

CHAPTER 2

Current Trends, Mixing Ratios, and Emissions of Ozone-Depleting Substances and Their Substitutes

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KEY FINDINGS

Measures of production, consumption, emission, and atmospheric abundances of ozone-depleting substances (ODSs) and their substitute chemicals provide a coherent picture of how the Montreal Protocol has brought about substantial changes in the chemical composition of the atmosphere. All measures point to a shift away from ozone-depleting substances and toward increases in substitute chemicals. This shift will continue to reduce stratospheric ozone depletion and has had notable climate benefits. These different measures, some of which are independent, are discussed separately here:

From data reported by industry for the globe and for the United States¹:

- Owing to the Montreal Protocol, by 2005, the summed, global annual production and consumption of ozone-depleting substances for uses regulated by this Protocol had decreased 95% from peak amounts reported during the late 1980s². Summed U.S. production and consumption of these substances for these regulated uses declined by 97-98% over this same period².
- Use of substitutes for the more potent ozone-depleting gases has increased over time, but these chemicals are much less efficient at depleting stratospheric ozone than the chemicals they replace³.
- Declines in overall U.S. consumption of ozone-depleting substances and substitute chemicals through 2005 for uses regulated by the Montreal Protocol have been more rapid than total global declines. When ozone-depletion influences are considered⁴, the fractional contribution

¹ Production and consumption amounts for uses of ODSs regulated by the Montreal Protocol were obtained from United Nations Environment Programme (UNEP) compilations of data reported to them (UNEP, 2007) and, for magnitudes of unregulated and unrestricted uses, from UNEP Technical Option committee reports (UNEP/MBTOC, 2007; UNEP/CTOC, 2007); global production data for HFCs was taken from IPCC-TEAP (2005).

² Consumption is defined here and in the Montreal Protocol as amounts produced plus imports minus exports of a substance or group of substances. Production is defined as amounts produced minus the sum of amounts destroyed or used in feedstock (non-dispersive) applications. Consumption should equal production on a global scale averaged over time. In this Key Finding, magnitudes of production and consumption have been multiplied by weighting factors that are Ozone Depletion Potentials (see footnote #4).

³ The more potent and abundant ozone-depleting gases referred to here include chlorofluorocarbons, or CFCs, halons, methyl chloroform, and carbon tetrachloride. Chemicals considered to be substitutes include the hydrochlorofluorocarbons, or HCFCs, and the hydrofluorocarbons, or HFCs.

⁴ Weighting factors are applied to consumption, production, emission and banks of ODSs throughout this document that approximate the ozone depletion influences and the direct or indirect climate effects of these chemicals so as to allow consideration of them on an equivalent basis and as sums. These weighting factors account for the wide range of influences different chemicals have on ozone and climate. In the case of ozone, the weighting factors are

of the United States to annual global consumption of ozone-depleting substances (ODSs) in data reported to UNEP⁵ for all regulated, dispersive uses decreased by more than half, from a mean of 24 (± 2)% in 1986-1994 to 10 (± 2)%, on average, during 2001-2005. This decline is noted despite an increase in U.S. consumption of methyl bromide (CH₃Br) relative to global consumption in recent years. When direct and indirect climate effects of these chemicals are considered⁴, the contribution of the United States to total global consumption of ODSs for regulated, dispersive uses also decreased from the late 1980s to 2005, though the precise magnitude of this decline is sensitive to our understanding of the indirect climate forcing from ODSs related to stratospheric ozone changes.

- Declines in U.S. consumption for uses regulated by the Montreal Protocol have been slightly faster than phase-out schedules for all developed countries in the adjusted and amended Montreal Protocol for most ODSs. Consumption for methyl bromide was notably larger than this scheduled allotment in 2005 and 2006 (by 4.3 and 4.1 ODP-kilotons [Kt], respectively) because of Critical Use Exemptions (CUEs)⁶.
- Global consumption of methyl bromide for all fumigation-related uses declined by a factor of two from 1997 to 2005 despite substantial consumption in applications not regulated or restricted by the Montreal Protocol. Nearly half (43%) of the global, industrially-derived emissions of CH₃Br during 2005 arose from QPS⁶ consumption not restricted or limited by the Montreal Protocol.
- U.S. consumption of CH₃Br for all fumigation uses declined 40% from 1997 to 2005 despite enhanced Critical Use Exemptions⁶ and QPS⁶ consumption since 2001. Enhanced Critical Use Exemptions caused the annual U.S. contribution to global CH₃Br consumption for regulated and restricted uses in data reported to UNEP to increase from 23 (± 4)% during 2000-2003 to 36 (± 1)% during 2004-2005. In the United States during 2001-2006, the additional consumption of methyl bromide for fumigation not restricted or limited by the Protocol (QPS use) was, on average, 57 (± 20)% of the amounts used and reported to UNEP⁵ for regulated applications and had increased by 13% per year, on average, during 2001-2005.
- The mix of ozone-depleting chemicals produced throughout the globe has changed over time in response to the Montreal Protocol. In 2005, global production weighted by Ozone Depletion Potentials (ODPs) for relevance to ozone depletion was dominated by chlorofluorocarbons, or CFCs, (50%), hydrochlorofluorocarbons or HCFCs (33%), and CH₃Br (11%); in the United States, ODP-weighted consumption was dominated by HCFCs (54%) and CH₃Br (34%). When weighted by overall climate influences [net Global Warming Potentials (GWPs)], global production in 2005 was accounted for primarily by HCFCs and hydrofluorocarbons (HFCs) in similar amounts, a somewhat lesser contribution from CFCs, and very small or negative contributions from halons, CH₃Br, and other chemicals. In the United States, direct and net GWP-weighted consumption was dominated by HFCs and HCFCs with only small contributions from CFCs and other ODSs. Current estimates of global HFC production have large uncertainties owing to restrictions on reporting production magnitudes when less than three manufacturers produce a given chemical.
- Future emission rates from banks⁷ will play a substantial role in determining future mixing ratios

Ozone Depletion Potentials (ODPs) with units of ODP-Tons or ODP-Kt; 1 ODP-Kt=1 billion grams multiplied by the ODP of a given chemical. In the case of climate, the weighting factors are 100-year direct or net Global Warming Potentials (GWPs), where net GWPs include the radiative influence of stratospheric ozone depletion. Units for quantities weighted by 100-year GWPs are expressed equivalently by, for example, GWP-Tons or gigatons (Gt) CO₂-equivalents. Additional descriptions of these weighting factors appear in Box 2.2 and the main chapter text, and tables of the weighting factors used here appear in Appendix 2A.

⁵ The United Nations Environment Programme (UNEP) compiles and publishes global and national statistics on production and consumption of ODSs based upon data reported to them in order to monitor compliance with the adjusted and amended Montreal Protocol (UNEP, 2007).

⁶ QPS refers to quarantine and pre-shipment use of an ODS, specifically CH₃Br. Though reporting requirements exist for this dispersive use, it is not restricted or scheduled for phase-out in the Montreal Protocol and these use magnitudes are not included in data published by UNEP to assess compliance with the Protocol. CUEs refer to Critical Use Exemptions for consumption of an ODS above existing Montreal Protocol allotments; they are approved only on a case-by-case basis and are included in amounts reported to and published by UNEP.

⁷ Banks represent the amount of a chemical that has been produced but not yet emitted or chemically altered. They exist either in reserve storage or in current applications. Bank magnitudes are derived from the U.S. EPA's Vintaging Model analysis of sales and use of ODSs and substitutes in the U.S. (U.S. EPA, 2007). Owing to a lack of available data at this time, U.S. bank estimates presented here do not include stockpiles of halons.

for some ODSs. Banks in the U.S. and throughout the globe in 2005 are estimated to have been 7 to 16 times larger than emissions during this year, when weighted by their potential influence on climate or ozone depletion. CFCs accounted for the largest fraction of 2005 banks in the United States and throughout the globe. The U.S. EPA has classified approximately one-quarter of U.S. banks in 2005 as being accessible (210 ODP-Kt⁸, roughly two-thirds, *i.e.*, approximately 140 ODP-Kt, accounted for by halons; and 1.9 (0.9-2.2) gigatons (Gt) carbon dioxide (CO₂)-equivalents, of which HCFCs account for approximately 1.0 (0.9-1.1) Gt CO₂-equivalents)⁸. Additional halon is likely present in stockpiles, but these amounts are not included in these estimates of U.S. banks owing to a lack of available data at this time.

- Emission histories derived from global ODS production and consumption data and assumed release functions have large uncertainties but suggest strong declines in global emissions of most ODSs other than HCFCs.

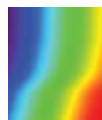
From national data quantifying applications that use ozone-depleting substances and substitutes the U.S. EPA has derived U.S. emission histories starting in 1985. Though these emissions estimates are recognized to have substantial uncertainties, they suggest that:

- Total emissions of ODSs and substitutes from the United States have declined substantially since the late 1980s. By 2005, U.S. emissions are estimated by the U.S. EPA to have declined by 81%, when emissions are weighted with factors relevant to ozone depletion. When weighted with factors relevant to climate, annual U.S. emissions of ODSs and substitutes including HFCs declined 74% (between 63 and 76% when indirect climate influences associated with ozone depletion are also included) over this same period.
- The United States accounted for a substantial fraction of global atmospheric mixing ratios of individual ODSs and HFCs measured in 2005, though precise quantification of these contributions is difficult owing to incomplete emission histories for most ODSs. The results suggest that U.S. emissions accounted for between 10 and 50% of the global atmospheric abundances of most ODSs and substitute chemicals measured in 2005, 17-42% of the tropospheric chlorine, 17-35% of the tropospheric bromine, and 15-36% of the tropospheric Equivalent Effective Chlorine (EECI)⁹ arising from these chemicals in that year.
- Changes in atmospheric chlorine and bromine inferred from U.S. emissions estimates of chemicals regulated by the Montreal Protocol have less uncertainty than absolute amounts. The data suggest that atmospheric chlorine from U.S. emissions has declined steadily since 1995, but atmospheric bromine from U.S. emissions in 2005 was similar to 1998 levels primarily as a result of recent increases in exempted critical uses⁶ and for QPS⁶ uses of CH₃Br.
- Atmospheric changes derived from U.S. emissions of chlorinated and brominated ODSs indicate a decline in total reactive halogen (EECI)⁹ arising from U.S. emissions through 2005, but a substantially slower rate of decline since 2003. The slower overall decline in 2004-2005 was because of the increases in U.S. emissions of brominated gases during these years (primarily CH₃Br).
- The direct climate influence (as direct radiative forcing)¹⁰ arising from the atmospheric abundances of ozone-depleting substances and substitute chemicals attributable to U.S.

⁸ Accessible banks are amounts of ODSs in use in fire extinguishers, refrigeration, and air conditioning sectors (not foams). While the accessible bank magnitude given was derived with direct GWP weighting, the ranges of bank magnitudes given in parentheses were derived with net GWPs, *i.e.*, where consideration of the indirect, ozone depletion influences of ODSs are included (see Box 2.2 for more details).

⁹ Equivalent Effective Chlorine, or EECI, is an index to approximately quantify the overall effect of ODSs on stratospheric ozone. It is calculated from surface measurements of ozone-depleting substances and accounts for the ODSs having different numbers of chlorine and bromine atoms, for the enhanced efficiency by which bromine atoms destroy ozone relative to chlorine, and the different rates at which ozone-depleting substances decompose in the stratosphere and liberate chemical forms of chlorine and bromine that can participate directly in stratospheric ozone-depleting reactions. Equivalent Effective Stratospheric Chlorine (EESC) is a related index, except that time lags associated with transporting air from the troposphere to the stratosphere are considered. These indices are described additionally in the text and in Box 2.7.

¹⁰ Direct radiative forcing is an estimate of the direct climate influence of a chemical and is expressed as energy per area (Watts per m²). It is calculated with knowledge of how a chemical absorbs infrared light in certain wavelength regions (its radiative efficiency) and is directly proportional to its atmospheric abundance for the less abundant greenhouse gases. Direct forcings do not include indirect radiative effects associated with feedbacks, such as those related to ozone depletion. Net forcings discussed in this chapter include the indirect forcings related to stratospheric ozone depletion (see Box 2.2 for further details).



emissions is estimated as having been between 0.067 and 0.16 W per m² in 2005. This U.S. contribution amounted to between 19 and 49% of the total global direct climate influence of these chemicals of 0.34 W per m². When indirect climate influences of ODSs related to stratospheric ozone depletion are considered, the U.S.-attributed forcing is between 0.04 and 0.18 W per m².

Direct observations of the atmosphere provide an independent assessment of the Montreal Protocol's success in reducing atmospheric abundances of ODSs and ozone-depleting chlorine and bromine. These observations show that:

- The global atmospheric abundances of all ODSs are responding to changes in global production and consumption magnitudes. Atmospheric mixing ratios of the most abundant CFCs, the most abundant chlorinated solvents, and CH₃Br are now decreasing. Increases are still observed for halon-1301, HCFCs, and HFCs. Methyl bromide mixing ratios have declined each year since global production was first reduced (1999), despite increases in Critical Use Exemptions recently, continued use in QPS⁶ applications, and substantial natural sources over which humans do not exert direct control.
- Global emissions magnitudes derived from global atmospheric data exhibit substantial declines since the 1980s, and provide independent confirmation of the large changes in global production and consumption as shown by UNEP⁵ in data reported to them. By 2005, global emissions had declined 77-82% compared to peak years, considering either the climate or ozone-depletion influences of ODSs and substitute chemicals.
- Tropospheric chlorine contained in all regulated ODSs and substitute chemicals has decreased since the early 1990s. Furthermore, measures of stratospheric chlorine show changes consistent with those observed in the troposphere. Stratospheric measurements also confirm that approximately 80% of stratospheric chlorine, which catalyzes ozone destruction, is from ODSs regulated by the Montreal Protocol. The remaining 20% is accounted for primarily by methyl chloride (CH₃Cl), though a small contribution (~2%) is from very short-lived chemicals.
- Tropospheric bromine from ODSs regulated by the Montreal Protocol has declined slowly since 1998. This decline has been dominated by tropospheric changes observed for CH₃Br. Measures of stratospheric bromine show changes consistent with those observed in the troposphere, though a decline in stratospheric bromine is not yet discernable. These stratospheric measurements indicate that approximately 50% of stratospheric bromine is from industrially produced halons and CH₃Br. The remainder is from naturally produced CH₃Br and from very short-lived chemicals produced primarily naturally.
- Observed changes in global atmospheric levels of ODSs containing chlorine and bromine demonstrate a substantial decline in the ozone-depleting halogen content of the atmosphere. The decrease since 1994 in the tropospheric halogen burden (EECI)⁹ accounted for by the long-lived ODSs considered here has been 20% of what would be needed to return EECI values to those in 1980 (*i.e.*, before substantial ozone depletion was observed). The decline in the shorter-lived gases methyl chloroform (CH₃CCl₃) and CH₃Br have contributed most to the observed decline. Decreases in stratospheric, ozone-depleting halogen (as Equivalent Effective Stratospheric Chlorine [EESC]) have been smaller because of the time delay associated with mixing tropospheric air into the stratosphere.
- The combined direct radiative forcing from ODSs and substitutes including HFCs is still increasing, but at a slower rate than in the 1980s. This trend arises primarily from slow declines in atmospheric abundances of CFCs and continued increases in abundances of HCFCs and HFCs. The total direct contribution of ODSs and substitutes was 0.34 W per m² in 2005 (it is 0.18-0.38 W per m² if the indirect ozone depletion forcing is included), compared to a contribution from CO₂, methane (CH₄), and nitrous oxide (N₂O) of 2.3 W per m².



INTRODUCTION

In an effort to heal the stratospheric ozone layer, schedules for the global phase-out of manmade ozone-depleting substances (ODSs) were set by the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer and its Amendments and Adjustments. This chapter

reviews the changes that have resulted from this international Protocol by assessing reported levels of ODS production and consumption, by deriving emissions with techniques independent of production and consumption estimates, by reporting on how these changes have influenced the atmospheric abundance of ODSs and chemicals used as substitutes, and by assessing

BOX 2.1: Key Issues

To facilitate a rapid phase-out of ODSs, the Montreal Protocol allowed the use of hydrochlorofluorocarbons (HCFCs) as interim substitutes for chlorofluorocarbons (CFCs). Temporary use of HCFCs was allowed because, even though HCFCs contain chlorine and are ODSs, they are much less efficient at causing stratospheric ozone depletion than the ODSs they replaced, and, therefore, have been considered as in-kind replacements to transition to a non-CFC world. Elimination of ODSs (including HCFCs) in nearly all applications is anticipated as the phase-out schedules run their course. Most uses of ODSs have been replaced with the non-ozone-depleting, non-chlorine-, and non-bromine-containing hydrofluorocarbons (HFCs) and other so-called “not-in-kind” alternatives (e.g., non-solvent-based cleaning processes, and hydrocarbon-based refrigerants). These changes have had a measurable influence on the global atmospheric abundance of these gases, with the result that the overall abundance of chlorine and bromine reaching the stratosphere has declined in recent years.

Therefore, the key issues, in the form of questions, that are related to ozone-depleting substances in the atmosphere and that are covered in this chapter, include:

- What is our best information on global production, consumption, and emissions of ozone-depleting substances, primarily CFCs and HCFCs, and HFCs, that are chlorine- and bromine-free, non-ozone-depleting, and longer-term replacements for CFCs and HCFCs? What are the associated uncertainties in these quantities?
- How can the combined influence of chlorinated and brominated ODSs in the stratosphere be quantified, and how is it likely to change in the future?
- What fraction of the produced ODSs is still sequestered and could be potentially released at a later date? (*i.e.*, what are the extents of the so-called “banks”?)
- What do the observations of ODS atmospheric abundances show about the levels of total atmospheric chlorine, bromine, and equivalent chlorine from these long-lived gases? In other words, are the atmospheric abundances actually responding as anticipated to restrictions set forth in the Montreal Protocol?

ODSs and halogenated chemicals used as substitutes have a second important property; they are efficient greenhouse gases (GHGs). As a result, they increase atmospheric heating and can influence climate. By requiring substantial reductions in global emissions of ODSs, the Montreal Protocol has led to societal benefits related to both stratospheric ozone depletion and climate change. The magnitude of this additional climate benefit has been diminished slightly, however, by small offsetting influences such as increased HFC emissions, and possibly by resulting stratospheric ozone increases, which may have a small warming influence. Therefore, it is important to know:

- What are the contributions of the various ODSs, and their substitutes, to climate forcing, in the past, now, and in the future?

Stratospheric ozone depletion is a global environmental issue. Yet, ODS emissions arise from various countries and regions. Also, the impact of ozone depletion is felt to different extents by different regions. Therefore, it is necessary to ask:

- What are the contributions of the United States to production and emissions of ODSs and substitute chemicals in the past?

This chapter attempts to address many of these issues to the extent possible for those that fall within the purview of this document.



In an effort to heal the stratospheric ozone layer, schedules for the global phase-out of manmade ozone-depleting substances (ODSs) were set by the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer and its Amendments and Adjustments.



how these atmospheric abundance changes have altered the influence of ODSs on stratospheric ozone depletion as well as their influence on climate. Furthermore, because this is a national assessment, this chapter provides estimates of these quantities for the United States and how they have changed over time.

This chapter is organized into six sections. In the first (Section 2.1), changes in reported production and consumption magnitudes of ODSs and substitute chemicals are discussed. These quantities provide important evidence elucidating how the Montreal Protocol has influenced human activities. The Protocol was written to control production and consumption of ODSs. Accordingly, countries report these quantities annually to the United Nations Environment Programme (UNEP) so that compliance with the Protocol can be assessed. The data are derived fundamentally from industry's records of production and international trade and provide the foundation for understanding how emissions of ODSs and substitute chemicals could change as a result of the Montreal Protocol. Limitations of the UNEP data are considered here through comparisons to AFEAS compilations (the Alternative Fluorocarbons Environmental Acceptability Study) (Section 2.1.2) and by considering the magnitudes of production and consumption for uses not regulated or restricted by the Protocol and, therefore, not included in the UNEP compilations (Section 2.1.3). Because the data compiled by UNEP are published on a country-by-country basis, a parallel analysis of U.S. consumption and production of ODSs and substitute chemicals is presented (Sections 2.1.4 and 2.1.5).

