D. Toohey, M. Peinemann, and P. Ross, Limits on the space launch market related to stratospheric ozone depletion, *Astropolitics*, 7, 50-82, doi: 10.1080/14777620902768867, 2009.
- Royal Society, *Geoengineering the Climate: Science, Governance and Uncertainty*, Report 10/09, London GB, The Royal Society, available: <http://royal-society.org/geoengineering-the-climate/>, 2009.
- Schauffler, S.M., E.L. Atlas, S.G. Donnelly, A. Andrews, S.A. Montzka, J.W. Elkins, D.F. Hurst, P.A. Romashkin, G.S. Dutton, and V. Stroud, Chlorine budget and partitioning during the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE), *J. Geophys. Res.*, 108 (D5), 4173, doi: 10.1029/2001JD002040, 2003.
- Scott, B.F., R.W. Macdonald, K. Kannan, A. Fisk, A. Witter, N. Yamashita, L. Durham, C. Spencer, and D.C.G. Muir, Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans, *Environ. Sci. Technol.*, 39 (17), 6555-6560, doi: 10.1021/es047975u, 2005.
- Scott, B.F., C.A. Moody, C. Spencer, J.M. Small, D.C.G. Muir, and S.A. Mabury, Analysis for

- perfluorocarboxylic acids/anions in surface waters and precipitation using GC-MS and analysis of PFOA from large-volume samples, *Environ. Sci. Technol.*, *40* (20), 6405-6410, doi: 10.1021/es061131o, 2006.
- Seedhouse, E., *Tourists in Space: A Practical Guide*, Springer Praxis Books, Chichester, U.K., doi: 10.1007/978-0-387-74644-9, 2008.
- Shine, K.P., On the cause of the relative greenhouse strength of gases such as the halocarbons, *J. Atmos. Sci.*, *48*, 1513-1518, doi: 10.1175/1520-0469(1991)048<1513:OTCOTR>2.0.CO;2, 1991.
- Shine K.P., The global warming potential—the need for an interdisciplinary retrieval, *Clim. Change*, *96*, 467-472, doi: 10.1007/s10584-009-9647-6, 2009.
- Smith, S.J., and T.M.L. Wigley, Multi-gas forcing stabilization with Minicam, *Energy J. Special Issue 3*, *27*, 373-392, in *Multi-Greenhouse Gas Mitigation and Climate Policy*, edited by F.C. de la Chesnaye and J.P. Weyant, International Association for Energy Economics, 2006.
- Soden, B.J., R.T. Wetherald, G.L. Stenchikov, and A. Robock, Global cooling after the eruption of Mount Pinatubo: A test of climate feedback by water vapor, *Science*, *296* (5568), 727-730, doi: 10.1126/science.296.5568.727, 2002.
- Solomon, S., and D.L. Albritton, Time-dependent ozone depletion potentials for short- and long-term forecasts, *Nature*, *357*, 33-37, doi: 10.1038/357033a0, 1992.
- Solomon, S., M. Mills, L.E. Heidt, W.H. Pollock, and A.F. Tuck, On the evaluation of ozone depletion potentials, *J. Geophys. Res.*, *97* (D1), 825-842, 1992.
- Solomon, S., R.W. Portmann, R.R. Garcia, L.W. Thomason, L.R. Poole, and M.P. McCormick, The role of aerosol variations in anthropogenic ozone depletion at northern midlatitudes, *J. Geophys. Res.*, *101* (D3), 6713-6727, 1996.
- Solomon, K.R., X. Tang, S.R. Wilson, P. Zanis, and A.F. Bais, Changes in tropospheric composition and air quality due to stratospheric ozone depletion, *Photochem. Photobiol. Sci.*, *2*, 62-67, doi: 10.1039/b211086e, 2003.
- Søvde, O.A., M. Gauss, I.S.A. Isaksen, G. Pitari, and C. Marizy, Aircraft pollution — a futuristic view, *Atmos. Chem. Phys.*, *7* (13), 3621-3632, doi: 10.5194/acp-7-3621-2007, 2007.
- SPARC CCMVal (Stratospheric Processes And their Role in Climate), *SPARC CCMVal Report on the Evaluation of Chemistry-Climate Models*, edited by V. Eyring, T.G. Shepherd, and D.W. Waugh, SPARC Report No. 5, WCRP-132, WMO/TD-No. 1526, available: [http://www.atmosph.physics.utoronto.ca/SPARC/ccmval\\_final/index.php](http://www.atmosph.physics.utoronto.ca/SPARC/ccmval_final/index.php), 2010.
- Stohl, A., P. Seibert, J. Arduini, S. Eckhardt, P. Fraser, B.R. Grealley, C. Lunder, M. Maione, J. Mühle, S. O'Doherty, R.G. Prinn, S. Reimann, T. Saito, N. Schmidbauer, P.G. Simmonds, M.K. Vollmer, R.F. Weiss, and Y. Yokouchi, An analytical inversion method for determining regional and global emissions of greenhouse gases: Sensitivity studies and application to halocarbons, *Atmos. Chem. Phys.*, *9* (5), 1597-1620, doi: 10.5194/acp-9-1597-2009, 2009.
- Sulbaek Andersen, M.P., D.R. Blake, F.S. Rowland, M.D. Hurley, and T.J. Wallington, Atmospheric chemistry of sulfuranyl fluoride: Reaction with OH radicals, Cl atoms and O<sub>3</sub>, atmospheric lifetime, IR spectrum, and global warming potential, *Environ. Sci. Technol.*, *43* (4), 1067-1070, doi: 10.1021/es802439f, 2009.
- Tabazadeh, A., K. Drdla, M.R. Schoeberl, P. Hamill, and O.B. Toon, Arctic “ozone hole” in a cold volcanic stratosphere, *Proc. Natl. Acad. Sci.*, *99* (5), 2609-2612, doi: 10.1073/pnas.052518199, 2002.
- Tanaka, K., B.C. O'Neill, D. Rokityanskiy, M. Obersteiner, and R.S.J. Tol, Evaluating global warming potentials with historical temperature, *Clim. Change*, *96*, 443-466, doi: 10.1007/s10584-009-9566-6, 2009.
- Tang, X., S. Madronich, T. Wallington, and D. Calamari, Changes in tropospheric composition and air quality, *J. Photochem. Photobiol. B: Biol.*, *46* (1-3), 83-95, doi: 10.1016/S1011-1344(98)00187-0, 1998.
- Taniguchi, N., T.J. Wallington, M.D. Hurley, A.G. Guschin, L.T. Molina, and M.J. Molina, Atmospheric chemistry of C<sub>2</sub>F<sub>5</sub>C(O)CF(CF<sub>3</sub>)<sub>2</sub>: Photolysis and reaction with Cl atoms, OH radicals, and ozone, *J. Phys. Chem. A*, *107* (15), 2674-2679, doi: 10.1021/jp0220332, 2003.
- TEAP (Technology and Economic Assessment Panel), *Task Force Decision XX/8 Report, Assessment of Alternatives to HCFCs and HFCs and Update of the TEAP 2005 Supplement Report Data*, coordinated by L. Kuijpers, and D. Verdonik, United Nations Environment Programme, Nairobi, Kenya, available: [http://ozone.unep.org/teap/Reports/TEAP\\_Reports/teap-may-2009-decisionXX-8-task-force-report.pdf](http://ozone.unep.org/teap/Reports/TEAP_Reports/teap-may-2009-decisionXX-8-task-force-report.pdf), 2009.
- Teller, E., L. Wood, and R. Hyde, Global warming and Ice Ages: I. Prospects for physics-based modulation of global change, *UCRL-JC-128715*, Lawrence Livermore National Laboratory, Livermore, California, U.S., 20 pp., 1997.
- Thompson, D.W.J., and S. Solomon, Interpretation of recent Southern Hemisphere climate change, *Science*, *296* (5569), 895-899, doi: 10.1126/