In the second section (Section 2.2), emissions magnitudes and changes are assessed because they provide a direct understanding of how policy decisions are altering human influences on the atmosphere. Global emissions are inferred from measured changes in the chemical composition of the remote atmosphere (the "top-down" method of estimation). Emissions derived in this way provide an important independent check on global production and consumption data reported to UNEP. Top-down estimates are also compared to "bottom up" global emission magnitudes estimates, which are derived from

sales data for different applications and time-dependent ODS leak rates from these different applications (AFEAS, 2007; UNEP/TEAP, 2006). As was the case for production and consumption, compound-dependent weighting factors related to stratospheric ozone depletion (Section 2.2.1) and climate (Section 2.2.2) are applied to emissions estimates to add relevance (see Box 2.2). Banks, *i.e.*, amounts of halocarbons that were produced but that have not been emitted to the atmosphere, account for a large fraction of present-day emissions for some halocarbons and are explored in Section 2.2.3. Banks are a particularly important topic because releases from banks account for much of the current emission of some ODSs, yet these releases are not restricted or addressed in the Protocol (Box 2.5). While U.S. regulations address recycling and venting of refrigerant, this represents a relatively small fraction of U.S. ODS banks and most, if not all, of this material will ultimately be vented to the atmosphere unless collected and destroyed. The contribution of emissions from other, non-restricted influences is discussed subsequently (Section 2.2.5).

Annual U.S. emissions of ODSs and substitute chemicals are estimated by U.S. EPA (2007) using a model analysis of sales and use within the United States (Section 2.2.5). U.S. emissions estimates are different from "top-down" global emissions estimates because they rely on the accuracy of industry-related production and sales data or assessments of market demand for ODSs and substitute chemicals. Comprehensive, independent assessments of U.S. emissions from atmospheric observations are not currently possible, though some useful conclusions are drawn from studies conducted to date (Section 2.2.6).

Atmospheric abundances of ODSs and substitute chemicals are discussed in Section 2.3. While emissions estimates provide a useful metric of how changes in human behavior are affecting the atmosphere, the influence of ODSs and substitute chemicals on stratospheric ozone and climate are dependent upon their atmospheric abundance, not rates of emission. The sensitivity of the atmosphere to emission magnitudes is determined by a chemical's persistence, which is quantified as an atmospheric lifetime.

Consistency between observed abundances of ODSs and substitute chemicals and calculated or expected abundances requires accurate estimates of both emissions and lifetimes (Section 2.3.1.1)

Halocarbon abundances in the remote atmosphere attributable to U.S. emissions are also derived for past years (Section 2.3.2). The U.S. contributions to global abundances are derived from histories of emissions since 1985 from the U.S. EPA (2007), and, for earlier years, a range of contributions of United States to global halocarbon emissions (Box 2.6).

Subsequently, the overall influences that the wide ranges of changes observed for individual gases are having or will have on ozone depletion (Section 2.4) and on climate forcing (Section 2.5) are discussed. Quantities such as total chlorine, total bromine, and Equivalent Effective Chlorine (EECl and EESC, see Box 2.7) are calculated to assess the changing influences on stratospheric ozone (Section 2.4). Radiative efficiencies are applied to observed atmospheric changes to assess the direct influence these forcings have on climate (Section 2.5). Indirect climate influences related to stratospheric ozone depletion arising from the use of ODSs are also considered.

Finally, though they are included throughout the document, findings related specifically to the United States are reviewed in Section 2.6. Results related to, for example, atmospheric abundances of ODSs calculated from consideration of U.S. emissions are summarized, as are the relative contributions of U.S. emissions to the measured global atmospheric abundances of ODSs and substitute chemicals (Box 2.6). Additional topics with enhanced relevance to U.S. policy are highlighted throughout the text in additional boxes. These include a discussion of methyl bromide (CH₃Br, Box 2.3) and HCFCs (Box 2.4).

Throughout this chapter different weighting factors are applied to quantities such as production, consumption and emission of ODSs. These weighting factors are useful for considering overall changes because different chemicals influence ozone and climate to different extents (see Box 2.2 for more

detail). With regard to stratospheric ozone, the weighting factors are Ozone Depletion Potentials (ODPs). With regard to climate, the weighting factors are 100-year Global Warming Potentials (GWPs). Two main influences are considered in the GWP calculations, the direct effect of a halocarbon on the radiative balance of the atmosphere, and the indirect influence arising from stratospheric ozone changes caused by a halocarbon. Here, the direct influence is accounted for by 100-year direct GWPs and the indirect influence is included by combining direct and indirect GWPs into net GWPs (see Box 2.2 for more detail). Different weighting factors are applied to atmospheric abundances of individual halocarbons to assess their influence on ozone or on the direct radiative forcing of the atmosphere. See Sections 2.4 and 2.5 for further discussion of these factors.

2.1 PRODUCTION AND CONSUMPTION OF OZONE-DEPLETING CHEMICALS AND THEIR SUBSTITUTES DERIVED FROM INDUSTRY ESTIMATES

2.1.1 Production and Consumption: Global Trends

Historical global data on production and consumption or sales of ozone-depleting chemicals are available through databases compiled from different countries by UNEP and from different companies by AFEAS (2007). The data provided by these organizations show how dramatically dispersive, regulated uses of ozone-depleting chemicals have changed over the past 20 years in response to the adjusted and amended 1987 Montreal Protocol on Substances that Deplete the Ozone Layer and to changing market conditions. Data are compiled on an annual basis by UNEP to assess compliance with the Montreal Protocol. The UNEP data provide more complete global coverage in recent years than AFEAS compilations but are not disaggregated by chemical in all instances; only production or consumption data aggregated by compound class are publicly available for CFCs, HCFCs, and halons. Other limitations include the UNEP data only being available for years since 1986, and not all countries have reported production or consumption figures to UNEP for all years. Despite these limitations, the UNEP compilation provides

Different chemicals influence ozone and climate to different extents. For this reason, weighting factors called Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) are useful for considering overall changes.



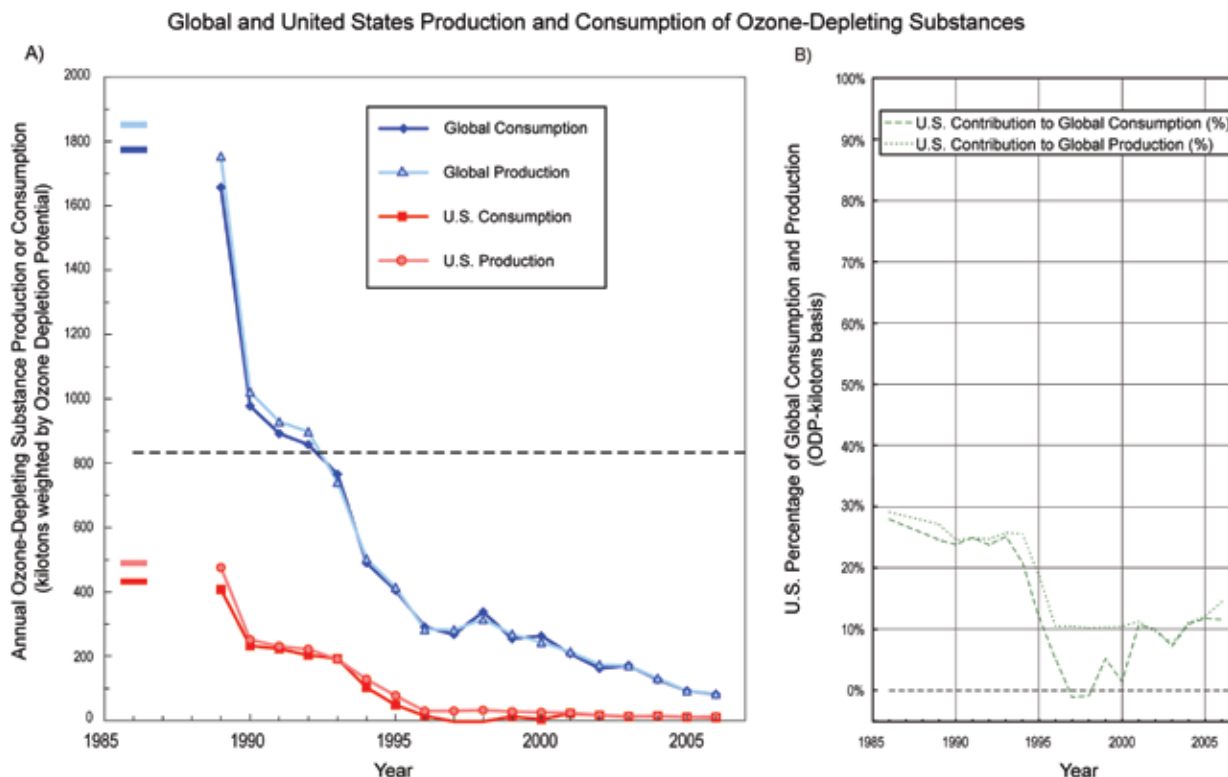


Figure 2.1 Panel A: Annual global production and consumption of all regulated ODSs and substitutes (dark and light blue solid lines) compared to similar quantities for the United States (dark and light red solid lines), as derived from data reported to UNEP (UNEP, 2007). Baseline production and consumption quantities are shown as separate bars with corresponding colors in 1986. All of these data are weighted by compound-dependent ODPs. Panel B: Percentage contributions of U.S. consumption and production to global totals. Negative consumption indicates exports being larger than the sum of imports plus production in a given year (see Section 2.1.4.1).

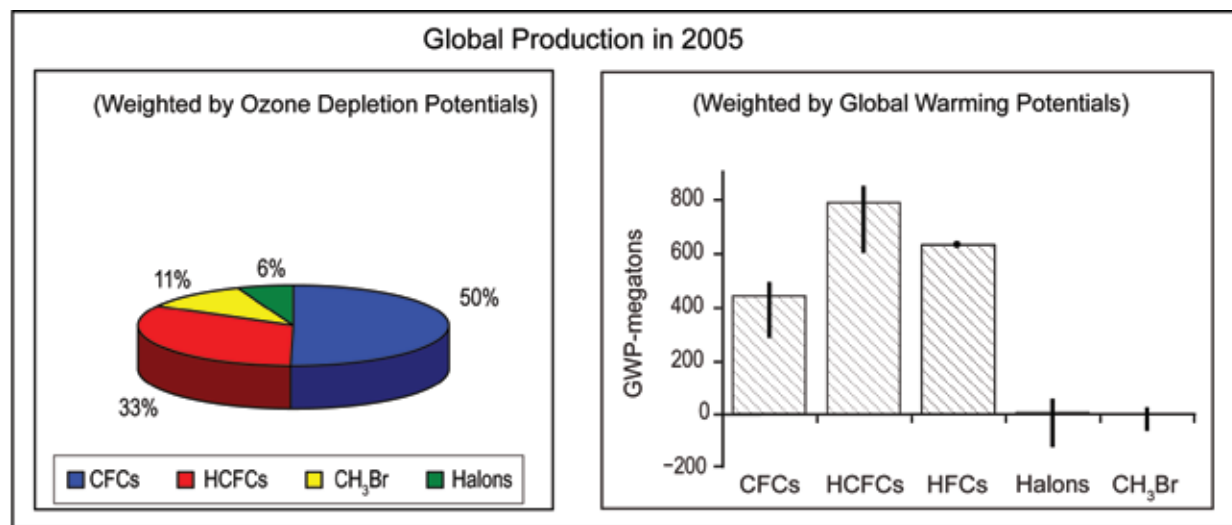


Figure 2.2 The contribution of different compound classes or compounds to total global, ODP-weighted production of ODS and substitute chemicals reported to UNEP for regulated uses for 2005 (left panel), and the global, GWP-weighted production of these chemicals in the same year (right panel) (UNEP, 2007; Personal communication, the UN Ozone Secretariat, 2007; AFEAS, 2007). The hatched bar heights in the right-hand panel were derived with direct GWPs; the given uncertainties represent weighting by net GWPs (see Box 2.2). HFC production includes only the portion of global HFC data reported by AFEAS (2007) for HFC-134a, HFC-125, and HFC-143a. For HFC-23, production was inferred from atmospheric data (Clerbaux and Cunnold *et al.*, 2007). Relative contributions of less than 1% are not included in these charts; note that the global CCl₄ ODP-weighted production was -7% during 2005, though its contribution was not included in this Figure. See Section 2.1.4.1 for additional discussion regarding negative consumption and production values.

Table 2.1 Declines in reported production or consumption and derived emission of ODSs and substitute chemicals (including HFCs) relative to magnitudes in the late 1980s.

Region	Production or Consumption Decline, 1989-2005 (%) ^a	Emission Decline Through 2005 (%) ^e
Weighted by Ozone Depletion Potentials		
Globe	95 ^b	82
United States	97-98 ^c	81
Weighted by 100-year Global Warming Potentials ^d		
Globe	81 (61-83) ^b	77 (77-84)
United States	87 (81-88) ^c	74 (71-75)
^a Considers production and consumption of ODSs for only dispersive uses restricted by the Montreal Protocol as shown by UNEP in data reported to them, plus HFC production and consumption or sales data without consideration of use. ^b Derived from the UNEP (2007) compilation of reported ODS production and consumption; AFEAS (2007) production data for HFC-134a, HFC-125, and HFC-143a; and HFC-23 production inferred from atmospheric data (Clerbaux and Cunbold <i>et al.</i> , 2007). ^c Derived from consumption of ODSs for restricted uses reported to UNEP (UNEP, 2007) but delineated by compound by the U.S. EPA; and the U.S. EPA (2007) vintaging model estimates for HFCs. ^d Declines indicated are calculated with direct GWP weighting but the ranges given in parentheses indicate the decline calculated when the indirect influence (and uncertainty) related to stratospheric ozone depletion is included in net GWP weighting factors (see Box 2.2). ^e Derived on a global scale from atmospheric data of ODSs and substitute chemicals and so includes all uses, regulated and not; derived on a U.S. scale from the U.S. EPA (2007) vintaging model estimates of emissions of ODSs and substitute chemicals. HFC global emissions in 2005 were interpolated from 2002 global estimates and the 2015 “business as usual” scenario in IPCC/TEAP (2005).		

critical data for assessing global and national changes in production and consumption for regulated uses of ODSs including CFCs, halons, carbon tetrachloride (CCl₄), methyl chloroform (CH₃CCl₃), HCFCs, and CH₃Br, particularly in recent years (UNEP, 2007). The data through 2005 indicate that annual global production and consumption of ODSs and substitutes for ODSs has declined by 1.6-1.7×10⁶ ODP-Tons since the Montreal Protocol was ratified (Figure 2.1). This corresponds to a 95% decline in both the ODP-weighted production and consumption of these chemicals across the globe by 2005 (Table 2.1) (see Box 2.2). The average total global production and consumption in 2004-2005 was approximately 1.1×10⁵ ODP-Tons per year.

In the data reported to UNEP aggregated by compound class, all classes showed declines in total global production and consumption during 2000-2005, though the relative decline was smallest for HCFCs (12 to 16%) and data for CCl₄ are quite variable year-to-year. Production and consumption of CFCs still dominates the ODP-weighted global totals. During 2005 ODP-weighted annual production (consumption) of CFCs accounted for 50% (48%), HCFCs 33% (34%), CH₃Br 11% (14%), and halons 6% (5%)

(CH₃CCl₃ and CCl₄ accounted for less than 1%) (Figure 2.2). Despite small declines in total production of HCFCs since 2000, the relative contribution of HCFCs increased substantially over this period so that by 2005 they accounted for 33% of total ODP-weighted production. Preliminary data suggest that global, ODP-weighted consumption of HCFCs equaled ODP-weighted consumption of CFCs in 2006.

Global production of ODSs and substitutes (unweighted data from UNEP, 2007; IPCC/TEAP, 2005) can be weighted by direct or net GWPs to estimate the potential influence that production could have on climate forcing (see Box 2.2) (Figure 2.3). When weighting by 100-year, direct GWPs is considered, the annual production of ODSs and substitutes declined by 8040 GWP-Mt from 1989 to 2005, which corresponds to a decline of 81% (Table 2.1) (Figure 2.3). A slightly smaller decline of 61 to 83% is calculated for global production through 2005 when net GWPs are used as weighting factors to account for the indirect influence of stratospheric ozone changes arising from the changing mix of ODSs (see Box 2.2). Increases in global HFC production have slowed the overall decline somewhat; production of HFCs

By 2005, annual global production and consumption of ozone-depleting substances (ODSs) and ODS substitutes declined by 1.6 to 1.7×10⁶ ODP-Tons since the Montreal Protocol was ratified.



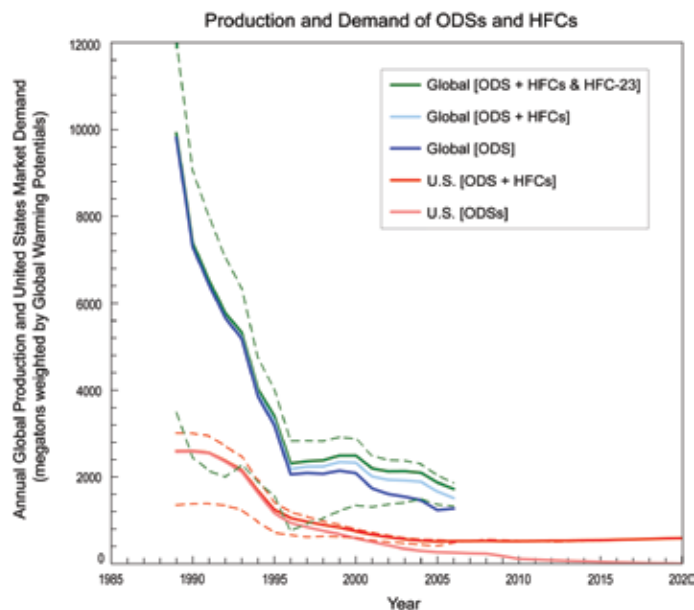


Figure 2.3 Global production of ODSs and HFCs compared to U.S. consumption estimates. Solid lines represent weighting by 100-year, direct GWPs. Dashed lines represent a range of total production or demand calculated with weighting by a range of net GWPs that include the indirect influence of stratospheric ozone on climate. A range of results, rather than a central value, is presented for net GWP weighting because of our incomplete understanding of how stratospheric ozone depletion has influenced climate (see Box 2.2). Results for subsets of different compound classes are also shown. Global ODS production derived from UNEP (2007) compilations (blue line) are compared to U.S. consumption data for ODSs (light red line). The additional influence of HFCs is shown on global (light blue and green lines) and U.S. scales (red line). The light blue line is derived by adding AFEAS global production data of HFC-134a, HFC-125, and HFC-143a (AFEAS, 2007) to the contribution of all ODSs. The green line includes additional inadvertent HFC-23 production derived from measured atmospheric trends (IPCC/TEAP, 2005; Clerbaux and Cunnold *et al.*, 2007). The contribution of HFCs to U.S. GWP-weighted production has been estimated from the U.S. EPA vintaging model (U.S. EPA, 2007). The contributions from other HFCs listed in Table 2.2 are not included here due to a lack of production information on global scales.

By 2004, annual global sales or consumption of CFCs and HCFCs declined by approximately 93% (1×10^6 ODP-Tons) since the late 1980s and since the Montreal Protocol went into force.

in 2005 is estimated here at approximately 630 GWP-Mt (production of HFC-134a, HFC-125, and HFC-143a from AFEAS [2007], and inadvertent production magnitudes of HFC-23 derived from atmospheric measurements [IPCC/TEAP, 2005]) (Figure 2.3).

Based upon these production figures and direct GWPs, CFCs accounted for 24%, HCFCs 42%, and HFCs 34% of the global, CO₂-equivalent production of all ODSs and their substitutes in 2005. The indirect influence associated with stratospheric ozone depletion alters these figures somewhat, though HCFCs and HFCs still account for the largest fraction of both direct and net GWP-weighted global production in 2005 (Figure 2.2). The contribution of HFCs

considered here is an underestimate because global production data on HFCs other than -134a, -125, -143a, and -23 are not currently available, though these four gases alone accounted for 95% of the global total, GWP-weighted demand for HFCs in 2002 (Campbell and Shende *et al.*, 2005).

2.1.2 Production and Consumption: Comparing UNEP and AFEAS Compilations

AFEAS has compiled production and sales data for individual compounds for many years (AFEAS, 2007). Though the data compiled by AFEAS and UNEP are not independent, they do allow for some cross checking and an assessment of consistency in the global totals reported for CFCs and HCFCs (Figure 2.4). The AFEAS compilation only includes data for some ODSs (CFCs, HCFCs, and HFCs) and only for a subset of companies around the globe that are producing ODSs and their substitutes. While this compilation accounted for most of global production and sales of CFCs and HCFCs in the 1980s and early 1990s, it has accounted for a smaller fraction since.

On an ODP-weighted basis, both the AFEAS and UNEP compilations show that by 2004 annual global sales or consumption of CFCs and HCFCs (weighted by chemical-specific ODPs) declined by approximately 1×10^6 ODP-Tons, or by 93%, since the late 1980s and since the ratification of the Montreal Protocol on Substances that Deplete the Ozone Layer by many countries (Figure 2.4). The totals from these two compilations during 1986-2004 are slightly different; annual AFEAS sales figures are $0.1 (\pm 0.03) \times 10^6$ ODP-Tons lower than consumption reported to UNEP, on average. This difference may represent errors in accounting or reporting of data, but is most likely the result of consumption outside the companies reporting to AFEAS, such as by countries operating under Article 5 of the Montreal Protocol (so-called “developing” countries). Since 1995, the annual UNEP – AFEAS difference has been $80 \pm 10\%$, on average, of the consumption reported by these Article 5 countries.

BOX 2.2: Weighting Factors

Accurately assessing the overall effect of changes in production, consumption, and emission of individual gases requires consideration of weighting factors that account for compound-dependent influences on ozone and climate (Clerbaux and Cunnold *et al.*, 2007; Daniel and Velders *et al.*, 2007). When considering the influence of ODS production, consumption, and emission on ozone depletion, Ozone Depletion Potentials (ODPs) are used. Units of these quantities are ODP-tons. When considering the direct or net influence of ODS on climate, direct or net 100-year Global Warming Potentials (GWPs) are used. Units on these quantities are GWP-tons or CO₂-equivalent tons. Ozone Depletion Potentials, direct and indirect Global Warming Potentials, and other compound-specific parameters used in this report are tabulated in Appendix 2A.

ODPs

Ozone Depletion Potentials represent the amount of global ozone destroyed by a particular ODS per unit mass compared to the amount destroyed by a reference gas (usually CFC-11) per unit mass. Ozone Depletion Potentials provide a simple way to compare ODSs with respect to their ability to deplete stratospheric ozone and have proved useful to scientists and policymakers since their initial development (Wuebbles, 1983). Ozone Depletion Potentials take into account the number of chlorine and bromine halogen atoms in a chemical, how rapidly these halogen atoms become released in the stratosphere, how reactive the halogen atoms are for ozone destruction (Cl vs. Br, for example), and how persistent the chemical is throughout the entire atmosphere (its lifetime). Steady-state ODPs are most commonly used and are applicable for longer time periods since they represent the steady-state ozone responses to ODS perturbations. Time-dependent ODPs also have been proposed (Solomon and Albritton, 1992) for use when a particular time horizon or the time-dependence of relative ozone destruction is of interest. Chapter 2 will use steady-state semi-empirical ODPs in this chapter (Solomon *et al.*, 1992), taken from Chapter 8 of the 2006 World Meteorological Organization (WMO) ozone assessment (Daniel and Velders *et al.*, 2007).

GWPs

Global Warming Potentials are analogous indices for comparing the integrated radiative impact of greenhouse gases (IPCC, 2007). They represent the cumulative radiative forcing of a unit mass of a gas relative to the same quantity for a unit mass of a reference gas (generally CO₂) over some time horizon (generally 100 years). Hence, the GWP provides an approximate measure of the relative integrated climate forcing of a GHG. While it is acknowledged to be an imperfect index, it is generally true that emission of a well-mixed gas that is characterized by a larger GWP than another well-mixed gas will lead to a greater climate response.

There are two components to GWPs that we will consider in this chapter. The first is from the direct effect of halocarbons. The addition of an ODS to the atmosphere initially leads to a reduction in the outgoing longwave radiation at the tropopause, causing a globally averaged warming. This results from the strong infrared absorption by the ODS, particularly in the transparent atmospheric window region (8-12 μm). The amount of the net radiative imbalance (down flux minus up flux) at the tropopause per unit mixing ratio increase in an ODS is called the “radiative efficiency” (e.g., units of W per m² per parts per billion by mole, ppb). The second component to GWPs considered in this chapter is from the destruction of ozone caused by ODSs. This ozone destruction leads to an additional radiative forcing that can be considered in discussions concerning the overall climate impact of ODSs. It is referred to as an “indirect” forcing because it is caused by the change in ozone (owing to ODSs) and not by the change in ODSs directly.

Our general approach in this chapter is to use direct GWPs as the primary weighting factors when considering climate-relevant magnitudes of production, consumption, or emission of ODSs. Uncertainties quoted on these direct GWP-weighted quantities, however, represent a range of net GWP weightings that include the rather uncertain indirect ODS forcing arising from stratospheric ozone depletion. The indirect and net GWPs are derived here from the indirect GWPs in WMO (2007) by considering the recent revision of the radiative forcing attributed to stratospheric ozone depletion from -0.15 ± 0.10 (IPCC, 2001) to -0.05 ± 0.1 W per m² (IPCC, 2007) (see Table 2A.3).



BOX 2.2: Weighting Factors *cont'd**Net GWPs*

Combining direct and indirect GWPs into net GWPs potentially leads to additional errors and has intentionally been avoided in IPCC/TEAP (2005) and WMO (2007). It is known that the direct and indirect processes will cause different spatial forcing, and it is possible that the climate response to these forcings will differ both in the global mean magnitude and in the spatial pattern (Joshi *et al.*, 2003). Therefore, it is inaccurate to think of direct and indirect GWPs or forcing as being additive. For example, if the direct and indirect GWPs were to exactly cancel each other, it is still expected that there would be a climate response. Nevertheless, in this chapter we have opted to use net GWPs in many situations. Our purpose in doing so is not to present a precise net GWP quantity, but to provide an approximate idea of how ozone destruction may affect some of the conclusions drawn from considering the direct effect alone. Doing so likely provides a more complete and accurate picture of overall climate forcing from ODSs than would be obtained from considering direct GWPs alone. Specifically, throughout the chapter, we provide analyses and conclusions based first on the more accurate direct GWPs and forcing. We then also consider net GWPs and forcing calculated assuming an indirect forcing for a total ODS-induced ozone depletion of -0.15 W per m^2 and $+0.05 \text{ W per m}^2$. These values are chosen to coincide with uncertainties on the $-0.05 \pm 0.10 \text{ W per m}^2$ IPCC (2007) ozone forcing estimate (\pm one-standard-deviation uncertainty). We neglect direct GWP uncertainties and other indirect GWP uncertainties, as we are not aware of a complete error analysis of these processes in the current literature.

GWP Uncertainties

The uncertainty in direct GWPs is stated to be about $\pm 35\%$ (\pm two-standard-deviation uncertainty), due primarily to uncertainties in the radiative efficiencies and lifetimes of the halocarbons and to uncertainties in the carbon cycle (see, e.g., IPCC, 2001; IPCC/TEAP, 2005; WMO, 2007; IPCC, 2007). Uncertainties in the carbon cycle are thought to lead to an uncertainty of about $\pm 15\%$ to the denominator of the GWP, or the CO_2 absolute GWP (IPCC, 2007). This error contributes to the uncertainty in the absolute GWP value, but affects each GWP in the same way. When one is more interested in comparing halocarbon direct GWPs than in the values themselves, an effective uncertainty level of something less than 35% can be assumed.

Uncertainties in the indirect GWPs have not been as well quantified. Two of the most important issues likely involve the absolute amount of forcing caused by the ozone depletion caused by ODSs, and the relationship between ODS-induced ozone forcing with Equivalent Effective Stratospheric Chlorine (EESC). IPCC (2007) has recently reduced the magnitude of the estimated forcing due to stratospheric ozone changes from -0.15 ± 0.10 (IPCC, 2001) to $-0.05 \pm 0.10 \text{ W per m}^2$. However, this forcing is due to the total ozone change, not only the ozone change due to ODSs. Because a better estimate does not currently exist, we will adopt this latest estimate and ignore the potential contribution of non-ODS processes to the value. It is not possible for us to estimate the error induced by this assumption at the current time. In the procedure for calculating indirect GWPs given in Daniel *et al.* (1995), there are assumed EESC “thresholds” that lead to discontinuities in the forcing/EESC relationship. Because of these forcing/EESC changes, indirect GWPs exhibit a dependence on the time of emission; this time dependence has likely been relatively small when compared to other uncertainties for emissions between 1970 and 2010 and will not be considered in this chapter. Nevertheless, this oversimplification of the forcing/EESC relationship leads to likely additional errors in the indirect GWPs that have not been quantified. Because of all the previously discussed uncertainties and errors, in this chapter, the indirect and net GWPs are used to provide a very general idea of how ozone depletion might affect conclusions obtained from a direct GWP weighting.

Indirect Forcing

The indirect forcing owing to ozone depletion and attributable to individual compounds, compound classes, or from the aggregate of U.S. emissions was estimated by scaling the global indirect forcing arising from global ozone depletion through 2005 ($-0.05 \pm 0.10 \text{ W per m}^2$) to the fraction of global Equivalent Effective Chlorine (EECI) attributable to the compound, a compound class, or the U.S. in 2005 (see Figure 2.15). This procedure suggests that the net forcing from ozone depletion attributable to U.S. ODS emissions was between 0.04 and 0.18 W per m^2 in 2005 (Figure 2.17).

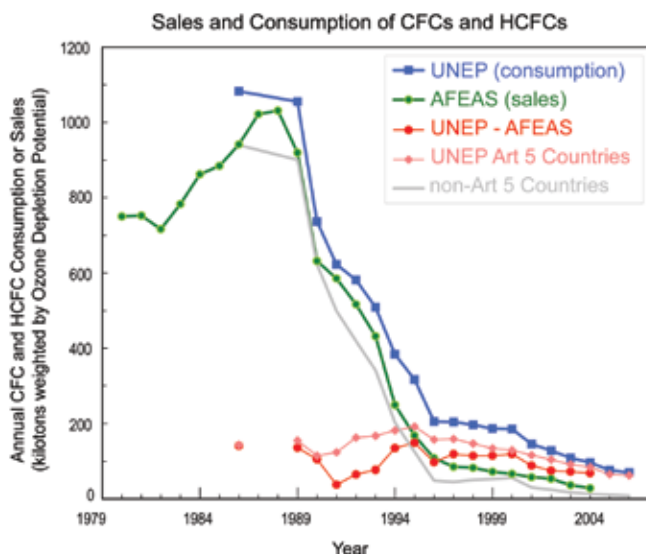


Figure 2.4 Comparison of annual AFEAS sales (green line) and annual UNEP consumption (blue line) totals for the aggregate of CFCs and HCFCs, weighted by Ozone Depletion Potential. Also shown is the annual difference (UNEP consumption minus AFEAS sales), and the magnitude of global consumption in countries operating under Article 5 of the Montreal Protocol, and non-Article 5 countries. Data were compiled by UNEP (2007) and AFEAS (2007).

During the years of highest consumption (1986-1990), the AFEAS compilation accounted for the majority of global consumption of CFCs and HCFCs. During the last decade, however, the data reported to UNEP suggest that 59 (± 8)% of global annual consumption was not included in the AFEAS compilation.

The accuracy of these data hinges on the reliability of sales and import-export magnitudes reported to AFEAS and UNEP by individual companies and nations. This is difficult to assess quantitatively with independent methods, though estimates of global emissions inferred from atmospheric observations provide an independent but qualitative confirmation that large decreases in production and consumption of ODSs have indeed occurred since the late 1980s. The smaller declines noted for emissions as compared to consumption or production (Table 2.1) likely arise in part because emissions of ODSs lag production by months to decades depending upon the specific application. The accuracy of production, consumption, sales, and emission data on a national basis is more difficult to assess by independent methods, though regional estimates of emissions and emission changes are an area of active research (Section 2.2.6).

The differences between the totals compiled by AFEAS and UNEP seem reasonable given the known differences in these databases. Finally, the consistency apparent in global total production and consumption data reported to UNEP suggests that the accounting of export and import activities has been reasonably accurate over time on a global scale (Figure 2.1).

2.1.3 Production and Consumption of ODSs and Substitutes Not Reported by AFEAS or in UNEP Compilations

In UNEP compilations, only production and consumption of ODSs for dispersive uses regulated by the Montreal Protocol are included. There is substantial additional production of ODSs for use as reagents in chemical manufacture of other substances (known as feedstock use) and for treatments to prevent the introduction or spread of pests and diseases during import/export of goods (known as quarantine and pre-shipment (QPS) processes) that are neither restricted by the Montreal Protocol nor included in the production and consumption data compiled by UNEP. Global production for feedstock uses was estimated at 3.2×10^5 ODP-Ton in 2002 (UNEP/CTOC, 2007), or about 1.9 times the total production of ODSs reported for dispersive uses in that year (UNEP, 2007). Emissions from this production are estimated to be 0.5% of amounts produced for feedstock use, but this estimate does not include any additional emissions that may occur during use. ODSs produced substantially as feedstocks include CFC-113, CCl_4 , CH_3CCl_3 , HCFC-22, HCFC-142b, CH_3Br , and halon-1301.

In addition to feedstock applications, methyl bromide is sold for QPS applications that are not restricted or limited by the Montreal Protocol. In 2005, global production for QPS uses of 0.8×10^4 ODP-tons was similar in magnitude to the non-QPS production reported to UNEP of 1.1×10^4 ODP-tons (UNEP/



The total decline in annual U.S. production or consumption of ozone-depleting substances (ODSs) for dispersive uses restricted by the Montreal Protocol since the late 1980s through 2005 was 0.4 to 0.5×10⁶ ODP-Tons. This represents a 97 to 98% decline in both U.S. production and consumption of ODSs over this period.



MBTOC, 2007). Based on data for CH₃Br use in QPS applications during 1999-2005, including this non-restricted production would increase UNEP-reported, global ODP-weighted production for all ODS by 2 to 9%, and it would influence the estimate of the total decline in ODP-weighted production since the late 1980s given in Table 2.1 only minimally (a decline of 94.3% when QPS is included, compared to 94.7%—rounded to 95% in this Table—when not included). Global production of CH₃Br for QPS is expected to increase in 2006-2007 (UNEP/MBTOC, 2007).

Production magnitudes for three HFCs are currently reported by AFEAS. These data are thought to account for a large fraction of total global HFC production. In 2003, estimates of HFC-134a global production capacity (Campbell and Shende *et al.*, 2005) exceeded AFEAS production data (AFEAS, 2007) for this compound by only 10%. Similar data for other HFCs are not currently available on a global or national basis primarily because of the relatively few number of production facilities. Most of HFC-23 in the atmosphere today arises from overfluorination during the production of HCFC-22 rather than direct production. As a result, production of HFC-23 can be estimated globally based upon emissions inferred from atmospheric measurement records (Clerbaux and Cunnold *et al.*, 2007) though this would be an underestimate if any HFC-23 produced during HCFC-22 manufacture were captured and destroyed. On national scales, HFC-23 production has been estimated from HCFC-22 production magnitudes (U.S. EPA, 2007).

2.1.4 Production and Consumption: United States Trends for ODSs and Substitutes

2.1.4.1 UNITED STATES PRODUCTION AND CONSUMPTION WEIGHTED BY OZONE-DEPLETION POTENTIAL (ODP)

Production and consumption magnitudes of ODSs for regulated, dispersive uses in the United States are reported to UNEP as part of requirements associated with being a signatory to the Montreal Protocol (UNEP, 2007). The data indicate large declines in U.S. production and consumption of most chemicals as a result of the adjusted and amended Montreal Protocol. The total decline in annual U.S. production or

consumption of ozone-depleting substances for dispersive uses restricted by the Protocol since the late 1980s through 2005 was 0.4-0.5×10⁶ ODP-Tons (Figure 2.1). This represents a 97-98% decline in both U.S. production and consumption of ODSs over this period (Table 2.1). The total U.S. ODP-weighted consumption and production of ODSs reported to UNEP for 2004-2005 averaged 1.2-1.3×10⁴ ODP-Tons per year.

An analysis of data reported to UNEP reveals that the contribution of the United States to total global ODS production and consumption for regulated, dispersive uses decreased from a mean of 25 (±2)% in 1986-1994 to 10 (±2)%, on average, during 2001-2005 (Figure 2.1). In the interim years (1996-2000) large differences between reported U.S. production and consumption are apparent owing to negative consumption of carbon tetrachloride. Negative consumption is reported when exports outweigh the sum of production plus imports, or when destruction of stockpiles or feedstock use outweighs production in any given year.

Though the mean contribution of the United States to global, ODP-weighted production and consumption of ODSs for regulated, dispersive uses has been 10 (±2)% since 2001, the contribution of different compound classes to this amount varies. Over this period the United States accounted for less than 3% of global annual consumption of CFCs, CH₃CCl₃, and halons, between 20 and 39% of HCFC annual consumption, and between 17 and 37% of CH₃Br annual consumption (UNEP, 2007).

The large range observed for some compounds and compound classes since 2001 reflects changes in U.S. contributions over this period. In data reported to UNEP (2007) during 2003-2005, the United States accounted for 22±2% of global HCFC consumption during these years (19±1% of production). This is notably lower than the U.S. contribution during the previous decade. During 1992-2002 the United States accounted for 38±3% of global HCFC consumption (40±4% of production). HCFCs accounted for over half of total U.S. consumption in 2005 weighted by ODP, the remaining consumption was CH₃Br (34%) and

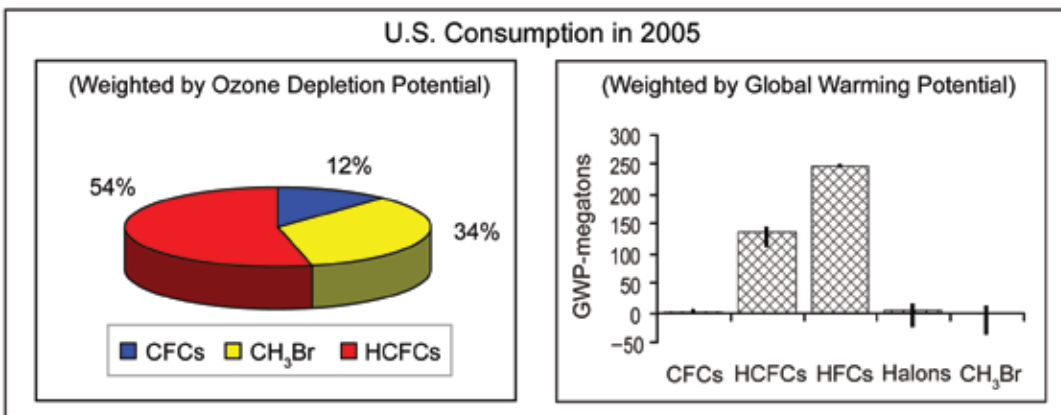


Figure 2.5 Contributions of different compound classes or individual compounds to total United States, ODP-weighted consumption or sales of ODSs and substitutes reported to UNEP for uses restricted by the Montreal Protocol or estimated by the U.S. EPA (left panel), and total United States, GWP-weighted consumption or sales of these chemicals in the same year (right panel) (UNEP, 2007; U.S. EPA, 2007). The hatched bar heights in the right-hand panel were derived with direct GWPs; the given uncertainties represent weighting by net GWPs (see Box.2.2). Relative contributions of less than 1% are not included in these charts; note that the U.S. CCl₄ ODP-weighted consumption was -16% during 2005, though this contribution was not included in the total or shown in the pie chart.

CFCs (12%); other compounds contributed less than 1% (Figure 2.5).

Consumption of CH₃Br in the United States for dispersive uses restricted by the Montreal Protocol has also varied in recent years. It decreased from 1999 to 2002 but then increased from 2003-2005 owing in part to Critical Use Exemptions (UNEP/MBTOC, 2007). The U.S. methyl bromide consumption in 2003-2005 was 1.3 to 2.8 times higher than consumption in 2002. Global consumption has declined fairly steadily since 1999 and, as a result, the U.S. contribution to global CH₃Br reported consumption for uses restricted by the Montreal Protocol increased from 23 ± 4% during 2000-2003 to 36 ± 1% during 2004-2005. Since 2005, amounts approved for Critical Use Exemptions (CUEs) in the United States have declined (UNEP/MBTOC, 2007).