- science.1069270, 2002.
- Tilmes, S., R. Müller, R.J. Salawitch, U. Schmidt, C.R. Webster, H. Oelhaf, C.C. Camy-Peyret, and J.M. Russell III, Chemical ozone loss in the Arctic winter 1991–1992, *Atmos. Chem. Phys.*, *8* (7), 1897–1910, doi: 10.5194/acp-8-1897-2008, 2008a.
- Tilmes, S., R. Müller, and R. Salawitch, The sensitivity of polar ozone depletion to proposed geoengineering schemes, *Science*, *320* (5880), 1201–1204, doi: 10.1126/science.1153966, 2008b.
- Tilmes, S., R.R. Garcia, D.E. Kinnison, A. Gettelman, and P.J. Rasch, Impact of geo-engineered aerosols on troposphere and stratosphere, *J. Geophys. Res.*, *114*, D12305, doi: 10.1029/2008JD011420, 2009.
- Tromp, T.K., M.K.W. Ko, J.M. Rodriguez, and N.D. Sze, Potential accumulation of a CFC-replacement degradation product in seasonal wetlands, *Nature*, *376*, 327–330, doi: 10.1038/376327a0, 1995.
- UBA (Umweltbundesamt), *Projections of Global Emissions of Fluorinated Greenhouse Gases in 2050*, B. Gschrey and W. Schwarz, German Federal Environment Agency (Umweltbundesamt), Report-no. UBA-FB 001318, available: <http://www.umwelt-daten.de/publikationen/fpdf-l/3866.pdf>, 2009.
- UNEP (United Nations Environment Programme), data on production and consumption of ozone depleting substances under the Montreal Protocol, downloaded from <http://www.unep.org/ozone>, Nairobi, Kenya, 2009.
- van Vuuren, D.P., B. Eickhout, P.L. Lucas, and M.D.G. Den Elzen, Long-term multi-gas scenarios to stabilise radiative forcing, *Energy J. Special Issue 3*, *27*, 201–233, in *Multi-Greenhouse Gas Mitigation and Climate Policy*, edited by F.C. de la Chesnaye and J.P. Weyant, International Association for Energy Economics, 2006.
- van Vuuren, D.P., M.G.J. den Elzen, P.L. Lucas, B. Eickhout, B.J. Strengers, B. van Ruijven, S. Wonink, and R. van Houdt, Stabilizing greenhouse gas concentrations at low levels: An assessment of reduction strategies and costs, *Clim. Change*, *81* (2), 119–159, doi: 10.1007/s10584-006-9172-9, 2007.
- Velders, G.J.M., S.O. Andersen, J.S. Daniel, D.W. Fahey, and M. McFarland, The importance of the Montreal Protocol in protecting climate, *Proc. Natl. Acad. Sci.*, *104* (12), 4814–4819, doi: 10.1073/pnas.0610328104, 2007.
- Velders, G.J.M., D.W. Fahey, J.S. Daniel, M. McFarland, and S.O. Andersen, The large contribution of projected HFC emissions to future climate forcing, *Proc. Natl. Acad. Sci.*, *106* (27), 10949–10954, doi: 10.1073/pnas.0902817106, 2009.
- Volk, C.M., J.W. Elkins, D.W. Fahey, G.S. Dutton, J.M. Gilligan, M. Loewenstein, J.R. Podolske, K.R. Chan, and M.R. Gunson, Evaluation of source gas lifetimes from stratospheric observations, *J. Geophys. Res.*, *102* (D21), 25543–25564, 1997.
- Von Sydow, L.M., A.B. Grimvall, H.B. Borén, K. Laniewski, and A.T. Nielsen, Natural background levels of trifluoroacetate in rain and snow, *Environ. Sci. Technol.*, *34*, 3115–3118, doi: 10.1021/es9913683, 2000.
- Wallington, T.J., W.F. Schneider, D.R. Worsnop, O.J. Nielsen, J. Sehested, W. DeBruyn, and J.A. Shorter, Environmental impact of CFC replacements — HFCs and HCFCs, *Environ. Sci. Technol.*, *28* (7), 320A–326A, 1994.
- Wallington, T.J., W.F. Schneider, J. Sehested, and O.J. Nielsen, Hydrofluorocarbons and stratospheric ozone, *Faraday Discuss.*, *100*, 55–64, 1995.
- Wallington, T.J., M.D. Hurley, and O.J. Nielsen, The radiative efficiency of HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H (H-Galden 1040x) revisited, *Atmos. Environ.*, *43*, 4247–4249, doi: 10.1016/j.atmosenv.2009.05.046, 2009.
- Wallington, T.J., M.P. Sulbaek Andersen, and O.J. Nielsen, Estimated photochemical ozone creation potentials (POC<sub>2</sub>s) of CF<sub>3</sub>CF=CH<sub>2</sub> (HFO-1234yf) and related hydrofluoroolefins (HFOs), *Atmos. Environ.*, *44* (11), 1478–1481, doi: 10.1016/j.atmosenv.2010.01.040, 2010.
- Wang, M., Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model, Version 1.8d.1, downloaded August 27, 2010, available: [http://www.transportation.anl.gov/modeling\\_simulation/GREET/](http://www.transportation.anl.gov/modeling_simulation/GREET/), 2010.
- Wagh, D.W., L. Oman, S.R. Kawa, R.S. Stolarski, S. Pawson, A.R. Douglass, P.A. Newman, and J.E. Nielsen, Impacts of climate change on stratospheric ozone recovery, *Geophys. Res. Lett.*, *36*, L03805, doi: 10.1029/2008GL036223, 2009.
- Wigley, T.M.L., A combined mitigation/geoengineering approach to climate stabilization, *Science*, *314* (5798), 452–454, doi: 10.1126/science.1131728, 2006.
- Wise, M., K. Calvin, A. Thomson, L. Clarke, B. Bond-Lamberty, R. Sands, S.J. Smith, and A. Janetos, J. Edmonds, Implications of limiting CO<sub>2</sub> concentrations for land use and energy, *Science*, *324* (5931), 1183–1186, doi: 10.1126/science.1168475, 2009.
- WMO (World Meteorological Organization), *Atmospheric Ozone 1985: Assessment of Our Understanding of the Processes Controlling its Present Distribution and Change* (3 volumes), Global Ozone Research and Monitoring Project—Report No. 16, Geneva, Switzerland, 1986.
- WMO (World Meteorological Organization), *Scientific Assessment of Stratospheric Ozone: 1989, Volume*

- I, Global Ozone Research and Monitoring Project—Report No. 20, Geneva, Switzerland, 1989.
- WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 1991*, Global Ozone Research and Monitoring Project—Report No. 25, Geneva, Switzerland, 1991.
- WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 1994*, Global Ozone Research and Monitoring Project—Report No. 37, Geneva, Switzerland, 1995.
- WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 1998*, Global Ozone Research and Monitoring Project—Report No. 44, Geneva, Switzerland, 1999.
- WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 2002*, Global Ozone Research and Monitoring Project—Report No. 47, Geneva, Switzerland, 2003.
- WMO (World Meteorological Organization), *Scientific Assessment of Ozone Depletion: 2006*, Global Ozone Research and Monitoring Project—Report 50, Geneva, Switzerland, 2007.
- Wuebbles, D.J., *The Relative Efficiency of a Number of Halocarbons for Destroying Stratospheric Ozone*, 11 pp., Lawrence Livermore National Laboratory, Livermore, CA, 1981.
- Wuebbles, D.J., Chlorocarbon emission scenarios: Potential impact on stratospheric ozone, *Geophys. Res. Lett.*, *88* (C2), 1433-1443, 1983.
- Wuebbles, D.J., Nitrous oxide: No laughing matter, *Science*, *326* (5949), 56-57, doi: 10.1126/science.1179571, 2009.
- Wuebbles, D.J., and K.O. Patten, Three-dimensional modeling of HCFC-123 in the atmosphere: Assessing its potential environmental impacts and rationale for continued use, *Environ. Sci. Technol.*, *43* (9), 3208-3213, doi: 10.1021/es802308m, 2009.
- Wuebbles, D.J., A. Douglass, B. Kärcher, W.-C. Wang, S. Baughcum, R.P. d'Entremont, A. Dessler, P. Ginoux, R. Herman, A. Heymsfield, I. Isaksen, D. Jacob, S. Lele, J. Logan, J. McConnell, R. Mialy, P. Minnis, D. Mitchell, D. Murphy, L. Pan, J. Penner, M. Prather, J. Rodriguez, K. Rosenlof, K. Sassen, R. Sausen, K. Shine, A. Tabazadeh, I. Waitz, P. Yang, and F. Yu, *Workshop on the Impacts of Aviation on Climate Change: A Report of Findings and Recommendations*, Partnership for Air Transportation Noise and Emissions Reduction, Report No. PARTNER-COE-2006-004, available: <http://web.mit.edu/aeroastro/partner/reports/climatewrksp-rpt-0806.pdf>, 2006.
- Wuebbles, D.J., D. Youn, K. Patten, D. Wang, and M. Martínez-Avilés, Metrics for ozone and climate: Three-dimensional modeling studies of ozone depletion potentials and indirect global warming potentials, in *Twenty Years of Ozone Decline. Proceedings of the Symposium for the 20<sup>th</sup> Anniversary of the Montreal Protocol*, edited by C. Zerefos, G. Contopoulos, and G. Skalkeas, 297-326, Springer Publishing, Dordrecht, The Netherlands, doi: 10.1007/978-90-481-2469-5, 2009.
- Youn, D., K.O. Patten, J.-T. Lin, and D.J. Wuebbles, Explicit calculation of indirect global warming potentials for halons using atmospheric models, *Atmos. Chem. Phys.*, *9* (22), 8719-8733, doi: 10.5194/acp-9-8719-2009, 2009.
- Youn, D., K.O. Patten, D.J. Wuebbles, H. Lee, and C.-W. So, Potential impact of iodinated replacement compounds CF<sub>3</sub>I and CH<sub>3</sub>I on atmospheric ozone: A three-dimensional modeling study, *Atmos. Chem. Phys.*, *10* (20), 10129-10144, doi: 10.5194/acp-10-10129-2010, 2010.
- Young, C.J., M.D. Hurley, T.J. Wallington, and S.A. Mabury, Atmospheric lifetime and global warming potential of a perfluoropolyether, *Environ. Sci. Technol.*, *40*, 2242-2246, doi: 10.1021/es052077z, 2006.
- Young, C.J., M.D. Hurley, T.J. Wallington, and S.A. Mabury, Molecular structure and radiative efficiency of fluorinated ethers: A structure-activity relationship, *J. Geophys. Res.*, *113*, D24301 doi: 10.1029/2008JD010178, 2008.
- Young, C.J., M.D. Hurley, T.J. Wallington, and S.A. Mabury, Atmospheric chemistry of CF<sub>3</sub>CF<sub>2</sub>H and CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>H: Kinetics and products of gas-phase reactions with Cl atoms and OH radicals, infrared spectra, and formation of perfluorocarboxylic acids, *Chem. Phys. Lett.*, *473*, 251-256, doi: 10.1016/j.cplett.2009.04.001, 2009.
- Yvon-Lewis, S.A., E.S. Saltzman, and S.A. Montzka, Recent trends in atmospheric methyl bromide: Analysis of post-Montreal Protocol variability, *Atmos. Chem. Phys.*, *9* (16), 5963-5974, doi: 10.5194/acp-9-5963-2009, 2009.