2.1.4.2 UNITED STATES CONSUMPTION WEIGHTED BY GLOBAL WARMING POTENTIAL (GWP)

United States consumption data for ODSs and substitutes (UNEP, 2007) has been combined with the U.S. EPA vintaging model estimates of HFC demand (U.S. EPA, 2007) to assess magnitudes and changes in U.S. consumption of halocarbons weighted by climate-relevant factors. The data suggest large declines in the consumption of ODSs and their substitutes when weighted by 100-year, direct GWPs (Figure

2.3). By 2005, the annual consumption of these chemicals had declined by approximately 2600 Mt CO₂-equivalents (87%, Table 2.1) from amounts reported and estimated for 1989. The ozone depletion arising from use of ODSs may have offset some of this warming influence. The magnitude of this offset can be approximated by considering net GWPs that include this indirect effect, though the uncertainties in this indirect influence are large (Box 2.2). With this indirect effect included, U.S. consumption of ODSs and substitutes declined by 81-88% from 1989 to 2005 (1305-3010 Mt of CO₂-equivalents). The total U.S. direct GWP-weighted consumption of ODSs and substitutes during 2004-2005 was nearly 400 Mt CO₂-equivalent (310-420 Mt CO₂-equivalent if the indirect influence associated with ozone depletion is included). The decline in CO₂-equivalent consumption has decreased slightly faster in the United States than across the globe; the contribution of the United States to total global ODS production and consumption for regulated, dispersive uses was 30% in 1989 and 21% in 2005 when direct GWP weighting is used. If net GWPs are considered, the U.S. contribution decreased from 24-48% in 1989 to 20-23% in 2005. Whereas in the late 1980s more than 90% of CO₂-equivalent U.S. consumption resulted from CFCs, in 2005 more than half of U.S. CO₂-equivalent consumption was of HFCs and nearly all the rest was of HCFCs (Figure 2.5).

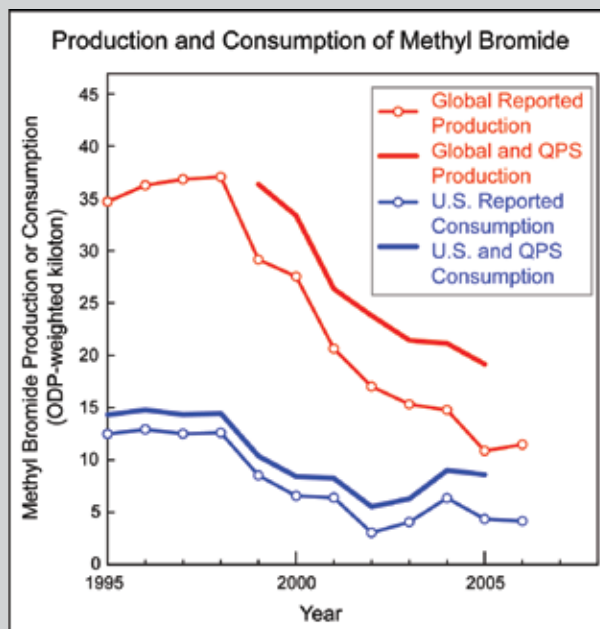
The decline in CO₂-equivalent consumption of ozone-depleting substances and substitute chemicals decreased slightly faster in the United States than across the globe from 1989 through 2005.



BOX 2.3: Focus on Methyl Bromide

Methyl bromide is unique among ODSs regulated by the Montreal Protocol for several reasons. First, natural processes emit substantial amounts, in addition to there being significant releases from industrial uses. Emissions arising from human-produced CH₃Br accounted for 30 (20-40)% of global emissions during the mid-1990s before industrial production was reduced in response to Montreal Protocol phase-out schedules (Clerbaux and Cunbold *et al.*, 2007). Since 1998, human production for all fumigant-related applications has declined by about 50%.

Second, a substantial fraction of industrial production is for dispersive applications not restricted by the Protocol. These unrestricted uses, primarily in quarantine and pre-shipment (QPS) applications, have increased recently and have led to a slower decline in total global CH₃Br production than suggested by UNEP values reported to them for assessing compliance with the Protocol. For example, during 2005 nearly half (43 (36-49%)) of the global, industrially derived emissions of CH₃Br were from uses not restricted by the Montreal Protocol (*i.e.*, QPS applications) and, therefore, were not included in the production and consumption data shown by UNEP as reported to them (Box Figure 2.3-1) (UNEP/MBTOC, 2007). Such use is expected to increase in the future (UNEP/MBTOC, 2007). In the United States, QPS consumption increased by about 13% per year, on average, during 2001-2006 (U.S.EPA, 2007), leading to an annual consumption 30 to 80% higher than the annual amounts reported to UNEP during these years.



Box Figure 2.3-1 Annual global production and U.S. consumption magnitudes for restricted uses reported to UNEP (UNEP, 2007) (lines with circles), which includes CUE amounts, compared to these reported amounts plus use in QPS applications considered (solid lines) (UNEP/MBTOC, 2007; U.S. EPA, 2007)(feedstock uses not included).

Third, declines in CH₃Br production and consumption have also been slowed by exemptions to protocol restrictions for critical uses (Critical Use Exemptions or CUEs) that have allowed substantial continued production and consumption past the 2005 phase-out in developed countries. Enhanced CUEs in the United States have resulted in higher annual consumption of CH₃Br and an increased United States/Global consumption ratio during 2004-2005 compared to 2002-2003 (Box Figure 2.3-1).

Despite increases in QPS use and enhanced CUEs in recent years and variability in underlying natural emissions, global atmospheric mixing ratios of CH₃Br have declined continuously since 1998 (Clerbaux and Cunbold *et al.*, 2007). While the United States contributed much to this atmospheric decrease through 2002, this U.S. trend reversed in 2003; the atmospheric abundance of bromine attributable to U.S. emissions was higher in 2004-2005 compared to 2002-2003 primarily because of enhanced QPS and CUEs consumption of CH₃Br in the United States (Figure 2.14).

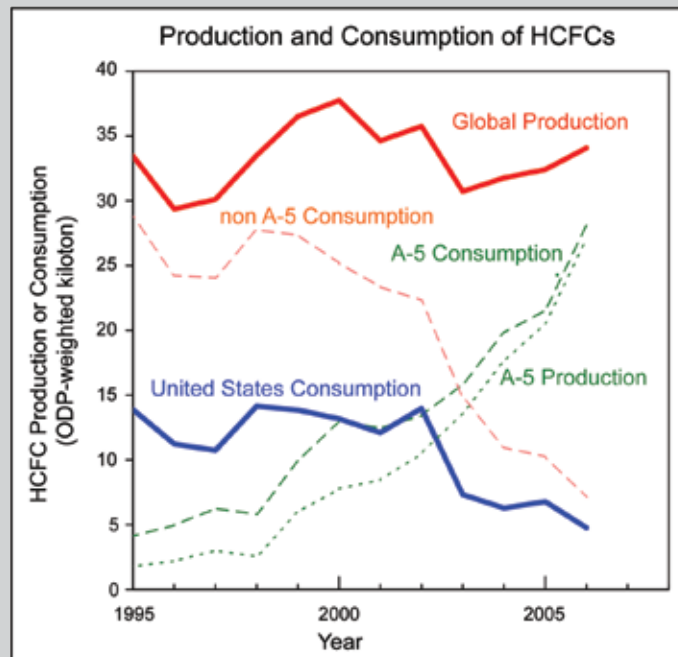


BOX 2.4: Focus on Hydrochlorofluorocarbons (HCFCs)

HCFCs were attractive substitutes for CFCs because they have similar properties to CFCs in many applications, but shorter lifetimes, generally fewer chlorine atoms per molecule, and, therefore, lower ODPs and GWPs.

In spite of these attributes, HCFCs still lead to stratospheric ozone depletion and affect climate. Hence, HCFCs are considered only temporary replacements for the most potent ODSs. Production of HCFC-22 causes an additional climate influence through the unintended formation of the byproduct HFC-23, itself a long-lived, potent greenhouse gas.

The temporary nature of HCFC use is reflected in how developed-country consumption totals have changed in recent years (Box Figure 2.4-1). Consumption has declined substantially in developed countries (non-Article 5) and in the United States in response to the HCFC phase-out outlined in the Protocol. Production on a global scale has remained relatively constant over this time, however, as production and consumption in developing countries (Article 5) have increased dramatically.



Box Figure 2.4-1 Annual production and consumption totals for HCFCs as reported to UNEP for dispersive and regulated uses, weighted by ODPs (UNEP, 2007). Global production (red line) is compared to U.S. consumption (U.S. Cons.; blue line), consumption in all developed countries (non Article 5; developed countries; red dashed line), and both consumption and production in developing countries (Article 5 country consumption and Article 5 country production; green dashed and dotted lines; developing countries).

U.S. EPA vintaging model estimates suggest that U.S. HCFC annual emissions have increased by about 10% since 2002, despite U.S. reported annual consumption during 2003-2005 being about half of what it was from 1995-2002 (Box Figure 2.4-1). This apparent discrepancy likely arises from the large bank of HCFCs; while HCFC emissions were similar to HCFC consumption in 2005 (~6 ODP-Kt) the HCFC bank was more than ten times larger (Box 2.5). In the U.S. during 2005, HCFC-22, HCFC-142b, and HCFC-141b accounted for 98% of all U.S. HCFC emissions. The remainder was contributed by HCFC-225 (1.2%), HCFC-124 (0.6%), and HCFC-123 (0.3%).

An increased awareness of the influence ODSs have on both climate and stratospheric ozone has led to recent proposals for more stringent HCFC limits to future use by several Parties to the Montreal Protocol, including the United States. The accepted proposal speeds up the production and consumption phase-out schedule for non-Article 5 and Article 5 countries and moves the Article 5 country consumption baseline year forward to 2009-2010 from 2015. This earlier baseline year is expected to reduce Article 5 country consumption beginning in at least 2013, the first year consumption limits would be in force. The potential future implications of this accepted proposal on the evolution of EESC are summarized in Chapter 5.

Emissions estimates allow an understanding of how human behaviors influence the atmospheric abundances of ODSs and their substitutes, and how that influence has changed over time as a result of international agreements (such as the Montreal Protocol) and other factors.



2.1.5 United States Production and Consumption of ODSs and Substitutes Not Included in Published UNEP Compilations

Production and consumption of ODSs for chemical feedstock purposes and of CH₃Br for QPS applications are not included in UNEP compilations because these uses are not restricted by the Montreal Protocol. While losses from feedstock applications are estimated to be small (0.5%, see Section 2.2.4), most CH₃Br used in QPS applications is emitted to the atmosphere (UNEP/MBTOC, 2007). Furthermore, amounts of CH₃Br used in QPS applications are substantial compared to amounts reported to UNEP for restricted uses and they have increased in recent years. For example, in the United States, annual consumption of CH₃Br in QPS applications during 2001-2006 was 1.8-2.9 Kt, or 57 (±20)% of annual consumption reported by the United States to UNEP for restricted uses; this QPS use had increased by about 13% per year, on average, over this period (U.S. EPA, 2007).

U.S. production data for HFCs are not publicly available either through UNEP, AFEAS, or the U.S. EPA. Estimates of HFC demand and sales, however, are made by the U.S. EPA through its vintaging model (U.S. EPA, 2007). These estimates show how HFC use in the United States has increased by a factor of three over the past decade, when use is weighted by compound-dependent GWPs. HFC use in the United States accounted for about two-thirds of the CO₂-equivalent consumption of ODSs and substitutes in 2005 (Figure 2.5). This vintaging model projects a doubling of CO₂-equivalent HFC use in the United States during 2005-2015 (U.S. EPA, 2007).

2.2 EMISSIONS: OZONE-DEPLETING CHEMICALS AND THEIR SUBSTITUTES

Emissions estimates allow an understanding of how human behaviors influence the atmospheric abundances of ODSs and their substitutes, and how that influence has changed over time as a result of international agreements (such as the Montreal Protocol) and other factors. Only after chemicals become emitted to the atmosphere do they contribute to ozone depletion and

radiative heating of the atmosphere. Nearly all ODSs produced ultimately become released to the atmosphere through direct emission (*e.g.*, use in aerosol cans) or leakage during use or upon disposal. Methyl bromide is an exception, because a substantial fraction that is produced and applied to soils becomes destroyed through hydrolysis and does not reach the atmosphere.

Global emissions can be estimated from production data, knowledge of release rates during production, use, and disposal of ODSs in different use applications, and information on the magnitude of sales for different end uses over time (AFEAS, 2007). Uncertainties can be significant in this “bottom-up” approach—but, in general, emissions are delayed after production with time lags that are application-dependent. Because these estimates rely on the production data considered in Section 2.1 of this chapter, they are not independent of them. Furthermore, restrictions on reporting of production and consumption for ODS and substitutes can substantially influence emission estimates, particularly when a limited number of manufacturers produce a specific chemical.

Independent estimates of global emissions can be derived from an analysis of atmospheric observations. This “top-down” approach provides an important independent check on production and consumption magnitudes reported to UNEP, and is critical for assessing global emissions considering the limitations of the “bottom-up” methodology. The observationally derived emissions are based on the measured change in the global atmospheric burden of an ODS relative to the expected rate of change in the absence of emissions. Accordingly, this calculation incorporates the atmospheric lifetime of the ODS, which is derived from laboratory measurements of destruction rate constants (via photolysis and or oxidation by the hydroxyl radical, OH) and model-derived parameters such as photolytic fluxes, OH abundances, and 3-D distributions of ODS atmospheric mixing ratios. This method of estimating emissions is susceptible to errors in measurement calibration, in estimating the global atmospheric burdens of trace gases in the entire atmosphere from a few measurement locations at Earth’s surface, in lifetime, and in the assumption (generally

applied) that all observed changes are the result of changes in emissions, not changes in loss rates. Atmospheric measurement techniques have improved over time to the extent that the majority of the uncertainty in this approach for long-lived ODSs is believed to arise from the estimates of lifetime and loss (UNEP/TEAP, 2006).

Global emissions for ODSs have been derived with these different techniques and have been compared and reviewed in past WMO Ozone Assessment Reports (2003; 2007) and in the IPCC/TEAP (2005). Particular discrepancies in bottom-up *versus* top-down emission magnitudes were noted in IPCC/TEAP (2005) for the years since 1990 and were investigated additionally in a special Emissions Discrepancies report (UNEP/TEAP, 2006). In this latter report, the potential for rapid-release applications and time-dependent release functions to influence bottom-up emissions estimates was explored and a more comprehensive analysis of top-down uncertainties was presented. For the compounds studied (CFC-11, CFC-12, HCFC-22, HCFC-141b, and HCFC-142b), the range (± 1 sigma) of emissions estimated with top-down and bottom-up methods overlapped in nearly all years and, therefore, were considered to be consistent estimates (Figure 2.6) (UNEP/TEAP, 2006). The uncertainty ranges are quite large in both approaches, however, such that the mean CFC-11 emissions estimated from these different methods differed generally by a factor of between 1.5 to 2. The overall trends in emissions estimated for these chemicals since 1990 were generally consistent, with the exception being HCFC-142b since 2000. While the bottom-up analysis suggests a rapid decline in emissions of this HCFC over this period, the top-down trends indicate only a small decline.

2.2.1 Global Emissions: Estimates Derived From Atmospheric Observations and Weighted by Ozone Depletion Potentials

Estimates of ODS emissions on a global scale have been derived for the past from a combination of atmospheric observations and industrial estimates (WMO Scenario A1, Daniel and Velders *et al.*, 2007). This emission history indicates substantial declines in total ODP-weighted emissions since 1990. By 2005, annual

emissions had declined nearly 1.1 ODP-Mt from peak emissions in 1988. This corresponds to an 82% decrease in global annual ODP-weighted emissions over this period (Figure 2.7; Table 2.1). Decreases in emissions of CFCs accounted for the majority of this decline (~80%). Decreases in emissions of CH_3CCl_3 and CCl_4 accounted for 6 and 8% of the decline, respectively; emissions decreases in halons and CH_3Br each accounted for 2-3% of the decline. Increases in HCFC ODP-weighted emissions have offset some of the overall decline since 1990; annual HCFC emissions increased from 1.1×10^4 in 1990 to 2.2×10^4 ODP-Tons in 2005. Total global

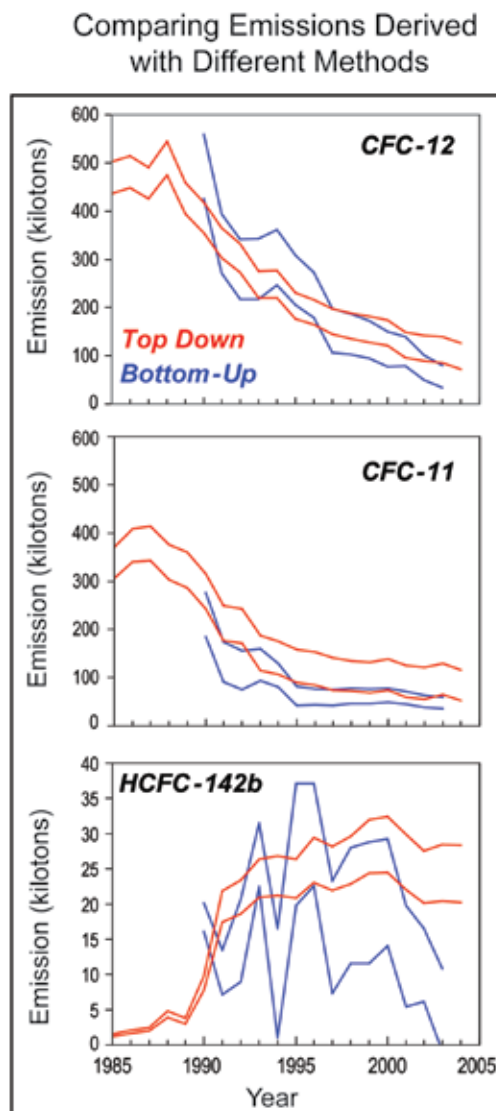


Figure 2.6 Comparison between global emissions derived from measured changes in the global atmospheric mixing ratio of CFC-12, CFC-11, and HCFC-142b (top down method; emissions bounded by red lines) and global emissions derived from an analysis of sales for different uses and estimates of releases from those uses over time (bottom-up method; emissions bounded by blue lines) (UNEP/TEAP, 2006).

By 2005, annual emissions of ozone-depleting substances declined by 82% from peak emissions in 1988.