## APPENDIX 5A

## TABLES

Table 5A-1. Direct Global Warming Potentials for selected gases.

| Industrial Designation or Common Name | Chemical Formula                                  | Radiative Efficiency <sup>a</sup><br>( $\text{W m}^{-2} \text{ppb}^{-1}$ ) | Lifetime <sup>b</sup><br>(years) | Global Warming Potential for Given Time Horizon |           |           |
|---------------------------------------|---|--|----------------------------------|---|-----------|-----------|
|                                       |   |  |                                  | 20 years  | 100 years | 500 years |
| Carbon dioxide                        | CO <sub>2</sub>                                   | $1.38 \times 10^{-5}$ <sup>c</sup>   |                                  | 1   | 1         | 1         |
| Nitrous oxide                         | N <sub>2</sub> O                                  | $3.03 \times 10^{-3}$  | 114                              | 289   | 298       | 153       |
| <b>Chlorofluorocarbons</b>            |   |  |                                  |   |           |           |
| CFC-11                                | CCl <sub>3</sub> F                                | 0.25   | 45                               | 6,730   | 4,750     | 1,620     |
| CFC-12                                | CCl <sub>2</sub> F <sub>2</sub>                   | 0.32   | 100                              | 11,000  | 10,900    | 5,200     |
| CFC-13                                | CCIF <sub>3</sub>                                 | 0.25   | 640                              | 10,800  | 14,400    | 16,400    |
| CFC-113                               | CCl <sub>2</sub> FCCIF <sub>2</sub>               | 0.30   | 85                               | 6,540   | 6,130     | 2,690     |
| CFC-114                               | CCIF <sub>2</sub> CCIF <sub>2</sub>               | 0.31   | 190                              | 7,890   | 9,180     | 6,330     |
| CFC-115                               | CCIF <sub>2</sub> CF <sub>3</sub>                 | 0.18   | 1,020                            | 5,290   | 7,230     | 9,120     |
| <b>Hydrochlorofluorocarbons</b>       |   |  |                                  |   |           |           |
| HCFC-21                               | CHCl <sub>2</sub> F                               | 0.14   | 1.7                              | 530   | 151       | 46        |
| HCFC-22                               | CHClF <sub>2</sub>                                | 0.20   | 11.9                             | 5,130   | 1,790     | 545       |
| HCFC-123                              | CHCl <sub>2</sub> CF <sub>3</sub>                 | 0.14   | 1.3                              | 273   | 77        | 24        |
| HCFC-124                              | CHClFCF <sub>3</sub>                              | 0.22   | 5.9                              | 2,110   | 619       | 188       |
| HCFC-141b                             | CH <sub>3</sub> CCl <sub>2</sub> F                | 0.14   | 9.2                              | 2,240   | 717       | 218       |
| HCFC-142b                             | CH <sub>3</sub> CClF <sub>2</sub>                 | 0.20   | 17.2                             | 5,390   | 2,220     | 678       |
| HCFC-225ca                            | CHCl <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> | 0.20   | 1.9                              | 429   | 122       | 37        |
| HCFC-225cb                            | CHClFCF <sub>2</sub> CClF <sub>2</sub>            | 0.32   | 5.9                              | 2,060   | 606       | 184       |
| <b>Hydrofluorocarbons</b>             |   |  |                                  |   |           |           |
| HFC-23                                | CHF <sub>3</sub>                                  | 0.19   | 222                              | 11,900  | 14,200    | 10,700    |
| HFC-32                                | CH <sub>2</sub> F <sub>2</sub>                    | 0.11   | 5.2                              | 2,470   | 716       | 218       |
| HFC-41                                | CH <sub>3</sub> F                                 | 0.02   | 2.8                              | 377   | 107       | 33        |
| HFC-125                               | CHF <sub>2</sub> CF <sub>3</sub>                  | 0.23   | 28.2                             | 6,290   | 3,420     | 1,070     |
| HFC-134                               | CHF <sub>2</sub> CHF <sub>2</sub>                 | 0.18   | 9.7                              | 3,420   | 1,110     | 339       |
| HFC-134a                              | CH <sub>2</sub> FCF <sub>3</sub>                  | 0.16   | 13.4                             | 3,730   | 1,370     | 416       |
| HFC-143                               | CH <sub>2</sub> FCHF <sub>2</sub>                 | 0.13   | 3.5                              | 1,240   | 352       | 107       |
| HFC-143a                              | CH <sub>3</sub> CF <sub>3</sub>                   | 0.13   | 47.1                             | 5,780   | 4,180     | 1,440     |
| HFC-152a                              | CH <sub>3</sub> CHF <sub>2</sub>                  | 0.09   | 1.5                              | 468   | 133       | 40        |
| HFC-227ea                             | CF <sub>3</sub> CHFCF <sub>3</sub>                | 0.26   | 38.9                             | 5,480   | 3,580     | 1,180     |
| HFC-236cb                             | CH <sub>2</sub> FCF <sub>2</sub> CF <sub>3</sub>  | 0.23   | 13.1                             | 3,560   | 1,290     | 392       |

Table 5A-1, continued.

| Industrial Designation or Common Name | Chemical Formula   | Radiative Efficiency <sup>a</sup><br>(W m <sup>-2</sup> ppb <sup>-1</sup> ) | Lifetime <sup>b</sup><br>(years) | Global Warming Potential for Given Time Horizon |           |           |
|---------------------------------------|--|---|----------------------------------|---|-----------|-----------|
|                                       |  |   |                                  | 20 years  | 100 years | 500 years |
| HFC-236ea                             | CHF <sub>2</sub> CHF <sub>2</sub> CF <sub>3</sub>                | 0.30  | 11                               | 4,170   | 1,410     | 430       |
| HFC-236fa                             | CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>                  | 0.28  | 242                              | 8,100   | 9,820     | 7,710     |
| HFC-245ca                             | CH <sub>2</sub> FCF <sub>2</sub> CHF <sub>2</sub>                | 0.23  | 6.5                              | 2,440   | 726       | 221       |
| HFC-245ea                             | CHF <sub>2</sub> CHFCHF <sub>2</sub>                             | 0.18 <sup>d</sup>   | 3.2                              | 983   | 280       | 85        |
| HFC-245eb                             | CH <sub>2</sub> FCHF <sub>2</sub> CF <sub>3</sub>                | 0.23 <sup>d</sup>   | 3.1                              | 1,220   | 346       | 105       |
| HFC-245fa                             | CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>                 | 0.28  | 7.7                              | 3,410   | 1,050     | 318       |
| HFC-263fb                             | CH <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>                  | 0.13 <sup>d</sup>   | 1.2                              | 365   | 104       | 31        |
| HFC-329p                              | CHF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> | 0.31 <sup>d</sup>   | 28.4                             | 4,640   | 2,530     | 792       |
| HFC-365mfc                            | CH <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>  | 0.22 <sup>d</sup>   | 8.7                              | 2,670   | 842       | 256       |
| HFC-43-10mee                          | CF <sub>3</sub> CHFCHF <sub>2</sub> CF <sub>3</sub>              | 0.40  | 16.1                             | 4,170   | 1,660     | 506       |
| <b>Chlorocarbons</b>                  |  |   |                                  |   |           |           |
| Methyl chloroform                     | CH <sub>3</sub> CCl <sub>3</sub>                                 | 0.06  | 5.0                              | 506   | 146       | 45        |
| Carbon tetrachloride                  | CCl <sub>4</sub>   | 0.13  | 26                               | 2,700   | 1,400     | 435       |
| Methyl chloride                       | CH <sub>3</sub> Cl   | 0.01  | 1.0                              | 45  | 13        | 4         |
| <b>Bromocarbons and Halons</b>        |  |   |                                  |   |           |           |
| Methyl bromide                        | CH <sub>3</sub> Br   | 0.01  | 0.8                              | 19  | 5         | 2         |
| Bromodifluoromethane                  | CHBrF <sub>2</sub>   | 0.14  | 5.2                              | 1,250   | 362       | 110       |
| Halon-1211                            | CBrClF <sub>2</sub>  | 0.30  | 16                               | 4,750   | 1,890     | 575       |
| Halon-1301                            | CBrF <sub>3</sub>  | 0.32  | 65                               | 8,480   | 7,140     | 2,760     |
| Halon-2402                            | CBrF <sub>2</sub> CBrF <sub>2</sub>                              | 0.33  | 20                               | 3,680   | 1,640     | 503       |
| <b>Fully Fluorinated Species</b>      |  |   |                                  |   |           |           |
| Nitrogen trifluoride                  | NF <sub>3</sub>  | 0.21  | 500                              | 13,300  | 17,500    | 18,500    |
| Sulfur hexafluoride                   | SF <sub>6</sub>  | 0.52  | 3,200                            | 16,300  | 22,800    | 32,600    |
| Trifluoromethylsulfur-pentafluoride   | SF <sub>5</sub> CF <sub>3</sub>                                  | 0.57  | 800 <sup>e</sup>                 | 13,200  | 17,800    | 21,400    |
| Perfluoromethane                      | CF <sub>4</sub>  | 0.10  | 50,000                           | 5,210   | 7,390     | 11,200    |
| Perfluoroethane                       | C <sub>2</sub> F <sub>6</sub>                                    | 0.26  | 10,000                           | 8,630   | 12,200    | 18,200    |
| Perfluoropropane                      | C <sub>3</sub> F <sub>8</sub>                                    | 0.26  | 2,600                            | 6,310   | 8,830     | 12,500    |
| Perfluorocyclopropane                 | c-C <sub>3</sub> F <sub>6</sub>                                  | 0.42  | ~3,000                           | 12,800  | 17,900    | 25,500    |
| Perfluorobutane                       | C <sub>4</sub> F <sub>10</sub>                                   | 0.33  | 2,600                            | 6,330   | 8,850     | 12,500    |
| Perfluorocyclobutane                  | c-C <sub>4</sub> F <sub>8</sub>                                  | 0.32  | 3,200                            | 7,310   | 10,300    | 14,700    |
| Perfluoropentane                      | C <sub>5</sub> F <sub>12</sub>                                   | 0.41  | 4,100                            | 6,510   | 9,150     | 13,300    |
| Perfluorohexane                       | C <sub>6</sub> F <sub>14</sub>                                   | 0.49  | 3,100                            | 6,620   | 9,290     | 13,300    |
| Perfluorodecalin                      | C <sub>10</sub> F <sub>18</sub>                                  | 0.56  | ~2,000                           | 5,530   | 7,700     | 10,600    |

Table 5A-1, continued.

| Industrial Designation or Common Name  | Chemical Formula   | Radiative Efficiency <sup>a</sup><br>(W m <sup>-2</sup> ppb <sup>-1</sup> ) | Lifetime <sup>b</sup><br>(years) | Global Warming Potential for Given Time Horizon |           |           |
|--|--|---|----------------------------------|---|-----------|-----------|
|  |  |   |                                  | 20 years  | 100 years | 500 years |
| <b>Halogenated Alcohols and Ethers</b> |  |   |                                  |   |           |           |
| HFE-125                                | CHF <sub>2</sub> OCF <sub>3</sub>  | 0.44  | 119                              | 13,700  | 14,200    | 7,510     |
| HFE-134                                | CHF <sub>2</sub> OCHF <sub>2</sub>   | 0.45  | 24.4                             | 11,930  | 5,960     | 1,840     |
| HFE-143a                               | CH <sub>3</sub> OCF <sub>3</sub>   | 0.27  | 4.8                              | 2,920   | 840       | 256       |
| HFE-227ea                              | CF <sub>3</sub> OCHFCF <sub>3</sub>  | 0.40  | 51.6                             | 8,170   | 6,180     | 2,200     |
| HFCE-235da2<br>(isoflurane)            | CHF <sub>2</sub> OCHClCF <sub>3</sub>  | 0.38  | 3.5                              | 1,650   | 470       | 143       |
| HFE-236ea2<br>(desflurane)             | CHF <sub>2</sub> OCHFCF <sub>3</sub>   | 0.44  | 10.8                             | 5,460   | 1,840     | 560       |
| HFE-236fa                              | CF <sub>3</sub> OCH <sub>2</sub> CF <sub>3</sub>                                   | 0.34  | 7.5                              | 3,240   | 988       | 300       |
| HFE-245cb2                             | CH <sub>3</sub> OCF <sub>2</sub> CF <sub>3</sub>                                   | 0.32  | 4.9                              | 2,350   | 680       | 207       |
| HFE-245fa1                             | CF <sub>3</sub> OCH <sub>2</sub> CHF <sub>2</sub>                                  | 0.30  | 6.6                              | 2,880   | 859       | 261       |
| HFE-245fa2                             | CHF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>                                  | 0.31  | 5.5                              | 2,540   | 740       | 225       |
| HFE-254cb2                             | CH <sub>3</sub> OCF <sub>2</sub> CHF <sub>2</sub>                                  | 0.28  | 2.5                              | 1,210   | 345       | 105       |
| HFE-329mcc2                            | CF <sub>3</sub> CF <sub>2</sub> OCF <sub>2</sub> CHF <sub>2</sub>                  | 0.49  | 22.5                             | 6,300   | 3,000     | 925       |
| HFE-338mcf2                            | CF <sub>3</sub> CF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>                   | 0.43  | 7.5                              | 3,150   | 963       | 293       |
| HFE-347mcc3                            | CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> OCH <sub>3</sub>                   | 0.34  | 5.0                              | 1,910   | 553       | 168       |
| HFE-347mcf2                            | CF <sub>3</sub> CF <sub>2</sub> OCH <sub>2</sub> CHF <sub>2</sub>                  | 0.41  | 6.6                              | 2,950   | 881       | 268       |
| HFE-356mec3                            | CF <sub>3</sub> CHFCF <sub>2</sub> OCH <sub>3</sub>                                | 0.30  | 3.8                              | 1,430   | 408       | 124       |
| HFE-356pcf2                            | CHF <sub>2</sub> CF <sub>2</sub> OCH <sub>2</sub> CHF <sub>2</sub>                 | 0.37  | 5.7                              | 2,580   | 754       | 229       |
| HFE-356pcf3                            | CHF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> OCHF <sub>2</sub>                 | 0.39  | 3.5                              | 1,710   | 488       | 148       |
| HFE-356pcc3                            | CHF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> OCH <sub>3</sub>                  | 0.33  | 3.8                              | 1,570   | 448       | 136       |
|  | (CF <sub>3</sub> ) <sub>2</sub> CHOCHF <sub>2</sub>                                | 0.41  | 21.2                             | 5,580   | 2,570     | 789       |
|  | (CF <sub>3</sub> ) <sub>2</sub> CFOCH <sub>3</sub>                                 | 0.31  | 3.7                              | 1,310   | 373       | 114       |
| HFE-43-10pccc124                       | CHF <sub>2</sub> OCF <sub>2</sub> OC <sub>2</sub> F <sub>4</sub> OCHF <sub>2</sub> | 1.02 <sup>d</sup>   | 13.5                             | 8,130   | 2,990     | 909       |
| HFE-7100 (HFE-449 blend)               | C <sub>4</sub> F <sub>9</sub> OCH <sub>3</sub>                                     | 0.31  | 4.7                              | 1,320   | 379       | 115       |
| HFE-7200 (HFE-569 blend)               | C <sub>4</sub> F <sub>9</sub> OC <sub>2</sub> H <sub>5</sub>                       | 0.30  | 0.8                              | 208   | 59        | 18        |
| HFE-236ca12                            | CHF <sub>2</sub> OCF <sub>2</sub> OCHF <sub>2</sub>                                | 0.66  | 25                               | 11,320  | 5,730     | 1,770     |
| HFE-338pcc13                           | CHF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub> OCHF <sub>2</sub>                | 0.87  | 12.9                             | 8,660   | 3,120     | 949       |
|  | (CF <sub>3</sub> ) <sub>2</sub> CHOH   | 0.28  | 1.9                              | 726   | 206       | 63        |
| <b>Miscellaneous</b>                   |  |   |                                  |   |           |           |
| Sulfuryl fluoride                      | SO <sub>2</sub> F <sub>2</sub>   | 0.22 <sup>d</sup>   | 36                               | 7,580   | 4,740     | 1,540     |

<sup>a</sup> Taken from WMO (2007), unless stated otherwise.