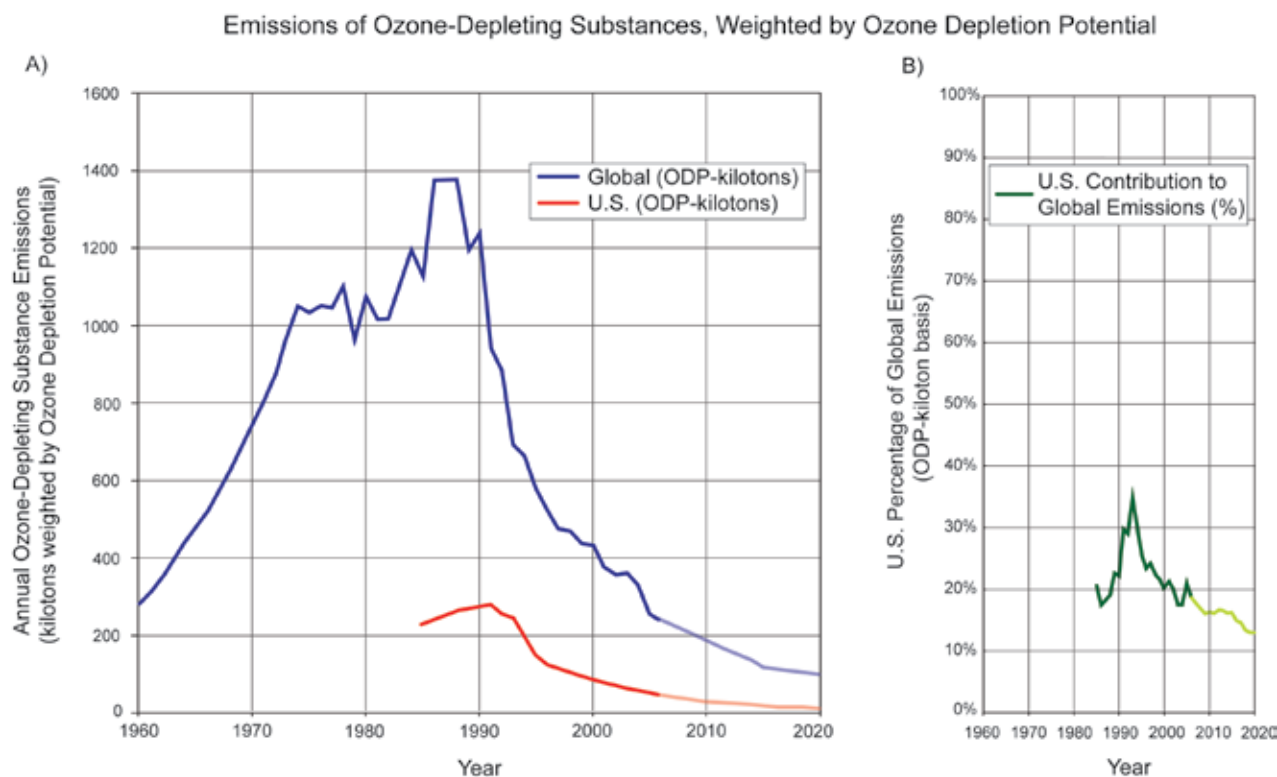


Figure 2.7 Panel A: Aggregated emissions of ODSs derived for the entire globe (blue line; Clerbaux and Cunnold *et al.*, 2007; Daniel and Velders *et al.*, 2007) and for the U.S. (red line; U.S. EPA, 2007) over time, weighted by ODP. Lighter lines represent projections into the future. Panel B: The percentage of emissions (weighted by ODP) contributed by the United States to the global total. Global emissions here are derived from atmospheric observations (Clerbaux and Cunnold *et al.*, 2007); U.S. emissions are inferred from a bottom-up analysis of sales data in the U.S. (U.S. EPA, 2007).

emissions of ODSs and substitutes amounted to 2.5×10^5 ODP-Tons in 2005. Because these global emissions estimates are derived from atmospheric observations, they include the influence of all processes releasing ODSs and substitutes to the atmosphere, including releases from non-reported, QPS, Critical Use Exemptions, and all others.

2.2.2 Global Emissions: Estimates Derived From Atmospheric Observations and Weighted by Global Warming Potentials

When the global emission history compiled as the WMO scenario A1 (Daniel and Velders *et al.*, 2007) is combined with global emissions derived for HFCs (Campbell and Shende *et al.*, 2005), the results indicate a substantial decline in total GWP-weighted emissions since the late 1980s when the climate influences of ozone depletion are not included (Figure 2.8). The overall decline in annual emissions amounted to 7270 GWP-Mt by 2005, which corresponds to a 77% decrease from peak global GWP-weighted emissions in 1988 (Table 2.1). With

weighting by net GWPs to include consideration of indirect forcing from ozone changes, the global decline in annual emission is estimated to be between 3600 and 8500 GWP-Mt, or a decline of 77-84%. The decline integrated between 1988 and 2005 amounts to a decrease of over 90 Gt CO₂-equivalents compared to constant emissions at 1988 levels. Declines in annual CFC emissions accounted for a decrease of 7900 (5330-8790) GWP-Mt by 2005, but this decline was partially offset by increases in HCFC and HFC annual emissions from 1990 to 2005 of 210 (150-230) and 530 GWP-Mt, respectively (numbers in parentheses represent quantities with a range of net GWP weightings; see Box 2.2).

In 2005, total global emissions of ODSs and substitutes are estimated to have been 2150 GWP-Mt (direct GWP weighting; a range of 675-2600 is calculated with the range of net GWPs). CFCs accounted for 810 (510-910), HCFCs 590 (470-630), and HFCs 625 GWP-Mt of this emission (HFC global emissions for 2005 were interpolated from 2002 estimates and for

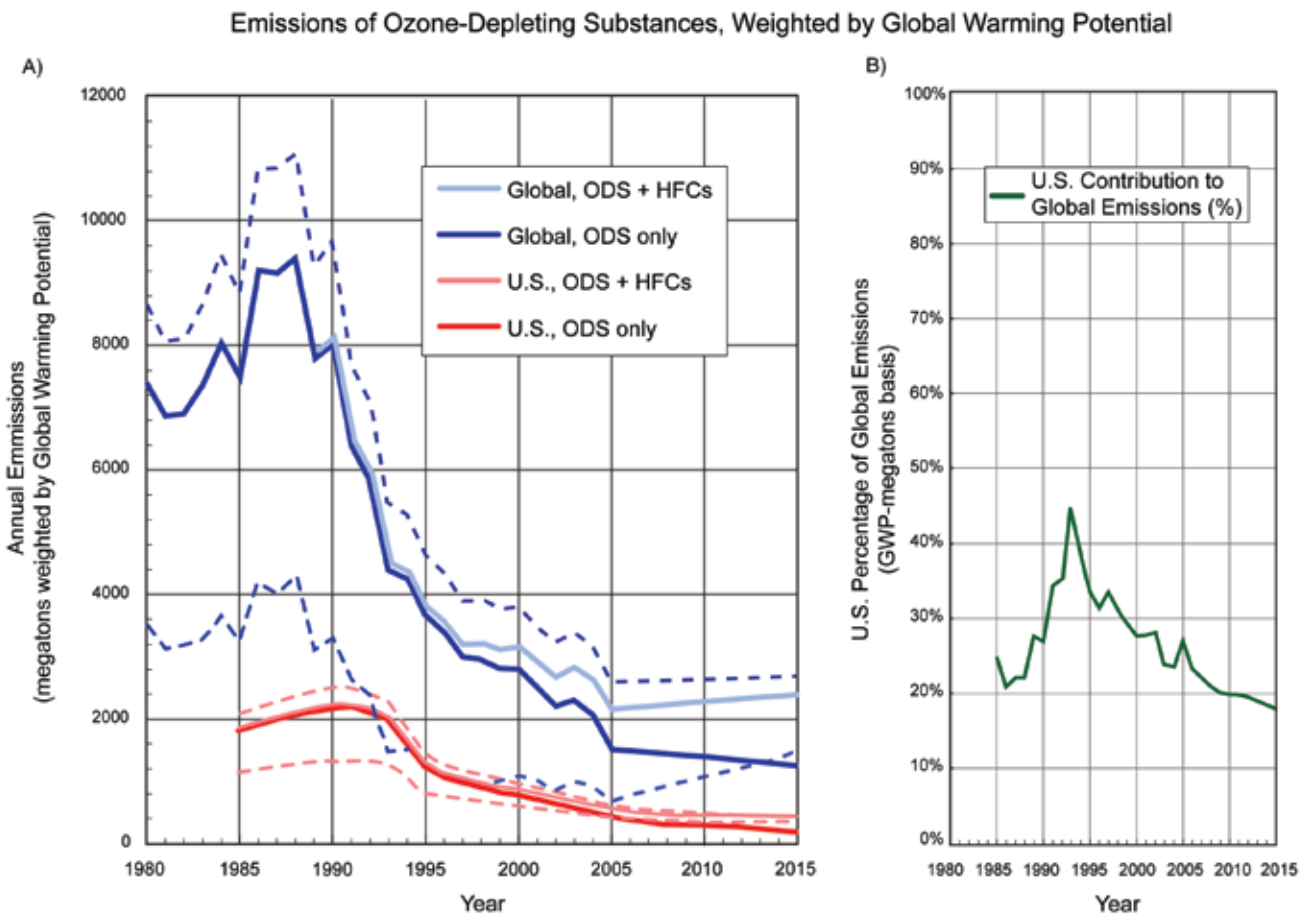


Figure 2.8 Panel A: Aggregated, GWP-weighted emissions of ODSs derived for the entire globe (blue lines; Clerbaux and Cunnold *et al.*, 2007; Daniel and Velders *et al.*, 2007) and for the U.S. (red lines; U.S. EPA, 2007). Solid lines represent weighting by direct GWPs (no indirect influences considered), and the lighter colored lines represent the contribution from emissions of HFCs, which were derived on the global scale from Campbell and Shende *et al.*, (2005) and for the U.S. (U.S. EPA, 2007). Dashed blue and red lines indicate the range in overall CO₂-equivalent emissions when the climate influence of stratospheric ozone depletion is included (as indirect GWPs). Panel B: The percentage of emissions (weighted by GWP) contributed by the United States to the global total. Global ODS emissions here are derived from atmospheric observations and global HFC emissions are derived from a combination of atmospheric observations and an analysis of production data (Campbell and Shende *et al.*, 2005; and AFEAS, 2007); U.S. ODS and HFC emissions are inferred from the vintaging model, which is a “bottom-up” analysis of sales and use data in the U.S. (U.S. EPA, 2007). U.S. HFC emissions include those from replacing ODS use and an additional small (~10-20% since 2001) contribution from unintended byproduct emission during HCFC-22 feedstock production.

business-as-usual scenario projections for 2015 [IPCC/TEAP, 2005]).

2.2.3 Global Emissions: The Contribution of Banks and Bank Sizes

“Banks” of ODSs exist where there are reserves of ODSs that potentially could be released at a later date. Though the magnitudes of banks are highly uncertain, the release of ODSs from these banks has become the most important factor in projecting future emissions of many ODSs (*e.g.*, CFCs and halons) for two main reasons. First, the production of CFCs and halons has diminished substantially and is expected to continue to decrease in the future in response to regulations of the Montreal

Protocol; and second, the applications for which CFCs are used today tend to release ODSs only over many years’ time. While the continuing production of HCFCs remains important to their future evolution in the atmosphere, the HCFCs banks are currently large enough so that future emissions will also be determined by their size and release rates from them.

The estimated sizes of banks, annual consumption, and annual emissions for the CFCs are shown in Figure 2.9 (see also Box 2.5). The United States’ contribution to these values is represented by the lower regions of each bar and amounts to nearly a quarter of global banks in 2005, when ODP weighting

Banks of ozone-depleting substances (ODSs) exist where there are reserves of ODSs that could potentially be released at a later date. The release of ODSs from these banks has become the most important factor in projecting future emissions of many ODSs.

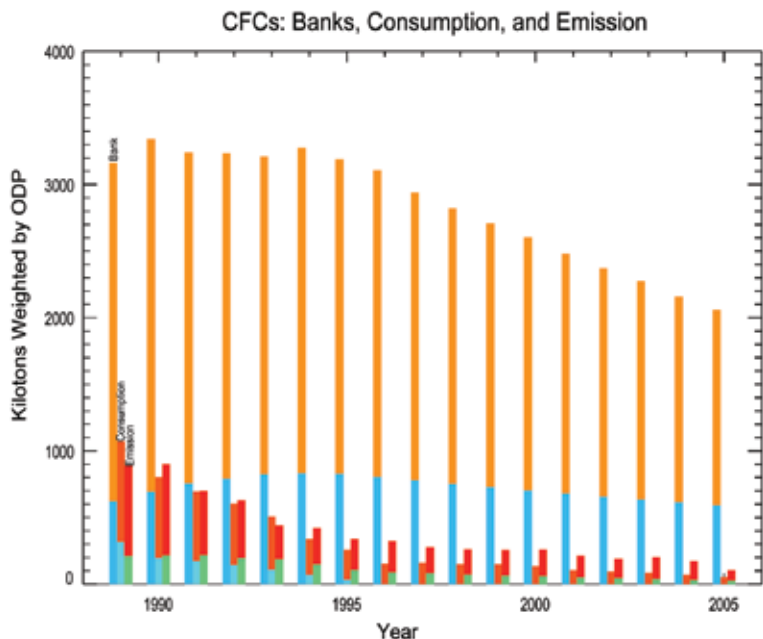


Figure 2.9 Time evolution of CFC banks, annual consumption, and annual emission, weighted by compound-dependent ODPs. The total height of the bars represents global values, while the lower blue/green portions represent the U.S. portions. Global banks are taken from WMO (Daniel and Velders *et al.*, 2007) with reliance on IPCC/TEAP (2005) bottom-up estimates used in combination with annual production and emission estimates. U.S. values are from the U.S. EPA vintaging model analysis of CFCs in the United States.

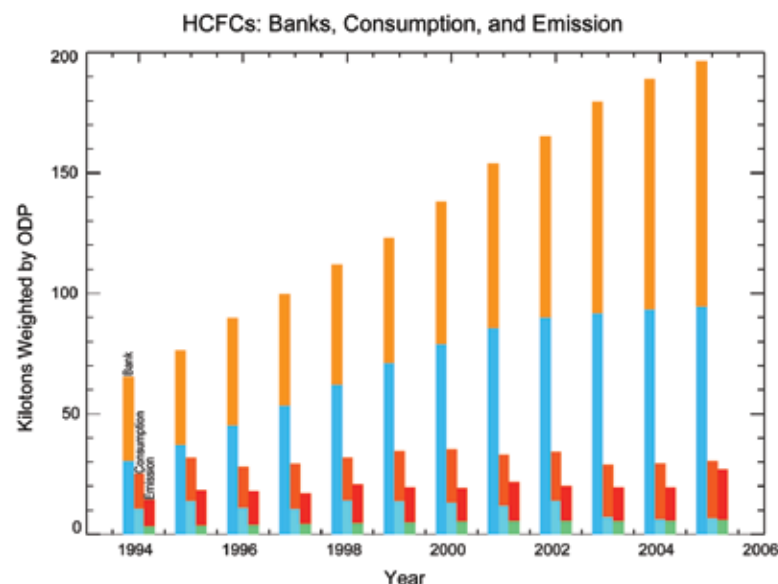


Figure 2.10 Time evolution of HCFC banks, annual consumption, and annual emission, weighted by compound-dependent ODPs. The total height of the bars represents global values, while the lower blue/green portions represent the U.S. portions. Global banks are taken from WMO (Clerbaux and Cunnold *et al.*, 2007; Daniel and Velders *et al.*, 2007) with reliance on IPCC/TEAP (2005) bottom-up estimates used in combination with annual production and emission estimates. U.S. values are from the U.S. EPA vintaging model analysis of HCFCs in the United States.

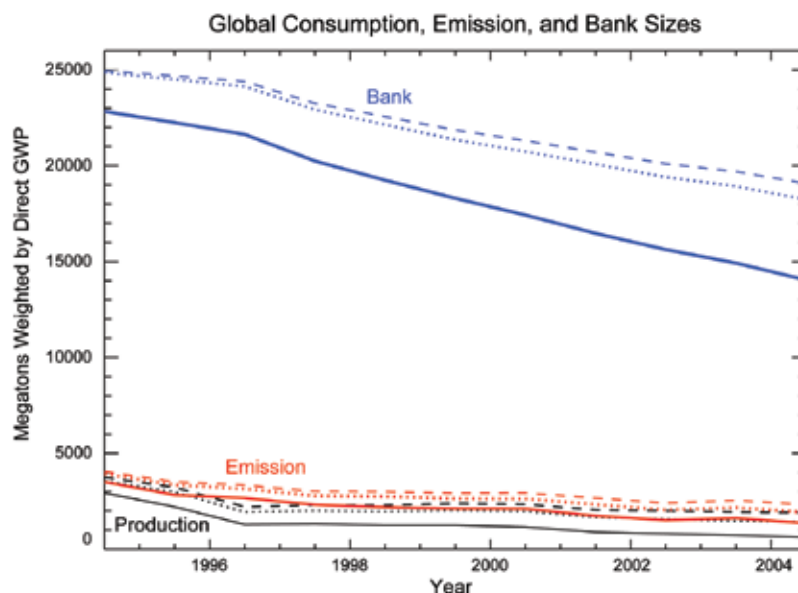
is considered. Both globally and domestically, the gradual decline of consumption is evident, with the size of the bank remaining as the most important driver of future emission. The importance of the bank is already apparent because the annual emission is substantially larger than the reported annual consumption, with the difference presumably coming from the bank.

The banks of the HCFCs similarly represent an important reservoir that will affect future U.S. and global emissions (Figure 2.10). However, because consumption of HCFCs has not been fully phased out in the developed world and is not yet limited in countries operating under Article 5 of the Montreal Protocol, current global consumption plays a larger relative role influencing current global emission rates than it does for the CFCs (Box 2.5).

Reducing future releases of ODSs from banks would necessitate recovering and destroying some of them. Technical feasibility and the economics of recovery necessarily play important roles in determining which ODS banks could be feasibly recovered and destroyed. Daniel and Velders *et al.* (2007) have evaluated test cases in which the 2007 total global banks of CFCs, HCFCs, or halons were recovered and destroyed in terms of the ozone benefits that could theoretically be achieved as a result. This information can be found in Chapter 5 of this report.

The direct GWP-weighted annual production and emissions are compared to the global bank sizes for CFCs, HCFCs, and HFCs in Figure 2.11. The only HFC considered in this calculation is HFC-134a because there is a lack of information regarding banks of other HFCs.

The decreases in global production, emissions, and bank sizes of the CFCs represent the largest changes and have led to overall decreases in these quantities for the sum of these compounds in a direct GWP-weighted sense. Although global banks for HFC-134a were still a small fraction of total direct GWP-weighted banks in 2005, banks of HCFCs have continued to increase over time and accounted for almost 25% of the total direct GWP-



Reducing future releases of ozone-depleting substances from banks would necessitate recovering and destroying some of them.

Figure 2.11 Comparison of direct GWP-weighted annual global production and emission with total bank sizes. Solid lines represent contributions of CFCs, dotted lines also include HCFCs, and dashed lines further add the HFC-134a contribution to the bank.

BOX 2.5: Banks of Ozone-Depleting Substances (ODS) and Substitute Chemicals

The term “bank” refers to an amount of chemical that currently resides in existing equipment or applications (including, for example, refrigerators, air conditioners, fire extinguishers, and foams) and stockpiles. Banked halocarbons are expected to be released to the atmosphere at some point in the future unless they are recovered and destroyed. Before scientists identified the relationship between chlorine- and bromine-containing halocarbons (now referred to as ozone-depleting substances, or ODSs) and stratospheric ozone, the majority of ODS usage was in fast-release applications like aerosol sprays and solvents. At that time, knowledge of the bank sizes was not critical to an understanding of current or even future projected ODS abundances.

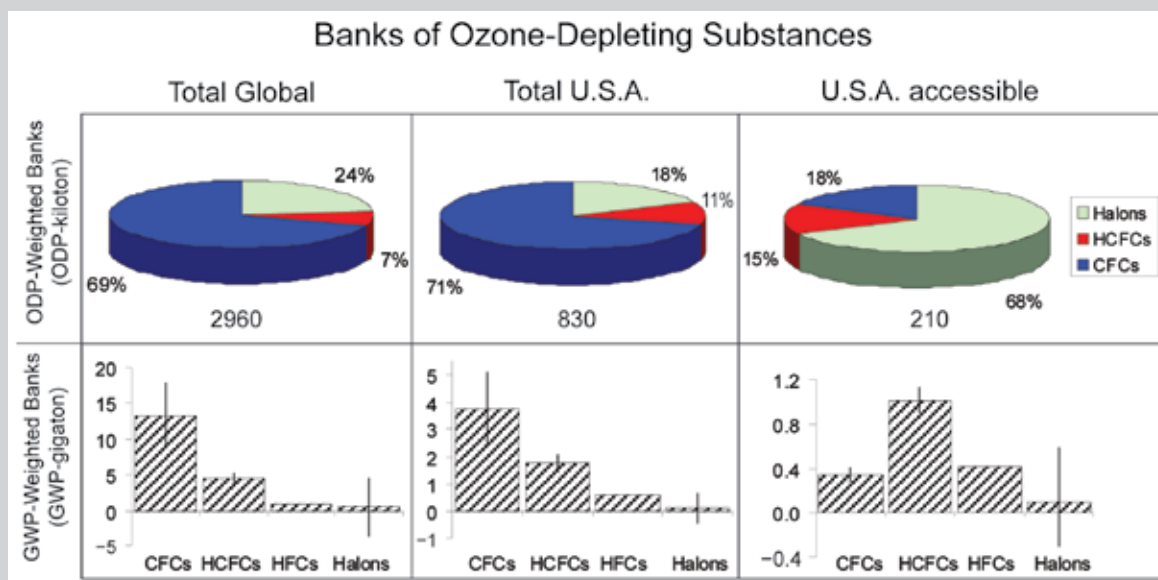
Today the situation is far different. Most ODSs are used in slow-release applications, many of which contain a significant quantity of a halocarbon compared to its current atmospheric abundance; this quantity is in some cases much larger than the amount of halocarbon emitted annually. Accurate knowledge of these bank sizes and rates of halocarbon emissions from banks is now important to the future projections of many halocarbon abundances and to the amount of ozone that these ODSs will destroy.

Estimates of current bank sizes are known to be highly uncertain, though various methods have been used to make these estimates. In ozone assessments prior to 2007 a “top-down” approach was used in which annual changes to bank sizes were determined from the difference between annual production estimates, taken from industry databases or reported amounts to UNEP, and annual emissions, estimated from atmospheric observations and global lifetimes. This method is particularly susceptible to systematic errors in production magnitudes and in the atmospheric lifetime of a chemical; significant errors can arise because the bank size is characterized often by small differences between large production and emission numbers and systematic errors can accumulate over time. A second method, which was discussed in IPCC/TEAP (2005) and is used in the U.S. EPA vintaging model, involves counting the number of application units that use a particular ODS and converting this information to a total bank size by knowing the amount of ODS typically residing in a single unit. This method is often called the “bottom-up” method and is independent of atmospheric lifetime estimates that influence top-down estimates.

Advantages and disadvantages of these methods are discussed in detail elsewhere (IPCC/TEAP, 2005; Daniel and Velders *et al.*, 2007). All have significant uncertainties, and in many cases, they do not agree particularly well. In the most recent WMO ozone assessment report (Daniel and Velders *et al.*, 2007), the bottom-up methodology for estimating the bank, in spite of acknowledged deficiencies, was thought to likely be more accurate than the top-down estimate and was used to project future halocarbon abundances.



BOX 2.5: Banks of Ozone-Depleting Substances (ODSs) and Substitute Chemicals *cont'd*



Box Figure 2.5-1 The size and contribution of different compound classes to 2005 banks estimated for the globe, for the U.S., and for the U.S. but classified as accessible (Daniel and Velders *et al.*, 2007; U.S.EPA, 2007). Top row includes bank estimates weighted by compound-dependent ODPs; banks in the bottom row have been weighted by direct (hatched bars) and net (indicated as uncertainties) GWPs (see Box 2.2). Pie charts show relative percentages; units refer to weighted total bank sizes, which are given at the bottom of each box in upper panel. Bar charts in lower panels give weighted absolute quantities; totals in the lower panels are 19 (5-24) GWP-Gt (or Gt CO₂-equivalents) for the global bank, 6.2 (2.9-7.3) GWP-Gt for the U.S. bank, and 1.9 (0.9-2.2) GWP-Gt for the U.S. accessible bank. Note that of the U.S. accessible bank, HCFCs accounted for approximately 1.0 (0.9-1.1) GWP-Gt. Note that halon stockpiles are not included in any of the U.S. bank estimates from the U.S. EPA owing to lack of available data at this time.

The current bank sizes have important scientific and policy implications. Because banks that are not captured will eventually be released into the atmosphere, inaction can result in increased ozone depletion and climate forcing. Banks vary in how technically and cost-efficiently they can be recovered so that emission to the atmosphere is avoided. The U.S. EPA has identified refrigeration, air conditioning, and fire protection banks as accessible and potentially recoverable; other banks may also be recoverable to different extents, albeit with potentially more effort and higher costs.

Sizes and relative contributions of different banks in 2005 weighted by different quantities are displayed in the figure (see Box Figure 2.5-1). When compared to annual emissions in 2005 (Figures 2.7 and 2.8), this analysis suggests that the 2005 total global and total U.S. banks were about 7 to 16 times larger (weighting by ODP or the range of net GWPs). 2005 accessible banks in the U.S. were about four times larger than U.S. annual emissions in that year (ODP or direct GWP weighting). For comparison, CO₂ global emissions from fossil fuel and cement production have been estimated at 27-30 Gt CO₂ in 2005 (IPCC, 2001). Furthermore, while CFCs account for the largest fraction of both global and U.S. banks in 2005 regardless of the weighting considered, they account for a much smaller fraction of the bank classified as accessible in the U.S. (HFCs not included). For 2005, halons accounted for two-thirds of the ODP-weighted, accessible U.S. bank and HCFCs a similar fraction of the GWP-weighted, accessible U.S. bank. The halon contributions to U.S. banks calculated here should be considered underestimates because stockpiles were likely non-zero in 2005.

weighted bank in that year. The 2005 global banks continue to represent an important reservoir in terms of climate forcing, equivalent to about 19 Gt of potential CO₂-equivalent emissions (Figure 2.11). When compared to

the reductions in emissions that already have resulted from compliance with the Montreal Protocol (more than 90 Gt integrated through 2005, direct GWP weighting), they represent a non-zero additional contribution to future

climate forcing and ozone depletion (see Section 2.2.1; Velders *et al.*, 2007). The importance of the Montreal Protocol and the quantification of the effect of future policy actions regarding global bank recovery and destruction have also been discussed in WMO (Daniel and Velders *et al.*, 2007), and IPCC/TEAP (2005) reports, and in Velders *et al.*, (2007). Consideration of the indirect forcing influences of ODSs associated with stratospheric ozone declines (and uncertainty in these influences) changes these figures somewhat. When weighted by a range of net GWPs, the 2005 global bank of ODSs and substitutes is estimated to be 5-24 GWP-Gt, comprised of 6-16 GWP-Gt of CFCs, 3-5 GWP Gt of HCFCs, and 0.9 Gt of HCFC-134a (See Box Figure 2.5-1; the uncertainty range stated in these figures represents the range of influences associated with net GWPs; see Box 2.2).

2.2.4 Global Emissions: The Influence of Non-restricted Uses and Other Factors

As indicated in Section 2.1.3 of this chapter, production of ODSs for chemical feedstock purposes is not restricted under the Montreal Protocol. ODP-weighted production of ODSs for feedstock purposes was approximately 1.8 times larger than overall production for dispersive uses reported to UNEP during 2002 (UNEP/CTOC, 2007). Emissions during production of the feedstock chemical are estimated to be 0.5%, which corresponds to 1600 ODP-Tons during 2002 based upon ODSs produced for chemical feedstock purposes, though this estimate does not include emissions that might arise after production. At a rate of 0.5% of production, this emission amounted to less than 1% of total ODP-weighted emission in 2002.

All production of HCFC-22, including feedstock-related production not restricted by the Montreal Protocol, has an added influence on the atmosphere that arises from HFC-23, which is created from over-fluorination as HCFC-22 is produced. Byproduct HFC-23 emissions account for most of the HFC-23 present in the atmosphere today (Clerbaux and Cunold *et al.*, 2007). Feedstock production of HCFC-22 accounted for approximately one-third of total HCFC-22 production in 2005

(Rand and Yamabe *et al.*, 2005). In a “business-as-usual” scenario regarding HCFC-production for restricted and feedstock purposes, HFC-23 emissions were projected to increase 60% from 2005 to 2015.

Production of CH₃Br for QPS purposes is also not restricted by the Montreal Protocol (Box 2.3). This global production was similar in magnitude to that used for restricted purposes in 2005. The emission rate for CH₃Br in QPS uses is estimated to be 78-90% of the amount produced (UNEP/MBTOC, 2007). Based upon 2005 production for restricted and non-restricted (feedstock and QPS) uses of CH₃Br, we estimate that global emissions from non-restricted applications accounted for nearly half (43 [36-49]%) of all anthropogenic CH₃Br emission during this year. Most of this non-restricted emission (more than 99%) is estimated to arise from QPS uses.

Unlike other restricted ODSs, a substantial amount of CH₃Br emission arises from the natural environment. These emissions arise from the oceans, wetlands, plants, and biomass burning; as a result, humans have little direct control over them. Emissions of CH₃Br arising from industrial production are estimated to have accounted for 30 (20-40)% of total global emissions during the 1990s before industrial production was curtailed (Clerbaux and Cunold *et al.*, 2007).

The magnitude of variability in non-industrial emissions of CH₃Br on annual and decadal time scales is not well known, and changes in these natural emissions could add to or offset the emission declines brought about by the Montreal Protocol. Despite these uncertainties, atmospheric data (Clerbaux and Cunold *et al.*, 2007) suggest that global emissions of CH₃Br have declined each year since industrial production was first reduced (1999).

2.2.5 United States Emissions and Banks: Estimates Derived by U.S. EPA Vintaging Models

While global emissions are fairly straightforward to derive from atmospheric measurements of the global background abundances of ODSs and substitutes, provided loss rates are known (Section 2.2), estimating emissions on

In 2005, global emissions from non-restricted applications accounted for nearly half of all anthropogenic CH₃Br emission. More than 99% of this non-restricted emission is estimated to arise from quarantine and preshipment use.



national or regional scales is more difficult. While regional atmospheric monitoring could potentially provide national estimates of emissions, to date such estimates have been sporadic and are based on very few sampling regions (Section 2.2.6). Instead, U.S. emissions have been estimated using “vintaging” models that incorporate data regarding application-specific sales, and leakage rates during and after use of ODSs and substitutes (see Box 2.6 for further description of the vintaging model). With this method the U.S. EPA has estimated annual, U.S. emissions of ODSs and their replacements since 1985 (U.S.EPA, 2007). The data compiled by the U.S. EPA covers industrial production for uses restricted by the Montreal Protocol and for non-restricted uses such as feedstock and QPS applications.

When weighted by chemical-specific ODP values, the U.S. emissions of ODSs and substitute chemicals peaked in 1991 and declined thereafter as a result of limits imposed upon production and consumption by the fully adjusted and amended Montreal Protocol (Figure 2.9). By 2005, total annual U.S. emissions of ODSs and substitute chemicals had declined by 226 ODP-Kt or by 81% (Table 2.1). Emissions have declined less from their peak than consumption or production (Table 2.1) because much of those ODSs are contained currently in in-use foams, fire extinguishers, and cooling devices. United States emissions of ODSs and substitutes are estimated to have been 52.7 ODP-Kt in 2005. Emissions for the substitute HCFCs have increased over this period; U.S. HCFC emissions in 2005 were nearly 6 ODP-Kt, which represents an increase of 3.5 ODP-Kt since 1990. U.S. HCFC emissions in 2005 were predominantly HCFC-22 (87%) and HCFC-141b (7%); other chemicals contributed lesser amounts (HCFC-142b 4%; HCFC-227ca/cb 1%; HCFC-124 0.6%; and HCFC-123 0.3%). Over half (55%) of the U.S. ODP-weighted emissions in 2005 were from CFCs, 25% were from halons, 9% were from CH₃Br, and 11% were from HCFCs.

The contribution of the United States to global ODP-weighted emissions has varied during the period of available data from 18 to 35% (1985-2005; Figure 2.7). When weighted by chemical-specific 100-year direct GWP values,

U.S. emissions estimated by the U.S. EPA suggest a reduction of 1640 GWP-Mt in annual emissions of ODSs and substitutes including HFCs by 2005 compared to 1991 when they were at their peak (a decrease of 74%; Figure 2.8; Table 2.1). When indirect influences are included, a U.S. emissions decline of 900-1880 GWP-Mt is estimated with net GWP weighting (see Box 2.2), which corresponds to a relative decline of 71-75% from peak emissions. The largest decline was for CFCs emissions, which accounted for 90-95% of the direct or net GWP-weighted total annual U.S. emissions in 1985-1995 and only 40-45% of these emissions in 2005. By 2005, direct or net GWP-weighted emissions of HCFCs accounted for about one-third and HFCs one-quarter of total annual U.S. emissions of ODSs and substitutes.

Independent assessments of ODS emissions in the United States are limited. One analysis derived CFC emissions by country during a single year, 1986 (McCulloch *et al.*, 1994). This investigation was based upon consumption data for 1986 compiled by UNEP, AFEAS delineations of use by individual CFCs specific to different geographic regions, and emissions of 86-98% of consumption in each year. These results suggest that emissions in 1986 were within 50% of those estimated by the U.S. EPA for CFC-12, CFC-113, CFC-114, and CFC-115, but a factor of three higher for CFC-11. This discrepancy likely arises because the U.S. EPA analysis suggests that U.S. emissions of CFC-11 were not typical of other nations during this period. In this report we have used the U.S. EPA estimates because they represent the most in-depth and comprehensive analysis of U.S. emissions available. In this analysis, an error range of -25% to +50% is applied to U.S. emission estimates of ODSs after 1985.

As was touched upon in the discussion of ODS banks on global scales, U.S. emissions of many ODSs are dominated currently by slow releases from banks. Bank magnitudes in the United States are estimated with the U.S. EPA’s vintaging model, though these estimates likely have large uncertainties. The vintaging model estimates banks as part of its calculation to estimate emissions through an analysis of the number of pieces of equipment in use, the charge size of ODS in the equipment,

The U.S. emissions of ozone-depleting substances (ODSs) and substitute chemicals peaked in 1991 and declined thereafter as a result of limits imposed by the Montreal Protocol. By 2005, total U.S. annual emissions of ODSs and substitute chemicals had declined by 81%.



the loss rate of ODS from these applications, and estimates of how these variables change over time with input from industry. The 2005 banks amounted to seven to sixteen years worth of emissions at rates estimated for 2005, depending upon weighting, or 830 ODP-Kt and 6.2 Gt CO₂-equivalents (direct GWP weighting; Box 2.5) (halon stockpiles not included).

The U.S. EPA vintaging model analysis does include an estimate of how much of the ODS banks are accessible for recovery, where “accessible” refers to ODSs in current air conditioning, refrigeration, and fire protection equipment. While banked halocarbons that are not considered accessible by the U.S. EPA could be recovered and destroyed with appropriate policy measures, market-based incentives, and/or certain technological advances, halocarbons that are not recovered and destroyed will eventually escape into the atmosphere. Banks in the United States that are classified by the U.S. EPA as being accessible amount to approximately 25-30% of the total U.S. bank (ODP, direct or net GWP weighting). Halons account for the majority of the ODP-weighted accessible U.S. bank in 2005, even when stockpiles are not included. HCFCs make up over two-thirds of the accessible GWP-weighted bank. Less than 15% of the total U.S. CFC bank in 2005 is considered accessible (8-14% when net GWP-weighted; ~6% when ODP-weighted) compared to over 30% of the U.S. HCFC bank (55-68% when net GWP-weighted and 37% when ODP-weighted) (Box 2.5).

Comparing these U.S. EPA vintaging model bank size estimates in 2005 with the global banks from WMO (Daniel and Velders *et al.*, 2007) gives that the United States contributed 21 and 26% to the global ODP- and direct GWP-weighted banks, respectively. In this year the U.S. accessible banks accounted for about 5 and 7% of the ODP- and direct GWP-weighted global banks. Future projections from these models suggest that the total U.S. bank will gradually account for less of the global bank over the next decade, shrinking to 14% and 17% of the global ODP- and direct GWP-weighted bank. Similarly, the U.S. accessible bank is projected to decrease to 2 and 4% of the ODP- and direct GWP-weighted global banks. The significance of these banks to integrated EESC

and to ODS recovery times will be addressed in Chapter 5.

Interpretation of these bank comparisons must include consideration of the different assumptions and techniques used to generate the U.S. and the global bank estimates. Although an error analysis has not been performed on either set of numbers, the uncertainties are potentially large, with this uncertainty representing an important gap in our current understanding.

2.2.6 United States Emissions: Derived From Atmospheric Data in Non-remote Areas

Techniques to estimate regional or national emissions of ODSs that are independent of sales data and vintaging models are currently being developed. They rely on high-frequency atmospheric observations (multiple samples per day) in air downwind of source regions. The enhancements observed for ODSs in these air masses can be proportional to emission rates from the upwind source region provided dilution and mixing influences are appropriately considered. These estimates are specific to the region most directly influencing the air reaching a measurement site. Unfortunately, U.S. emissions have been derived using this method with data from only a small number of sites that may not capture regional variations in ODS use and emission rates. The extrapolations are made to the entire United States, for example, based upon population or by reference to enhancements observed in co-measured trace gases whose national emission rates are thought to be better quantified on a national scale (such as carbon monoxide or sulfur hexafluoride).

While the uncertainties associated with this general method can be substantial and estimates have been made for only a small number of years, such an approach offers the only independent test of U.S. emission estimates derived from production and sales data in vintaging models (U.S. EPA, 2007). Estimates of U.S. emissions have been made for selected CFCs, CH₃CCl₃, and CCl₄ over 1996-2003 based on individual studies in California and in the northeast. The results point to a clear decline in U.S. emissions of CFC-12 over this period (Clerbaux and Cunbold *et al.*, 2007). Although U.S. emissions derived for CFCs from these

Halocarbons that are not recovered from banks and destroyed will eventually escape into the atmosphere.



Because most ozone-depleting substances and their substitutes have lifetimes of a year or more, they are fairly well-mixed in the atmosphere. As a result, hemispheric and global atmospheric changes can be well captured by measurements at only a few remote sites.



estimates are generally lower than from the U.S. EPA, those for CCl_4 and CH_3CCl_3 are generally higher. On an ODP- or GWP-weighted basis, total U.S. emissions of ODSs derived from observations during 2002-2003 were about half of those estimated by the U.S. EPA's vintaging model analysis. Because it is not known which method is more accurate, no modifications were applied to the history of ODS emissions compiled by the U.S. EPA (2007).

2.3 CHANGES IN THE ATMOSPHERIC ABUNDANCE OF OZONE-DEPLETING CHEMICALS AND THEIR SUBSTITUTES

2.3.1 Global Atmospheric Abundances

The influence an atmospheric trace gas has on ozone or climate generally scales with its atmospheric abundance. Atmospheric abundances reflect the integration of past emissions and how persistent a trace gas is in the atmospheric environment (*i.e.*, its global lifetime). A measure of international efforts to minimize the deleterious environmental influences of ODSs and substitutes is found in how successful they are in reducing the atmospheric abundance of these chemicals.

Long-term changes in the global atmospheric abundances of ODSs and substitute chemicals are estimated with different techniques. The atmospheric abundances of the full suite of organic ODSs are generally determined at a small number (less than ten) of remote locations at Earth's surface by independent national and international scientific organizations. These determinations are either made in real time by direct injection of ambient air into on-site instrumentation, or via the analysis of flask samples collected at remote sites and subsequently shipped to a central laboratory. Measurements of the most abundant ODSs (*e.g.*, CFC-12, CFC-11, and HCFC-22) are also made with ground-based infrared solar absorption spectroscopy at selected sites across the globe. The absorption spectroscopy method provides a measure of the total column abundance of these gases above a point on Earth's surface. Measurements are also made with absorption spectroscopy instrumentation onboard satellites. These instruments provide global observations for the most abundant

ODSs. Long-term spectroscopic measurements of these chemicals reveal trends consistent with those observed with ground-based, flask or *in situ* sampling techniques and so are not shown here (Clerbaux and Cunnold *et al.*, 2007).

Because most ODSs and their substitutes have lifetimes of a year or more, they are fairly well-mixed in the atmosphere. As a result, hemispheric and global atmospheric changes can be well captured by measurements at only a few remote sites. Evidence for this can be found in the good agreement noted between global surface mixing ratios derived from the different array of sampling locations and analytical techniques used by these independent organizations. Global surface means derived from these independent laboratories typically agree within a few percent, and often the small discrepancies (typically less than 5%) that do exist for the most abundant ODSs can be attributed to calibration differences (UNEP/TEAP, 2006). Further evidence of this can be found in the consistent measures of atmospheric composition changes provided by spectroscopic total column measurements and those provided by ground-based, *in situ* discrete sample analysis or flask sampling (Clerbaux and Cunnold *et al.*, 2007).