<sup>b</sup> Taken from Chapter 1, unless stated otherwise.

<sup>c</sup> Assumes CO<sub>2</sub> mixing ratio is 378 parts per million (ppm).

<sup>d</sup> See Table 5-2.

<sup>e</sup> Midpoint of range given in Chapter 1.

**Table 5A-2. Assumptions made in obtaining production and emission estimates for the baseline (A1) scenario.**

| <b>General Approach for All Species</b>  |   |
|--|---|
| <p>Production: For the years when production is reported to UNEP, reported values (or best estimates of production values for cases in which reporting is incomplete) are used. Before this, WMO (2007) production values are generally used. In the future, annual figures are determined from the lesser of the Protocol limitations and the most recent annual estimates.</p> <p>Emission: For the years when mixing ratio observations are available, emissions are calculated using the box model described in Daniel and Velders et al. (2007) with the lifetimes of Appendix Table 5A-1. Emissions before this are usually consistent with WMO (2007) but are also forced to yield mixing ratios that meld smoothly into the measurement record. Future emissions are determined using a fixed annual bank release fraction, calculated as the average ratio over the past 10 years between the annual emissions and estimated bank plus production.</p> <p>Bank: The bank assumed to be in place at the start of the measurement record is set at such a value that the IPCC (2009) bank for 2008 is attained. The bank at the end of each year is equal to the bank at the beginning of the year plus production during that year minus emissions during that year.</p> |   |
| <b>Approach for Specific Species</b>   |   |
| <b>Species</b>   | <b>Description</b>  |
| CFC-11   | <p>Production:<br/> 1950–1985: WMO (2007)<br/> 1986, 1989–2008: UNEP (2009)<sup>a</sup>, 1987–1988 interpolated from 1986 and 1989 values<br/> 2009–2010: Approved critical-use exemptions for non-Article 5(1) countries<br/> 2010: Approved critical-use exemptions for Article 5(1) countries, 2009 value interpolated from 2008 and 2010 values. All critical-use exemptions for CFCs are assumed to be CFC-11<br/> After 2010: No production</p> <p>Emission:<br/> 1979–2008: Emissions calculated from observed global abundance trends<br/> 2009–2100: Annual emissions are a constant fraction of 0.05 of the bank, extrapolated from the previous years</p> <p>Bank:<br/> 1979 bank set to 1,705 Kt to attain a 2008 bank of 1,420 Kt (TEAP, 2009). The bank projected for 2008 in the previous Assessment was 1,380 Kt.</p> |
| CFC-12   | <p>Same as CFC-11, except:<br/> Annual emissions from 2009–2100 are a constant fraction of 0.15 of the bank</p> <p>Bank:<br/> 1979 bank set to 941 Kt to attain a 2008 bank of 394 Kt (TEAP, 2009). The bank projected for 2008 in the previous Assessment was 499 Kt.</p>  |
| CFC-113  | <p>Same formalism as for CFC-11, except:<br/> Annual emissions from 2009–2100 are a constant fraction of 0.5 of the estimated bank. (Although our scenario has a non-zero bank in 2010, according to TEAP (2009) the bank has been zero since 2002.)</p>  |
| CFC-114  | <p>Same formalism as for CFC-11 except:<br/> Bank calculated based on historic production and emission data<br/> Annual emission from 2009–2100 is a constant fraction of 0.1 of the estimated bank</p>   |
| CFC-115  | <p>Same as CFC-11, except:<br/> Emissions from 2009–2100 are a constant fraction of 0.02 of the bank</p> <p>Bank:<br/> 2008 bank of 16 Kt (TEAP, 2009)</p>  |

Table 5A-2, continued.

| Approach for Specific Species    |   |
|----------------------------------|---|
| CCl <sub>4</sub>                 | <p>Production and bank not considered due to gaps in our understanding of the origin of much of the global emission</p> <p>Emission:</p> <p>1951–1979: WMO (2003)</p> <p>1980–2008: Emissions calculated from observed global abundance trends</p> <p>2009–2050: Emissions decrease by 6% per year (average derived from observations and a 26-year lifetime during 2004 to 2008)</p> <p>2051–2100: No emission</p>   |
| CH <sub>3</sub> CCl <sub>3</sub> | <p>Production not explicitly considered</p> <p>Emission:</p> <p>1950–1978: WMO (2003)</p> <p>1979–2008: Emissions calculated from observed global abundance trends</p> <p>2009–2014: Emission equal to the 2004–2008 average</p> <p>2015–2100: No emission</p>  |
| HCFC-22                          | <p>Production:</p> <p>1950–1988: WMO (2003)</p> <p>1989, 1992–2008: UNEP (2009)<sup>a</sup>, 1990–1991 interpolated from 1989 and 1992 values</p> <p>Non-Article 5(1) countries: 2009 production is 2004–2008 average; 2010–2013 Montreal Protocol phase-out schedule applied</p> <p>The base level HCFC consumption in non-Article 5(1) countries is calculated as the consumption in 1989 + 2.8% of the 1989 CFC consumption (ODP-weighted). In WMO (2007), the 2.8% of the CFC consumption was assigned completely to HCFC-22. In this Assessment it is distributed over the three main HCFCs based on their historic production. This results in larger future emissions of HCFC-141b and HCFC-142b.</p> <p>Article 5(1) countries: 2009–2012 is linearly extrapolated from 2004–2008; 2013–2040 Montreal Protocol phase-out schedule applied</p> <p>Emission:</p> <p>1950–1992: Emissions calculated to yield mixing ratios consistent with WMO (2007)</p> <p>1993–2008: Emissions calculated from observed global abundance trends</p> <p>2009–2100: Assume an annual bank release fraction of 0.18 (average of 2002–2008)</p> <p>Bank:</p> <p>1993 bank set to 302 Kt to attain a 2008 bank of 1,618 Kt (TEAP, 2009). The bank projected for 2008 in the previous Assessment was 2,083 Kt.</p> |
| HCFC-141b                        | <p>Production as in HCFC-22</p> <p>Emission:</p> <p>1990–2008: Emissions calculated from observed global abundance trends</p> <p>2009–2100: Annual emissions calculated assuming a bank release fraction of 0.05 (average of 2003–2008)</p> <p>Bank:</p> <p>1994 bank set to 115 Kt to attain a 2008 bank of 941 Kt (TEAP, 2009). The bank projected for 2008 in the previous Assessment was 961 Kt.</p>  |
| HCFC-142b                        | <p>Production as in HCFC-22</p> <p>Emission:</p> <p>1979–2008: Emissions calculated from observed global abundance trends</p> <p>2009–2100: Annual emissions calculated assuming a bank release fraction of 0.11 (average of 1999–2008)</p> <p>Bank:</p> <p>1993 bank set to 95 Kt to attain a 2008 bank of 273 Kt (TEAP, 2009). The bank projected for 2008 in the previous Assessment was 211 Kt.</p>   |

Table 5A-2, continued.

| Approach for Specific Species |   |
|-------------------------------|---|
| Halon-1211                    | <p>Production:</p> <p>1986, 1989–2008: UNEP (2009), 1987–1988 interpolated from 1986 and 1989 values<br/> non-Article 5(1) countries: zero production from 2009–2100<br/> Article 5(1) countries: 2009 production is 2006–2008 average; zero from 2010–2100</p> <p>Emission:</p> <p>1950–1992: WMO (2007)<br/> 1993–2008: Emissions calculated from observed global abundance trends<br/> 2009–2100: Annual emissions calculated assuming a bank release fraction of 0.075 (average of 1999–2008)</p> <p>Bank:</p> <p>1993 bank is set to 128 Kt to attain a 2008 bank of 74 Kt (TEAP, 2009). The bank projected for 2008 in the previous Assessment was 86 Kt.</p>   |
| Halon-1301                    | <p>Production as in halon-1211</p> <p>Emission:</p> <p>1950–1992: WMO (2007)<br/> 1992–2008: Emissions calculated from observed global abundance trends<br/> 2009–2100: Annual emissions calculated assuming a bank release fraction of 0.04 (average of 1999–2008)</p> <p>Bank:</p> <p>1992 bank is set to 74 Kt to attain a 2008 bank of 47 Kt (TEAP, 2009). The bank projected for 2008 in the previous Assessment was 31 Kt.</p>  |
| Halon-1202                    | Same as WMO (2007)  |
| Halon-2402                    | <p>Production as in halon-1211</p> <p>Emission:</p> <p>1970–2003: based on WMO (2007), but adjusted to meld smoothly into the measurement record<br/> 2004–2008: Emissions calculated from observed global abundance trends<br/> 2009–2100: Annual emissions calculated assume a bank release fraction of 0.08 (average of 2004–2008)</p> <p>Bank:</p> <p>1995 bank is set to 20 Kt to allow the emissions meld smoothly into the emissions derived from observations. The corresponding 2008 bank of 9.1 Kt is much larger than from TEAP (2009) of 1.3 Kt. A bank of 1.3 Kt would result in emissions a factor of 8 smaller than derived from observations for 2004–2008. The bank projected for 2008 in the previous Assessment was 1.8 Kt.</p>  |
| CH <sub>3</sub> Br            | <p>Production/emissions from Yvon-Lewis et al. (2009): natural production/emission (102 Kt), gasoline (5.7 Kt), biomass (11.3 Kt), biofuel (6.1 Kt), non QPS-fumigation. Parenthetical values for anthropogenic sources are emission estimates for 1996 and 2007 (Yvon-Lewis et al., 2009 and references therein) and are held constant into the future.<br/> QPS production from 1995–2008 from UNEP (2009), held constant at 11.2 Kt (2004–2008 average) for 2009–2100<br/> Approved critical-use exemptions (CUE) for 2009–2011 (no CUE after 2011)</p> <p>Emissions:</p> <p>1950–2008: Emissions calculated from surface observations and derived from South Pole firm measurements (using a global lifetime of 0.75 years to be consistent with Yvon-Lewis et al., 2009)<br/> 2009–2100: Fumigation emissions equal 0.6 times production for fumigation. The combination of anthropogenic and natural emissions, constrained by the total emissions derived from observations of concentrations, leads to an anthropogenic fraction of total emissions of 0.30</p> |

**Table 5A-2, continued.**

| <b>Approach for Specific Species</b> |   |
|--------------------------------------|---|
| (CH <sub>3</sub> Br, continued)      | Bank: in 1992, in agreement with Montzka et al. (2003) (see also Chapter 1).<br>No bank considered  |
| CH <sub>3</sub> Cl                   | Emission:<br>1950–1995: Global emissions derived from firn measurements at the South Pole<br>1996–2100: Emissions held constant at 1995 levels, as in WMO (2003) and WMO (2007) |

<sup>a</sup> Estimated in cases in which reporting is not complete or reporting is made in compound classes rather than individually. The production data for each species in each year is obtained from UNEP (2009) and is consistent with the totals for each group of species as usually reported by UNEP.

**Table 5A-3. Mixing ratios (ppt) of the ODSs considered in the baseline (A1) scenario<sup>1</sup>.** Values are for the beginning of the corresponding year. Potentially important short-lived gases that may currently contribute 3–8 ppt of stratospheric bromine and 40–130 ppt of stratospheric chlorine (see Chapter 1) are not shown in the table.

|      | CFC-11 |        | CFC-113 |         | CFC-115 |                  | CH <sub>3</sub> CCl <sub>3</sub> |         | HCFC-22   |           | HCFC-141b  |            | Halon-1211 |            | Halon-1202         |                    | Halon-1301 |      | Halon-2402 |     | CH <sub>3</sub> Br | CH <sub>3</sub> Cl |
|------|--------|--------|---------|---------|---------|------------------|----------------------------------|---------|-----------|-----------|------------|------------|------------|------------|--------------------|--------------------|------------|------|------------|-----|--------------------|--------------------|
|      | CFC-11 | CFC-12 | CFC-113 | CFC-114 | CFC-115 | CCl <sub>4</sub> | CH <sub>3</sub> CCl <sub>3</sub> | HCFC-22 | HCFC-141b | HCFC-142b | Halon-1211 | Halon-1202 | Halon-1301 | Halon-2402 | CH <sub>3</sub> Br | CH <sub>3</sub> Cl |            |      |            |     |                    |                    |
| 1955 | 3.3    | 14.3   | 1.2     | 2.6     | 0.0     | 42.3             | 0.1                              | 1.0     | 0.0       | 0.0       | 0.0        | 0.0        | 0.0        | 0.0        | 0.0                | 0.0                | 0.0        | 0.0  | 0.0        | 6.3 | 491.3              |                    |
| 1960 | 9.5    | 29.5   | 1.9     | 3.8     | 0.0     | 52.1             | 1.5                              | 2.1     | 0.0       | 0.0       | 0.0        | 0.0        | 0.0        | 0.0        | 0.0                | 0.0                | 0.0        | 0.0  | 0.0        | 6.5 | 510.3              |                    |
| 1965 | 23.5   | 58.8   | 3.1     | 5.0     | 0.0     | 64.4             | 4.7                              | 4.9     | 0.0       | 0.0       | 0.0        | 0.0        | 0.0        | 0.0        | 0.0                | 0.0                | 0.0        | 0.0  | 0.0        | 6.7 | 528.1              |                    |
| 1970 | 52.8   | 114.3  | 5.5     | 6.5     | 0.2     | 75.9             | 16.2                             | 12.1    | 0.0       | 0.0       | 0.0        | 0.0        | 0.0        | 0.0        | 0.0                | 0.0                | 0.0        | 0.0  | 0.0        | 7.0 | 539.9              |                    |
| 1975 | 106.1  | 203.1  | 10.4    | 8.3     | 0.6     | 85.5             | 40.0                             | 23.8    | 0.0       | 0.2       | 0.12       | 0.01       | 0.04       | 0.06       | 0.01               | 0.04               | 0.06       | 0.01 | 0.04       | 7.4 | 545.8              |                    |
| 1980 | 161.9  | 297.4  | 19.0    | 10.7    | 1.3     | 93.3             | 81.6                             | 42.5    | 0.0       | 0.4       | 0.42       | 0.01       | 0.24       | 0.15       | 0.01               | 0.24               | 0.15       | 0.01 | 0.24       | 7.7 | 548.3              |                    |
| 1981 | 170.3  | 313.9  | 21.5    | 11.1    | 1.5     | 94.8             | 88.3                             | 46.6    | 0.0       | 0.5       | 0.52       | 0.01       | 0.31       | 0.17       | 0.01               | 0.31               | 0.17       | 0.01 | 0.31       | 7.8 | 548.6              |                    |
| 1982 | 179.2  | 329.9  | 25.3    | 11.6    | 1.8     | 95.8             | 93.0                             | 50.7    | 0.0       | 0.5       | 0.63       | 0.02       | 0.39       | 0.19       | 0.02               | 0.39               | 0.19       | 0.02 | 0.39       | 7.9 | 548.9              |                    |
| 1983 | 187.4  | 346.7  | 29.2    | 12.0    | 2.1     | 97.1             | 97.2                             | 54.8    | 0.0       | 0.6       | 0.75       | 0.02       | 0.49       | 0.21       | 0.02               | 0.49               | 0.21       | 0.02 | 0.49       | 8.0 | 549.1              |                    |
| 1984 | 196.0  | 363.9  | 32.5    | 12.4    | 2.4     | 98.2             | 101.7                            | 58.8    | 0.0       | 0.7       | 0.88       | 0.02       | 0.61       | 0.24       | 0.02               | 0.61               | 0.24       | 0.02 | 0.61       | 8.1 | 549.3              |                    |
| 1985 | 205.4  | 381.2  | 37.3    | 12.9    | 2.8     | 99.6             | 106.1                            | 62.7    | 0.0       | 0.7       | 1.04       | 0.02       | 0.74       | 0.26       | 0.02               | 0.74               | 0.26       | 0.02 | 0.74       | 8.2 | 549.4              |                    |
| 1986 | 215.8  | 399.3  | 42.0    | 13.4    | 3.1     | 100.8            | 110.0                            | 66.9    | 0.0       | 0.8       | 1.22       | 0.02       | 0.89       | 0.29       | 0.02               | 0.89               | 0.29       | 0.02 | 0.89       | 8.2 | 549.5              |                    |
| 1987 | 227.0  | 419.2  | 47.4    | 14.0    | 3.5     | 102.5            | 112.3                            | 71.5    | 0.0       | 0.8       | 1.44       | 0.02       | 1.06       | 0.32       | 0.02               | 1.06               | 0.32       | 0.02 | 1.06       | 8.3 | 549.6              |                    |
| 1988 | 238.0  | 438.4  | 54.4    | 14.5    | 3.9     | 103.6            | 118.0                            | 76.7    | 0.0       | 0.9       | 1.69       | 0.03       | 1.25       | 0.35       | 0.03               | 1.25               | 0.35       | 0.03 | 1.25       | 8.4 | 549.7              |                    |
| 1989 | 247.7  | 459.6  | 61.3    | 15.0    | 4.3     | 104.9            | 122.5                            | 82.5    | 0.0       | 1.0       | 1.98       | 0.03       | 1.46       | 0.38       | 0.03               | 1.46               | 0.38       | 0.03 | 1.46       | 8.5 | 549.8              |                    |
| 1990 | 256.2  | 477.5  | 67.6    | 15.4    | 4.7     | 106.5            | 127.2                            | 88.2    | 0.0       | 1.2       | 2.27       | 0.03       | 1.66       | 0.41       | 0.03               | 1.66               | 0.41       | 0.03 | 1.66       | 8.6 | 549.8              |                    |
| 1991 | 262.2  | 491.0  | 73.8    | 15.7    | 5.1     | 106.3            | 130.0                            | 93.7    | 0.0       | 1.8       | 2.54       | 0.03       | 1.84       | 0.44       | 0.03               | 1.84               | 0.44       | 0.03 | 1.84       | 8.7 | 549.9              |                    |
| 1992 | 265.2  | 500.7  | 78.7    | 15.8    | 5.6     | 105.3            | 131.4                            | 99.1    | 0.1       | 2.8       | 2.79       | 0.03       | 1.97       | 0.46       | 0.03               | 1.97               | 0.46       | 0.03 | 1.97       | 8.9 | 549.9              |                    |
| 1993 | 267.8  | 510.1  | 81.6    | 15.9    | 6.0     | 104.7            | 130.1                            | 103.9   | 0.3       | 3.9       | 3.02       | 0.04       | 2.20       | 0.49       | 0.04               | 2.20               | 0.49       | 0.04 | 2.20       | 9.0 | 549.9              |                    |
| 1994 | 267.8  | 517.1  | 83.0    | 16.0    | 6.4     | 104.0            | 121.5                            | 109.2   | 1.2       | 5.1       | 3.20       | 0.04       | 2.48       | 0.51       | 0.04               | 2.48               | 0.51       | 0.04 | 2.48       | 9.1 | 549.9              |                    |
| 1995 | 267.4  | 523.8  | 83.6    | 16.1    | 6.8     | 103.2            | 110.3                            | 113.6   | 2.7       | 6.3       | 3.34       | 0.04       | 2.63       | 0.52       | 0.04               | 2.63               | 0.52       | 0.04 | 2.63       | 9.2 | 550.0              |                    |
| 1996 | 266.8  | 528.9  | 83.7    | 16.2    | 7.1     | 102.5            | 97.8                             | 119.4   | 4.5       | 7.3       | 3.50       | 0.05       | 2.60       | 0.51       | 0.05               | 2.60               | 0.51       | 0.05 | 2.60       | 9.1 | 550.0              |                    |
| 1997 | 266.0  | 533.5  | 83.6    | 16.3    | 7.4     | 101.3            | 83.4                             | 124.2   | 6.4       | 8.4       | 3.66       | 0.05       | 2.67       | 0.51       | 0.05               | 2.67               | 0.51       | 0.05 | 2.67       | 9.1 | 550.0              |                    |
| 1998 | 264.5  | 536.4  | 83.3    | 16.4    | 7.6     | 100.5            | 70.6                             | 128.7   | 8.2       | 9.3       | 3.80       | 0.05       | 2.70       | 0.51       | 0.05               | 2.70               | 0.51       | 0.05 | 2.70       | 9.2 | 550.0              |                    |
| 1999 | 263.3  | 539.0  | 82.9    | 16.4    | 7.7     | 99.8             | 59.3                             | 134.7   | 10.1      | 10.3      | 3.92       | 0.05       | 2.73       | 0.51       | 0.05               | 2.73               | 0.51       | 0.05 | 2.73       | 9.3 | 550.0              |                    |
| 2000 | 261.7  | 541.0  | 82.3    | 16.5    | 7.9     | 98.6             | 49.7                             | 139.5   | 11.8      | 11.4      | 4.02       | 0.04       | 2.84       | 0.50       | 0.04               | 2.84               | 0.50       | 0.04 | 2.84       | 8.9 | 550.0              |                    |
| 2001 | 260.1  | 542.8  | 81.8    | 16.5    | 8.0     | 97.7             | 41.6                             | 144.7   | 13.5      | 12.4      | 4.11       | 0.04       | 2.85       | 0.50       | 0.04               | 2.85               | 0.50       | 0.04 | 2.85       | 8.5 | 550.0              |                    |
| 2002 | 258.3  | 543.4  | 81.1    | 16.5    | 8.0     | 96.6             | 34.6                             | 150.9   | 14.8      | 13.2      | 4.17       | 0.03       | 2.87       | 0.50       | 0.03               | 2.87               | 0.50       | 0.03 | 2.87       | 8.2 | 550.0              |                    |
| 2003 | 255.9  | 543.5  | 80.3    | 16.5    | 8.1     | 95.6             | 28.9                             | 155.4   | 16.1      | 13.9      | 4.22       | 0.03       | 2.88       | 0.49       | 0.03               | 2.88               | 0.49       | 0.03 | 2.88       | 8.2 | 550.0              |                    |
| 2004 | 253.9  | 543.4  | 79.6    | 16.5    | 8.2     | 94.7             | 24.1                             | 160.3   | 17.0      | 14.5      | 4.25       | 0.02       | 2.95       | 0.49       | 0.02               | 2.95               | 0.49       | 0.02 | 2.95       | 8.0 | 550.0              |                    |