A summary of measured trends for ODSs reveals a wide range of changes in atmospheric mixing ratios for these chemicals and their substitutes, primarily as a result of changes in production and emission brought about by the Montreal Protocol on Substances that Deplete the Ozone Layer (Figure 2.12). As of 2005, the surface mixing ratio and total column burden of the most abundant and long-lived CFC, CFC-12, had begun to decline slowly after reaching a plateau a few years earlier (Clerbaux and Cunnold *et al.*, 2007). Mixing ratios of other ODSs, including CFC-11, CFC-113, CCl_4 , CH_3CCl_3 , and CH_3Br , have declined persistently over the past five to ten years at rates ranging from -0.5% per year to -18% per year. Halons have been slower to respond to production restrictions, though most data indicate that the atmospheric accumulation of these bromine-containing chemicals has slowed in recent years. Rates of accumulation for halon-1211 and halon-1301 estimated by

Global Mean Surface Mixing Ratios

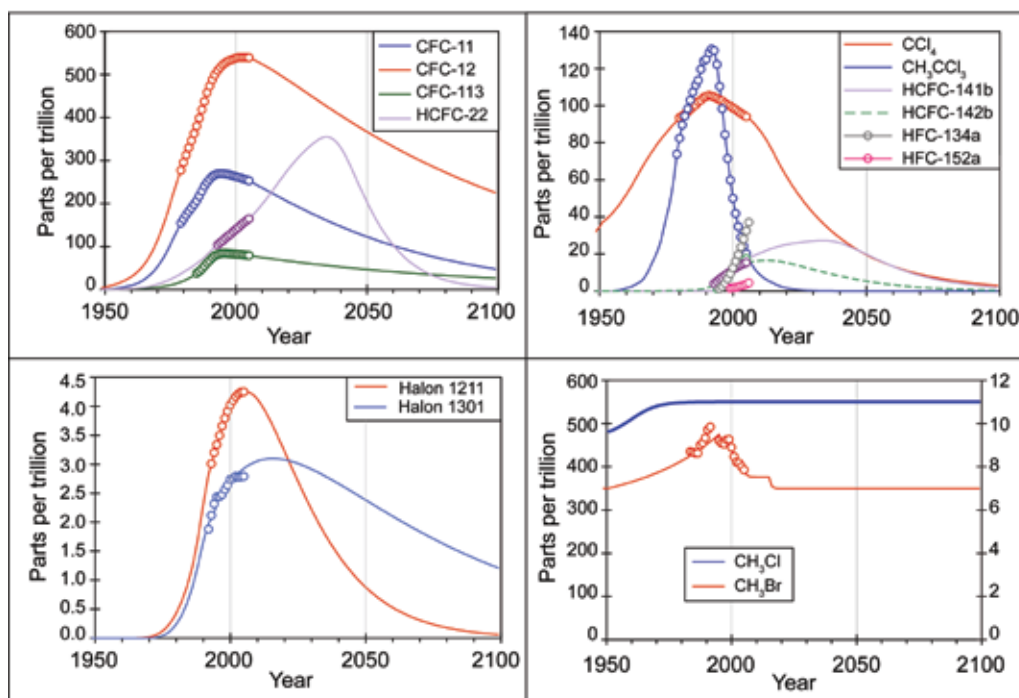


Figure 2.12 Global surface mixing ratios of ODSs and substitute chemicals observed from surface sampling networks (open circles), and as estimated for the past and future in WMO scenario AI (Clerbaux and Cunnold *et al.*, 2007; Daniel and Velders *et al.*, 2007). Past projections are based on histories derived from the analysis of archived air samples, the analysis and modeling of firn-air (air trapped in uncompacted snow in the polar regions) samples, and historic industrial production data.

different laboratories during 2003-2004 range from 0 to 3.2% per year.

Global atmospheric mixing ratios of HCFCs (the chlorine-containing substitutes for CFCs and other ODSs) continue to increase (Clerbaux and Cunnold *et al.*, 2007). The most abundant HCFC, HCFC-22, was present in the background atmosphere at nearly 170 ppt (parts per trillion by mole) in 2005 and has increased fairly steadily at 4 (± 1) % per year for over a decade. Other HCFCs are one-tenth as abundant (or less) in the global atmosphere but increased during 2003-2004 at relative rates similar to HCFC-22. For example, though the global mixing ratio of the least abundant HCFC, HCFC-123, was on the order 0.06 ppt in 2004, its mixing ratio increased at about 6% per year during 2003-2004.

Global atmospheric mixing ratios of HFCs, which are in-kind substitutes that do not contribute any Cl or Br to the atmosphere, have increased quite substantially over the past decade (Clerbaux and Cunnold *et al.*, 2007). HFC-134a is the most abundant of these

substitutes; the global mean surface mixing ratio in the beginning of 2006 was 36 ppt, and it was increasing at a rate of approximately 4.5 ppt per year. The long-lived HFC-23 is the second most abundant HFC; global measured mixing ratios in 2005 were approximately 20 ppt and were increasing. A number of other HFCs have been measured in the remote atmosphere at mixing ratios of a few ppt. After HFC-134a and HFC-23, the HFCs currently emitted in the most significant quantities are HFC-143a and HFC-125.

2.3.1.1 GLOBAL ATMOSPHERIC ABUNDANCES OF OZONE-DEPLETING SUBSTANCES AND SUBSTITUTE CHEMICALS: MEASURED VS. EXPECTED MIXING RATIOS

As of 2005, the initial success of the Montreal Protocol in reducing the threat that ODSs pose to the stratospheric ozone layer is made clear by noting that production declines have led to declining mixing ratios or mixing ratios that are increasing more slowly for all regulated ODSs not considered to be substitutes. The atmospheric response to decreasing production varies for different gases owing to differences



Table 2.2 The most abundant ODSs and substitute chemicals.

Compound	Lifetime (years)	Tropospheric Chlorine or Bromine Contribution (ppt)			EECI Contribution (%) ^c	ODS	ODS Substitute	Regulation ^a
		1985	1995	2005	2005			
CFCs					45%			
CFC-II	45	622	808	759	21%	X		M
CFC-I2	100	763	1046	1078	18%	X		M
CFC-II3	85	114	252	237	5%	X		M
CFC-II4	300	25	34	34	0.3%	X		M
CFC-II5	1,700	3	8	9	0.1%	X		M
HCFCs					2.5%			
HCFC-22	12	61	112	165	1.6%	X	X	M
HCFC-141b	9.3	0	5	35	0.7%	X	X	M
HCFC-142b	17.9	0	6	15	0.2%	X	X	M
HCFC-123	1.3			0.06 ^b	0.002%	X	X	M
HCFC-124	5.8			1.7 ^b	0.02%	X	X	M
Other Chlorocarbons					25%			
CH ₃ CCl ₃	5	324	330	60	1.8%	X		M
CCl ₄	26	398	412	376	11%	X		M
CH ₃ Cl	1	550	550	550	12% ^c	X		None
Bromocarbons					28%			
CH ₃ Br	0.7	8.6	9.5	7.9	15% ^c	X		MA
Halon-1211	16	1.1	3.3	4.2	8%	X		M
Halon-1301	65	0.7	2.3	2.9	3%	X		M
Halon-2402	20	0.4	0.8	0.7	1.4%	X		M
HFCs					0%			
HFC-23	270	0	0	0	0		X	K
HFC-125	29	0	0	0	0		X	K
HFC-134a	14	0	0	0	0		X	K
HFC-143a	52	0	0	0	0		X	K
HFC-152a	1.4	0	0	0	0		X	K

^a "M" represents regulation by the Montreal Protocol, "K" by the Kyoto Protocol, and "MA" is used to show that only the anthropogenic portion of CH₃Br production and consumption is regulated. Lifetimes are from WMO (Clerbaux and Cunnold *et al.*, 2007) and halogen abundances are from WMO Scenario A1 (Daniel and Velders *et al.*, 2007), which are derived from atmospheric observations.

^b Mixing ratios for these HCFCs are for 2004, not 2005 (Clerbaux and Cunnold *et al.*, 2007).

^c Bold percentages are calculated for the entire compound class. Methyl chloride and methyl bromide fractions are calculated including natural and manmade components. If only manmade emissions of CH₃Cl and CH₃Br were included (*i.e.*, assuming anthropogenic contributions in 2005 of 0 ppt for CH₃Cl and 1.25 ppt (7.9 - 9.5×0.7) for CH₃Br), the percentages calculated for 2005 abundances would be CFCs: 59%; HCFCs: 3.3%; Other Chlorocarbons: 17%; Other Bromocarbons: 20%; CH₃Br: 3.1%.

in release rates from the applications in which the chemicals were used, and the persistence of the chemicals in the atmosphere. For example, CH_3CCl_3 was used in cleaning applications in which release to the atmosphere followed sales with only a short delay (generally less than one year). This, combined with its relatively short lifetime of approximately five years, resulted in rapid atmospheric decreases once production was curtailed (Figure 2.12). The atmospheric abundance of CH_3CCl_3 has declined since 1998 at near its lifetime-limited exponential rate, which is approximately 20% per year.

Conversely, CFC-11 and CFC-12 were used largely in foam and refrigeration applications in which they only slowly escaped to the atmosphere over decades. This, combined with atmospheric lifetimes of 45 to 100 years, has resulted in only slowly declining atmospheric mixing ratios (Figure 2.12; Table 2.2). The maximum rate of decline in the atmospheric abundance of a chemical with a global lifetime of 100 years, such as CFC-12, is 1% per year and would be observed only if emissions were negligible.

Atmospheric mixing ratios of halons also have been slow to respond to production declines (Table 2.2). This delay is attributable to large banks of chemical in fire-protection installations that are released to the atmosphere during use, servicing, and from leakage, and in the case of halon-1301, its relatively long lifetime.

Carbon tetrachloride is used as a feedstock for production of CFC-11 and CFC-12. As production of these CFCs decreased, so did global emissions and atmospheric mixing ratios of CCl_4 . Atmospheric declines have not been as rapid as expected, however, given a lifetime of 26 years. The slower than expected decline suggests the presence of substantial unaccounted emissions (30 to 40 Gg per year since the mid-1990s, or greater than 35% of estimated emissions) or large errors in the estimate of the CCl_4 global lifetime (approximately 26 years; Table 2.2).

The decline in CH_3Br mixing ratios was somewhat faster than expected in response to production declines after 1998, though for this chemical the magnitude of the expected

decline hinges on an accurate understanding of the relative importance of industrial emissions compared to emissions from the natural environment (Clerbaux and Cunnold *et al.*, 2007). The measured decline has been more variable than observed for other ODSs, perhaps because of interannual variability in nonindustrial sources of this chemical, such as biomass burning. Despite these influences over which humans have little direct control, the global mean atmospheric mixing ratio of this chemical through 2006 has decreased each year since 1999, when the gradual phase-out of industrial production and consumption began in developed countries.

Increases in production of ODS substitutes (HCFCs and HFCs) have led to increases in atmospheric mixing ratios for these compounds over the past two decades (Clerbaux and Cunnold *et al.*, 2007).

2.3.1.2 ATMOSPHERIC ABUNDANCES: ON THE ROLE OF VARIATIONS IN LOSS RATES

Atmospheric abundances of ODSs represent a balance between emissions and loss. The Montreal Protocol has resulted in declining emissions of all regulated ODSs not considered to be substitutes. Atmospheric mixing ratios begin to decrease as the natural processes that decompose trace gases in the atmosphere outweigh emissions. For ODSs and their substitutes these natural loss pathways include photolytic destruction primarily in the stratosphere and, for ODSs containing C-H chemical bonds, photochemical oxidation by the hydroxyl radical.

Both loss processes can vary in strength over time because they are influenced by the physical and chemical state of the atmosphere. Accordingly, long-term or short-term variations in rates of photolysis and photo-oxidation have the potential to influence atmospheric mixing ratios in a way that is independent of emission changes brought about by the Montreal Protocol. Estimates of the magnitudes of these loss changes suggest that they are generally small over multi-decadal periods, though it has been suggested that decadal changes in hydroxyl radical abundance can be as large as 15% (Clerbaux and Cunnold *et al.*, 2007). Furthermore, OH reaction rate constants

The atmospheric response to decreasing production varies for different gases owing to differences in release rates from the applications in which the chemicals were used, and the persistence of the chemicals in the atmosphere.



BOX 2.6: On Deriving Atmospheric Abundances from U.S. Emissions

Atmospheric abundances of long-lived ODSs and substitute chemicals can be calculated from an emission history and a simple box model (IPCC/TEAP, 2005; WMO, 2007). A box model includes the influence of emissions and loss rates (or atmospheric lifetimes) to derive atmospheric abundances over time. This common and widely accepted approach is used in this report to estimate atmospheric mixing ratios of ODSs and substitutes arising solely from U.S. emissions of these chemicals. U.S. emission histories are derived over an entire period of ODS use based upon assumptions regarding a potential range of United States/Global emission ratios before 1985 and estimates from a vintaging model analysis thereafter (U.S. EPA, 2007) (Box Table 2.6-1). The U.S. EPA vintaging model is a bottom-up modeling approach that considers market size, amount of ODS in each unit of equipment or application, and ODS substitution trends in order to estimate time-dependent, annual emissions and bank sizes. In the absence of U.S. production or use data for most years before 1985, a number of assumptions were made in order to bracket likely U.S. emissions during these early years. Such assumptions are essential for estimating U.S. contributions to CFC abundances, for example, because much of the pre-1985 emissions of these long-lived chemicals are still present in the atmosphere today. In 1974, as the public became aware of the threat posed to the ozone layer by ODSs, CFC use in fast-release applications in the U.S. was dramatically curtailed. This likely resulted in substantial changes in U.S. emissions of CFCs then. Accordingly, a different approach was used to derive ranges of potential U.S. CFC emissions during 1975-1984 compared to before 1975 (Box Table 2.6-1).

Box Table 2.6-1 Methodology for Deriving Limits to Compound-Specific, Annual U.S. Emissions*:

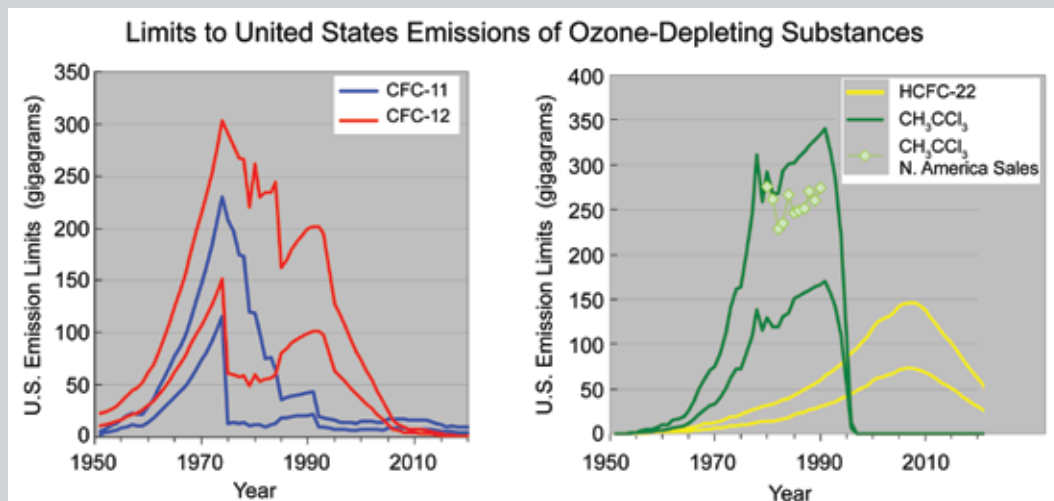
	Upper Range (emission or emission fraction)	Lower Range (emission or emission fraction)
Pre 1975		
CFCs	$[GE] \times 0.67$	$[GE] \times 0.33$
Non-CFCs	$GE_{US/Global(1985-1990)} \times 1.5$	$GE_{US/Global(1985-1990)} \div 1.5$
HFC-23	$\alpha \times GPF_{(HCFC-22)US/Global(1985-1990)} \times 1.2$	$\alpha \times GPF_{(HCFC-22)US/Global(1985-1990)} \times 0.9$
1975-1984		
CFCs	interpolate $[GE] \times 0.67$ in 1975 to $GE_{US/Global(1985-1990)} \times 2$ in 1984	$GE_{US/Global(1985-1990)} \div 2$
Non-CFCs	$GE_{US/Global(1985-1990)} \times 1.5$	$GE_{US/Global(1985-1990)} \div 1.5$
HFC-23	$\alpha \times GPF_{(HCFC-22)US/Global(1985-1990)} \times 1.2$	$\alpha \times GPF_{(HCFC-22)US/Global(1985-1990)} \times 0.9$
1985-2005		
All HFCs	U.S. EPA (2007) +20%	U.S. EPA (2007) -10%
All others	U.S. EPA (2007) +50%	U.S. EPA (2007) -25%
* where GE = global annual emissions; $GE_{US/Global(1985-1990)}$ refers to the mean U.S./global emission fraction over the period 1985 to 1990 determined from a ratio of compound-specific emissions from the U.S. EPA (2007) vintaging model and WMO scenario A1 global emissions (Daniel and Velders <i>et al.</i> , 2007); and $GPF_{(HCFC-22)US/Global(1985-1990)}$ refers to the mean U.S./global production fraction for HCFC-22 during 1985 to 1990 in data reported by AFEAS (2007) and by the U.S. EPA (2007) and the assumption that HFC-23 emissions were proportional to HCFC-22 production during those years. Alpha (α) indicates the fraction of HFC-23 emitted for a given amount of HCFC-22 produced (~1% by mass, U.S. EPA[2007])		

The main uncertainties in calculating atmospheric mixing ratios associated with U.S. emissions are associated with U.S. emission magnitudes and, for some gases, global atmospheric lifetimes. Emission errors stem from uncertainty in the ability of the U.S. EPA vintaging model to accurately capture the mean annual emissions from the many varied applications in which ODSs were used since 1985. Though a chemical-specific uncertainty analysis has not been performed by the U.S. EPA, an uncertainty analysis has been performed on 2005 emissions derived by the U.S. EPA vintaging model for the high-GWP, ODS substitutes as a group (HFCs and PFCs). This analysis, performed with Monte-Carlo techniques, indicated a 95% confidence interval of -9% to +20% on 2005 emissions estimated for this class of compounds.

Compound-specific uncertainties and uncertainties for earlier years are likely to be somewhat larger, though the ODS consumption and production tracking system required for compliance with the Montreal Protocol has added to data reliability.

BOX 2.6: On Deriving Atmospheric Abundances from U.S. Emissions *cont'd*

Given these considerations, we have augmented the uncertainties derived for the high-GWP ODS substitutes by a factor of approximately 2.5 to derive a lower and upper range of -25% to +50% on compound-specific, annual emission estimates derived from the vintaging model during the 1985 to 2005 period.



Box Figure 2.6-1 Ranges estimated for U.S. emissions derived from the analysis presented in Box Table 2.6-1; units are Gg, or 10^9 g. These U.S. emissions estimates are compared to North American sales data for CH_3CCl_3 (green points; Midgley and McCulloch, 1999). These data show reasonable consistency within the ranges estimated here for U.S. emissions, considering that the U.S. accounted for approximately 95% of North American consumption of this chemical in the late 1980s (UNEP, 2007) and that releases of CH_3CCl_3 generally occurred within a year after sales. Data to allow similar comparisons for other chemicals are not available.

These approaches have yielded estimates to expected upper and lower ranges to U.S. emissions of ODSs and substitute chemicals (Box Figure 2.6-1).

Errors on calculated atmospheric mixing ratios that are associated with lifetime uncertainties depend upon the use period of an ODS relative to its lifetime. For chemicals that have been emitted for a period that is small compared to their lifetimes (CFC-12 and HFC-23, for example), lifetime uncertainties are relatively small. For other gases such as CH_3Br and CH_3CCl_3 where their use period is long relative to their atmospheric lifetime, lifetime uncertainties are more substantial.

Errors associated with the simple box-model approach are thought to be substantially smaller than the errors already discussed, especially in the case of ODSs whose atmospheric lifetimes are comparable to or much longer than atmospheric mixing times (see, for example, UNEP/TEAP, 2006; Clerbaux and Cunnold *et al.*, 2007).

are temperature sensitive; increases in reaction rates of approximately 10% between OH and CH_4 , HCFCs, and HFCs are calculated for a 5°C increase in temperature. Because oxidation by OH is the primary means by which these gases are removed from the atmosphere, compound lifetimes would change similarly. Finally, future changes in large-scale atmospheric circulation patterns have been predicted in some models in response to increased radiative forcing from elevated greenhouse gas abundances and would likely also shorten lifetimes for ODSs where stratospheric losses are relatively important (Section 4.4.1).