|      | CFC-11  |         | CFC-113 |                  | CFC-115                          |         | CH <sub>3</sub> CCl <sub>3</sub> |           | HCFC-22    |            | HCFC-141b  |                    | Halon-1211         |      | Halon-1301 |     | CH <sub>3</sub> Br |  |
|------|---------|---------|---------|------------------|----------------------------------|---------|----------------------------------|-----------|------------|------------|------------|--------------------|--------------------|------|------------|-----|--------------------|--|
|      | CFC-114 | CFC-114 | CFC-114 | CCl <sub>4</sub> | CH <sub>3</sub> CCl <sub>3</sub> | HCFC-22 | HCFC-141b                        | HCFC-142b | Halon-1202 | Halon-1301 | Halon-2402 | CH <sub>3</sub> Cl | CH <sub>3</sub> Br |      |            |     |                    |  |
| 2005 | 251.6   | 542.7   | 78.8    | 16.6             | 8.3                              | 8.3     | 93.7                             | 20.1      | 165.5      | 17.5       | 15.1       | 4.26               | 0.02               | 3.03 | 0.48       | 7.9 | 550.0              |  |
| 2006 | 249.4   | 541.8   | 78.2    | 16.5             | 8.3                              | 8.3     | 92.7                             | 16.7      | 172.2      | 17.8       | 15.8       | 4.27               | 0.01               | 3.06 | 0.48       | 7.7 | 550.0              |  |
| 2007 | 247.2   | 539.8   | 77.6    | 16.5             | 8.4                              | 8.4     | 91.6                             | 14.1      | 179.3      | 18.6       | 16.9       | 4.24               | 0.01               | 3.12 | 0.48       | 7.6 | 550.0              |  |
| 2008 | 245.1   | 537.7   | 76.8    | 16.5             | 8.4                              | 8.4     | 90.4                             | 11.7      | 187.3      | 19.0       | 18.2       | 4.19               | 0.01               | 3.15 | 0.47       | 7.5 | 550.0              |  |
| 2009 | 243.3   | 535.3   | 76.2    | 16.4             | 8.4                              | 8.4     | 89.0                             | 9.8       | 195.2      | 19.6       | 19.3       | 4.14               | 0.00               | 3.18 | 0.47       | 7.2 | 550.0              |  |
| 2010 | 240.9   | 532.5   | 75.6    | 16.4             | 8.4                              | 8.4     | 87.6                             | 8.3       | 206.8      | 20.3       | 20.5       | 4.07               | 0.00               | 3.20 | 0.46       | 7.2 | 550.0              |  |
| 2011 | 238.4   | 529.4   | 74.8    | 16.3             | 8.4                              | 8.4     | 86.0                             | 7.1       | 218.6      | 21.1       | 21.7       | 3.99               | 0.00               | 3.22 | 0.46       | 7.2 | 550.0              |  |
| 2012 | 235.8   | 525.9   | 74.0    | 16.3             | 8.4                              | 8.4     | 84.5                             | 6.1       | 230.9      | 22.1       | 22.9       | 3.91               | 0.00               | 3.24 | 0.45       | 7.2 | 550.0              |  |
| 2013 | 233.1   | 522.3   | 73.2    | 16.2             | 8.4                              | 8.4     | 82.8                             | 5.3       | 243.6      | 23.2       | 24.2       | 3.82               | 0.00               | 3.26 | 0.44       | 7.1 | 550.0              |  |
| 2014 | 230.4   | 518.4   | 72.3    | 16.2             | 8.4                              | 8.4     | 81.2                             | 4.6       | 255.7      | 24.4       | 25.4       | 3.72               | 0.00               | 3.27 | 0.44       | 7.1 | 550.0              |  |
| 2015 | 227.6   | 514.4   | 71.5    | 16.1             | 8.4                              | 8.4     | 79.5                             | 4.1       | 267.1      | 25.6       | 26.6       | 3.62               | 0.00               | 3.28 | 0.43       | 7.1 | 550.0              |  |
| 2020 | 213.0   | 492.8   | 67.4    | 15.8             | 8.4                              | 8.4     | 70.9                             | 1.5       | 301.8      | 30.9       | 30.9       | 3.08               | 0.00               | 3.29 | 0.38       | 7.1 | 550.0              |  |
| 2025 | 197.8   | 470.3   | 63.6    | 15.5             | 8.4                              | 8.4     | 62.4                             | 0.5       | 299.8      | 34.1       | 32.4       | 2.55               | 0.00               | 3.26 | 0.32       | 7.1 | 550.0              |  |
| 2030 | 182.6   | 448.0   | 59.9    | 15.1             | 8.4                              | 8.4     | 54.4                             | 0.2       | 265.4      | 34.4       | 31.2       | 2.06               | 0.00               | 3.19 | 0.27       | 7.1 | 550.0              |  |
| 2035 | 167.7   | 426.5   | 56.5    | 14.7             | 8.4                              | 8.4     | 47.0                             | 0.1       | 208.0      | 31.9       | 27.8       | 1.65               | 0.00               | 3.09 | 0.22       | 7.1 | 550.0              |  |
| 2040 | 153.5   | 405.8   | 53.3    | 14.4             | 8.4                              | 8.4     | 40.3                             | 0.0       | 151.0      | 27.9       | 23.3       | 1.30               | 0.00               | 2.97 | 0.18       | 7.1 | 550.0              |  |
| 2045 | 139.9   | 386.1   | 50.2    | 14.0             | 8.4                              | 8.4     | 34.4                             | 0.0       | 105.0      | 23.5       | 18.9       | 1.01               | 0.00               | 2.85 | 0.15       | 7.1 | 550.0              |  |
| 2050 | 127.2   | 367.3   | 47.4    | 13.6             | 8.4                              | 8.4     | 29.2                             | 0.0       | 71.1       | 19.3       | 14.9       | 0.78               | 0.00               | 2.71 | 0.12       | 7.1 | 550.0              |  |
| 2055 | 115.4   | 349.4   | 44.7    | 13.3             | 8.4                              | 8.4     | 24.2                             | 0.0       | 47.5       | 15.6       | 11.6       | 0.60               | 0.00               | 2.57 | 0.09       | 7.1 | 550.0              |  |
| 2060 | 104.4   | 332.4   | 42.1    | 12.9             | 8.3                              | 8.3     | 20.0                             | 0.0       | 31.5       | 12.4       | 9.0        | 0.46               | 0.00               | 2.43 | 0.07       | 7.1 | 550.0              |  |
| 2065 | 94.4    | 316.2   | 39.7    | 12.6             | 8.3                              | 8.3     | 16.5                             | 0.0       | 20.8       | 9.8        | 6.8        | 0.35               | 0.00               | 2.29 | 0.06       | 7.1 | 550.0              |  |
| 2070 | 85.2    | 300.7   | 37.4    | 12.3             | 8.3                              | 8.3     | 13.6                             | 0.0       | 13.7       | 7.7        | 5.2        | 0.26               | 0.00               | 2.16 | 0.05       | 7.1 | 550.0              |  |
| 2075 | 76.8    | 286.1   | 35.3    | 12.0             | 8.3                              | 8.3     | 11.2                             | 0.0       | 9.0        | 6.1        | 3.9        | 0.20               | 0.00               | 2.02 | 0.04       | 7.1 | 550.0              |  |
| 2080 | 69.1    | 272.1   | 33.3    | 11.6             | 8.2                              | 8.2     | 9.3                              | 0.0       | 5.9        | 4.7        | 3.0        | 0.15               | 0.00               | 1.90 | 0.03       | 7.1 | 550.0              |  |
| 2085 | 62.2    | 258.8   | 31.4    | 11.3             | 8.2                              | 8.2     | 7.6                              | 0.0       | 3.9        | 3.7        | 2.2        | 0.11               | 0.00               | 1.77 | 0.02       | 7.1 | 550.0              |  |
| 2090 | 55.9    | 246.2   | 29.6    | 11.1             | 8.2                              | 8.2     | 6.3                              | 0.0       | 2.6        | 2.9        | 1.7        | 0.08               | 0.00               | 1.66 | 0.02       | 7.1 | 550.0              |  |
| 2095 | 50.2    | 234.2   | 27.9    | 10.8             | 8.2                              | 8.2     | 5.2                              | 0.0       | 1.7        | 2.2        | 1.3        | 0.06               | 0.00               | 1.55 | 0.01       | 7.1 | 550.0              |  |
| 2100 | 45.1    | 222.8   | 26.3    | 10.5             | 8.1                              | 8.1     | 4.3                              | 0.0       | 1.1        | 1.7        | 0.9        | 0.05               | 0.00               | 1.44 | 0.01       | 7.1 | 550.0              |  |

<sup>1</sup>Note: Areas are shaded for compounds in years when mixing ratio values are forced to equal global estimates inferred from observations. The pre-1995 global mixing ratio trend for CH<sub>3</sub>Br was derived from SH firm data by including a time-varying hemispheric ratio that increased linearly from 1.0 in 1940 to 1.3 in 1995 (see Section 1.2.1.6 of Chapter 1). This is based on the concurrent decline in the measured hemispheric difference and industrially averaged emissions since 1998, and suggests a mean hemispheric mixing ratio difference close to 0 ppt for CH<sub>3</sub>Br in preindustrial times. Previously, a constant hemispheric ratio had been used. CH<sub>3</sub>Cl mixing ratios before 1995 were also derived from South Pole firm data (Butler et al., 1999). From 1995 onward, global means of CH<sub>3</sub>Br are based on surface observations, while global means of CH<sub>3</sub>Cl are held constant (Chapter 1). All other shaded areas are from atmospheric observations from one or more measurement networks (Chapter 1).

**Table 5A-4. Halocarbon indirect GWPs from ozone depletion using the EESC-based method described in Daniel et al. (1995).** Values have been updated for the new scenarios and fractional release values. Indirect forcing from ozone depletion is also now assumed to continue even after EESC drops below the 1980 level, consistent with our understanding that this level does not represent a threshold value for ozone depletion. Uncertainties in direct GWPs represent 35% of the direct value; uncertainties in the indirect GWPs reflect the uncertainty in stratospheric ozone radiative forcing quoted in IPCC ( $-0.05 \pm 0.10$  W/m<sup>2</sup>) even though that forcing is not attributed to only halocarbons.

| Gas                              | Direct GWP |   |       | Indirect GWP |   |        |
|----------------------------------|------------|---|-------|--------------|---|--------|
| CFC-11                           | 4,750      | ± | 1,660 | -1,630       | ± | 3,250  |
| CFC-12                           | 10,900     | ± | 3,810 | -1,270       | ± | 2,540  |
| CFC-113                          | 6,130      | ± | 2,150 | -1,310       | ± | 2,630  |
| CFC-114                          | 9,180      | ± | 3,210 | -562         | ± | 1,120  |
| CFC-115                          | 7,230      | ± | 2,530 | -137         | ± | 275    |
| HCFC-22                          | 1,790      | ± | 630   | -58          | ± | 116    |
| HCFC-123                         | 77         | ± | 27    | -25          | ± | 50     |
| HCFC-124                         | 619        | ± | 217   | -30          | ± | 60     |
| HCFC-141b                        | 717        | ± | 252   | -158         | ± | 316    |
| HCFC-142b                        | 2,220      | ± | 780   | -97          | ± | 193    |
| HCFC-225ca                       | 122        | ± | 42    | -27          | ± | 54     |
| HCFC-225cb                       | 606        | ± | 214   | -39          | ± | 78     |
| CH <sub>3</sub> CCl <sub>3</sub> | 146        | ± | 53    | -212         | ± | 424    |
| CCl <sub>4</sub>                 | 1,400      | ± | 490   | -1,300       | ± | 2,600  |
| CH <sub>3</sub> Br               | 5          | ± | 2     | -851         | ± | 1,700  |
| Halon-1211                       | 1,890      | ± | 660   | -11,720      | ± | 23,430 |
| Halon-1301                       | 7,140      | ± | 2,500 | -27,060      | ± | 54,130 |
| Halon-2402                       | 1,640      | ± | 570   | -19,780      | ± | 39,570 |