2.3.2 The United States Contribution to Global Atmospheric Abundances

Atmospheric mixing ratio histories can be derived from a record of U.S. ODS emissions, estimates of global loss rates (lifetimes), and a simple global box model (Box 2.6). Mixing ratios calculated in this way can be compared to measured and calculated global mixing ratios to estimate the contribution of U.S. emissions to the atmospheric abundance of ODSs and substitute chemicals in the past and future. Though uncertainties in this analysis are large, the results suggest that U.S. emissions of ODSs and substitutes account for between 10

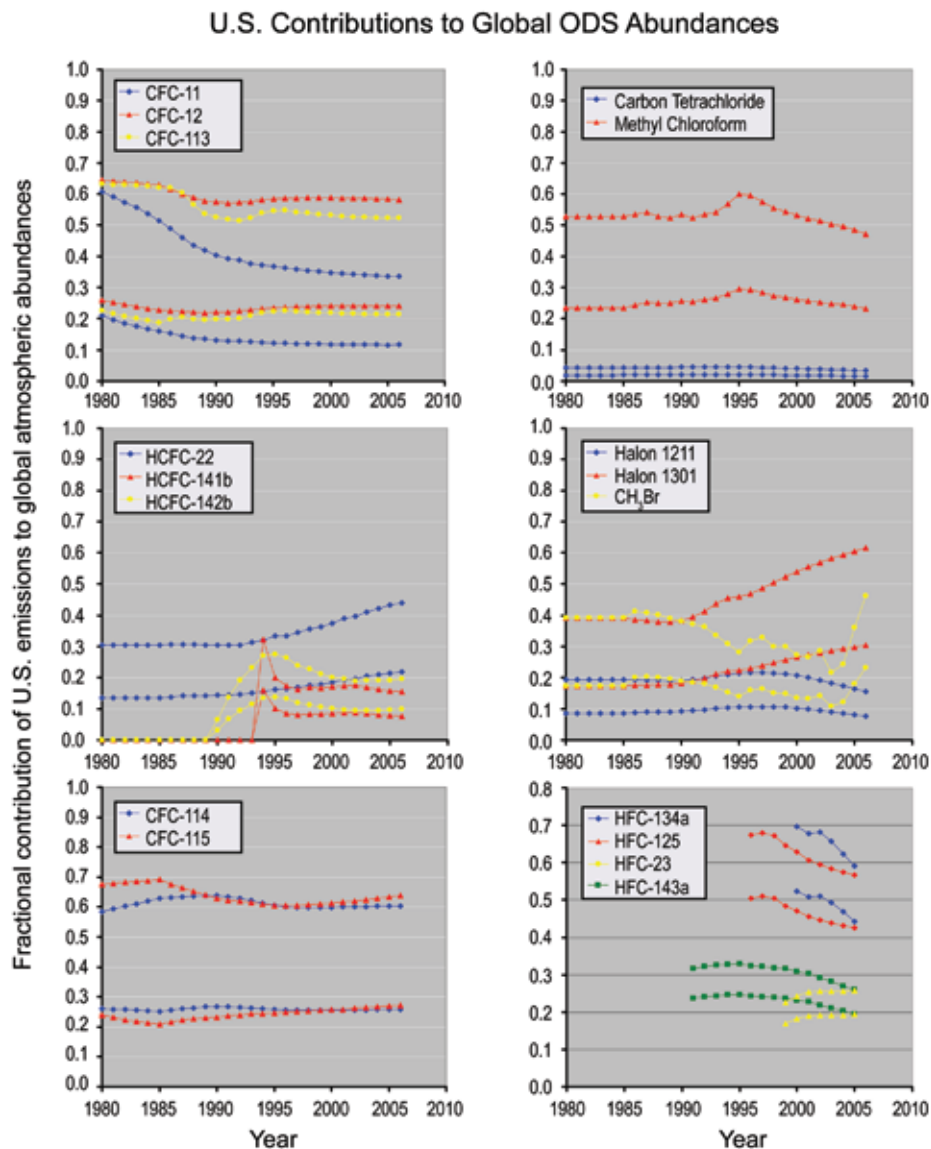


Figure 2.13 Upper and lower ranges to the fractional contributions of U.S. industrial emissions to global atmospheric abundances of ODSs and substitute chemicals over time (see Box 2.6 for the derivation of U.S. emissions and a discussion of uncertainties). For HFC-23, emission from production of HCFC-22 for ODS substitution and feedstock uses is included. For the HFCs, results are only displayed for years when global mixing ratios are greater than 1 ppt. Methyl bromide emissions arising from natural processes are not included, *i.e.*, 146,000 Metric Tons of emission per year (Clerbaux and Cunnold *et al.*, 2007; Daniel and Velders *et al.*, 2007).

and 50% of the global atmospheric abundance measured for most gases in the present-day atmosphere (Figure 2.13). These estimates are most uncertain for the long-lived CFCs because the substantial and poorly constrained emissions that occurred before 1985, when U.S. EPA estimates begin, still contribute significantly to atmospheric abundances today. Uncertainties are smaller for gases having shorter lifetimes and shorter emission histories (*i.e.*, where a higher percentage of total emissions have occurred after 1985).

The smallest fractional contributions of U.S. emissions to present-day mixing ratios are calculated for CCl₄, CFC-11, HCFC-142b, HCFC-141b, and halon-1211. Larger contributions are estimated for some other CFCs, CH₃CCl₃, HCFC-22, halon-1301, CH₃Br, and some HFCs (Figure 2.13).

The largest increases in U.S. contributions in recent years are calculated for CH₃Br, HCFC-22, and halon-1301. The increased fractional contribution of U.S. CH₃Br emissions to its atmospheric abundance arises from

increases in U.S. consumption compared to global consumption since 2002 (Section 2.1.4 and Box 2.3). The U.S. fractional contribution to atmospheric mixing ratios of halon-1211, HCFC-141b, CH_3CCl_3 and some HFCs has decreased in recent years (Figure 2.13).

2.4 THE ATMOSPHERIC ABUNDANCE OF AGGREGATED CHLORINE AND BROMINE FROM LONG-LIVED ODSs

Many different chemicals contribute to atmospheric chlorine and bromine, such as sea salt, pool disinfectants, CFCs, and HCFCs. Only those with longer lifetimes (greater than months) and lower water solubilities escape scavenging by aerosols and rain, however, and become efficiently transported to the stratosphere and contribute to ozone depletion (ODSs such as CFCs, HCFCs, halons, CH_3Br , and others). Hence, tropospheric burdens of these long-lived ODSs are closely monitored because they provide a useful measure of changes and amounts of chlorine and bromine being transported to the stratosphere and that will ultimately become available for catalyzing the destruction of stratospheric ozone.

Stratospheric abundances of chlorine and bromine are more difficult to regularly measure with high precision. Such measurements are useful, however, to discern whether amounts and changes in stratospheric chlorine and bromine are well described by the total amount of chlorine or bromine measured in long-lived ODSs at Earth's surface. Stratospheric measurements take advantage of the fact that in the upper stratosphere, nearly all organic compounds have become photo-oxidized and chlorine and bromine exist primarily in only one or two chemical forms (*e.g.*, hydrogen chloride, HCl, and chlorine nitrate, ClONO_2 ; and bromine oxide, BrO, for example). As a result, stratospheric measurements of these few inorganic chemicals provide an integrated estimate of how ozone-depleting halogen levels are changing, and whether or not these changes are consistent with ODS observations in the lower atmosphere.


2.4.1 Atmospheric Chlorine

As a result of the restrictions on production and consumption of ODSs brought about by the Montreal Protocol, the abundance of chlorine measured in long-lived gases has been decreasing in the lower atmosphere since 1995 and has continued to decrease through 2004 (Clerbaux and Cunnold *et al.*, 2007). Global tropospheric chlorine in long-lived chemicals was 3.44 ppb in 2004, or 0.25 ppb below the peak observed in the early 1990s. The rate of tropospheric decline in total chlorine from all regulated ODSs during 2003-2004 was slightly slower than four years earlier, as the influence of CH_3CCl_3 continued to diminish; the mean decline during 2003-2004 was 20 ppt per year (0.6% per year).

Approximately 80-85% of organic chlorine in long-lived trace gases measured in the troposphere is accounted for by gases regulated by the Montreal Protocol (CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, HCFC-22, HCFC-142b, HCFC-141b, HCFC-124, HCFC-123, CH_3CCl_3 , CCl_4 , and halon-1211). Most of the remaining 15% (or 550 ppt Cl) is accounted for by methyl chloride, a chemical having predominantly (greater than 95%) non-industrial sources. Atmospheric mixing ratios of CH_3Cl have been relatively constant over the past decade, though year-to-year variations on the order of a few percent can be observed at Earth's surface during years with enhanced biomass burning (Clerbaux and Cunnold *et al.*, 2007).

Small additional amounts of chlorine (~2% of the sum from regulated ODSs and CH_3Cl , or 50-80 ppt Cl) may be contributed by short-lived gases such as CH_2Cl_2 , CHCl_3 , C_2Cl_4 , and others (Law and Sturges *et al.*, 2007). Tropospheric observations suggest that mixing ratios of some of these gases have decreased in recent years.

Because HCl and ClONO_2 have quite low abundances in the lower atmosphere, total column measurements of HCl and ClONO_2 from surface-based spectroscopic instruments provide an independent measure of stratospheric chlorine changes (Clerbaux and Cunnold *et al.*, 2007). These measurements show that, after many years of consistent increases, total column inorganic chlorine mixing ratios peaked in the mid-to-late 1990s and have since



Approximately 80 to 85% of organic chlorine in long-lived trace gases measured in the troposphere is accounted for by gases regulated by the Montreal Protocol. Most of the remaining 15% is accounted for by methyl chloride, a chemical having predominantly non-industrial sources.

declined. The declines have lagged behind the decreases observed at Earth's surface by a few years because of time lags associated with transporting air in the lower atmosphere to the stratosphere.

Satellite-based spectroscopic instruments also have the potential to measure changes in stratospheric chlorine abundance over time (Clerbaux and Cunnold *et al.*, 2007). To date, however, long-term trends determined from these instruments have added uncertainty from numerous complications related to small unexplained offsets in HCl measured by different instruments, substantial unexplained variability in the longest record (Halogen Occultation Experiment), and relatively short data records for other instruments that offer higher precision (Atmospheric Chemistry Experiment and Microwave Limb Sounder).

Despite these issues, satellite instruments have provided an important independent measure of stratospheric chlorine mixing ratios (Clerbaux and Cunnold *et al.*, 2007). Results from these instruments demonstrate that mixing ratios of chlorine observed in the upper stratosphere

are well explained by measured tropospheric abundances of long-lived ODSs regulated by the Protocol plus a contribution from CH_3Cl of approximately 15%. The scatter among results from different instruments prevents a precise estimate of the contribution of short-lived gases to stratospheric chlorine, but they do suggest it is on the order of a few percent, consistent with the tropospheric observations.

As of 2004, ground-based air sampling results show that CFCs still account for most of the long-lived Cl in the troposphere, (62% in 2004; Clerbaux and Cunnold *et al.*, 2007). The abundance of the three most abundant CFCs has peaked or is decreasing in the troposphere, with declines in CFC abundances accounting for about half of the decline in total tropospheric Cl in 2004 (-9 ppt Cl per year). Methyl chloroform still strongly influences total chlorine trends despite its dramatically reduced atmospheric abundance; in 2004 it accounted for more than half of the observed decline in Cl (-13.5 ppt Cl per year). Carbon tetrachloride has declined fairly steadily at a rate of 1 ppt per year and has accounted for an annual change in tropospheric chlorine of -4 ppt Cl per year during the past

As of 2004, the abundance of the three most abundant CFCs had peaked or was decreasing in the troposphere, with declines in CFC abundances accounting for about half of the decline in total tropospheric chlorine in that year.

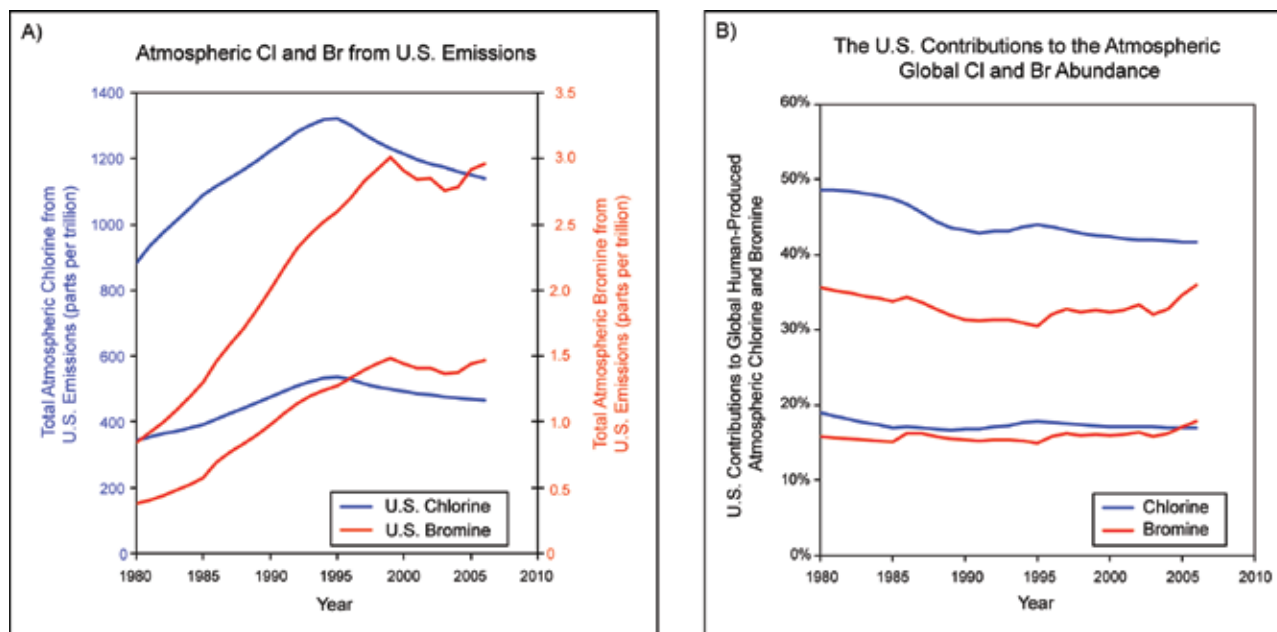


Figure 2.14 A) Estimated ranges of the tropospheric abundance of Cl and Br from U.S. emissions of all regulated ODSs. These ranges are from upper and lower estimates of U.S. emissions (see Box 2.6 for additional information). B) Estimated ranges in the fractional contribution of U.S. emissions to global atmospheric mixing ratios arising from industrial production of ODSs. In both panels, only emissions arising from industrial production of ODSs for restricted uses plus QPS uses of CH_3Br were considered; global and U.S. emissions of CH_3Cl and CH_3Br from natural processes are not included in these calculations. Chemicals included in these estimates of total Cl: CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, HCFC-22, HCFC-142b, HCFC-141b, HCFC-123, HCFC-124, CH_3CCl_3 , CCl_4 , and halon-1211; and of total Br include: CH_3Br , halon-1211, halon-1301, and halon-2402.

decade. In 2004 CH_3CCl_3 accounted for 2% (65 ppt Cl) and CCl_4 accounted for 11% (375 ppt Cl) of all long-lived Cl in the troposphere. (These declines total more than 100% owing to the offsetting increases observed for chlorine from HCFCs.)

HCFCs continue to increase in the atmosphere as they are used as substitutes for CFCs and other ODSs (Clerbaux and Cunnold *et al.*, 2007). They accounted for 6% of total tropospheric Cl in 2004, and chlorine from HCFCs increased at a rate of nearly 8 ppt Cl per year during that year. Though the increase in Cl from HCFCs during 2004 was significantly slower than observed in 1996-2000, near-term projections of production and use, and continued observations since the publishing of the latest WMO Scientific Assessment of Ozone Depletion Report (Clerbaux and Cunnold *et al.*, 2007), show accelerating growth rates since 2004.

Tropospheric chlorine attributable to U.S. emissions of long-lived ODSs also has declined since the early 1990s (Figure 2.14). The U.S. contribution to global tropospheric chlorine from all regulated ODSs (excluding consideration of CH_3Cl) is estimated as being between 17 and 42% in 2005. Despite this large uncertainty range, estimates of the rate of change have smaller uncertainties and suggest that the U.S. relative contribution to global atmospheric chlorine from regulated ODSs has remained fairly constant over the past decade.

2.4.2 Atmospheric Bromine

Bromine in the stratosphere catalyzes the destruction of ozone with a per-atom efficiency that is approximately 60 times that of chlorine (WMO, 2007). As a result, small mixing ratios of stratospheric bromine play an important part in controlling stratospheric ozone abundances. Bromine also differs from chlorine because emissions from regulated uses account for a smaller fraction of the inorganic bromine measured in the stratosphere. Whereas chlorine emissions from uses regulated by the Montreal Protocol accounted for approximately 80-85% of stratospheric chlorine at its peak abundance, emissions of bromine regulated by the Protocol accounted for approximately 50% of the bromine measured in the stratosphere at its

peak abundance of 20-22 ppt (estimated by assuming 30% of 9.5 ppt from CH_3Br as arising from regulated uses, plus 8 ppt Br from halons) (Law and Sturges *et al.*, 2007).

Chemicals containing bromine that are regulated by the Montreal Protocol include halons and methyl bromide, though methyl bromide has both natural and anthropogenic emissions. When both natural and anthropogenic sources of CH_3Br are considered together with the bromine from halons, these chemicals accounted for approximately 80-90% of total bromine reaching the stratosphere in 1998. Surface-based measurements show that total tropospheric bromine from these chemicals peaked in 1998 and has since declined (Clerbaux and Cunnold *et al.*, 2007). By mid-2004, tropospheric bromine from these gases was 0.6 to 0.9 ppt below the peak amount. The decline was entirely a result of declining CH_3Br mixing ratios. By 2004 the tropospheric mean CH_3Br mixing ratio had declined by 1.3 ppt (14%) from its peak in 1998. Although the rate of decline of CH_3Br was variable over this period, global mixing ratios of CH_3Br have declined each year during this period as global production decreased. Global atmospheric mixing ratios of the halons were still increasing slowly in 2004, albeit at slower rates than in earlier years (2004 rates of increase for the halons were less than 0.1 ppt per year). Continued increases in halon mixing ratios arise from continued production allowed in developing nations and slow leakage rates from large banks of halons in developed countries in fire extinguishers that are still in use.

Trends in global mean bromine accounted for by short-lived gases are not easily measured from ground-based stations, because of the high variability observed and the potential for local influences to dominate measured abundances and changes. In these instances, data from firn air (air trapped in uncompacted snow in the polar regions) have improved our understanding of historical changes in the atmospheric abundance of these chemicals. Firn air integrates atmospheric abundances over decadal periods so short-term variations are smoothed, but local influences could mask broader changes. Atmospheric histories of short-lived brominated chemicals such as dibromomethane (CH_2Br_2) and bromoform

Whereas chlorine emissions from uses regulated by the Montreal Protocol accounted for approximately 80-85% of stratospheric chlorine at its peak abundance, emissions of bromine regulated by the Protocol accounted for approximately 50% of the bromine measured in the stratosphere at its peak abundance.



BOX 2.7: Equivalent Effective Chlorine (EECI) and Equivalent Effective Stratospheric Chlorine (EESC)

The threat posed to the ozone layer from ODSs is not directly proportional to the summed mixing ratios of these chemicals in the troposphere. Instead, it depends upon the number of chlorine and bromine atoms contained in the ODSs, how rapidly the ODSs degrade once they reach the stratosphere and liberate ozone-depleting forms of chlorine and bromine, and the abundance of bromine relative to chlorine contained in the mix of ODSs reaching the stratosphere (given that bromine is 60 times more reactive, on average, than chlorine). To account for these influences, indices have been developed to estimate changes in the burden of reactive stratospheric halogen in a simple manner based on observed changes in tropospheric abundances of ODSs.

Equivalent Effective Chlorine (EECI) is one such index used here and elsewhere (WMO, 2007) to quantify overall changes in reactive halogen trends based upon the measured mix of ODSs in the troposphere. The timing associated with EECI changes correspond to the dates those changes were measured in the troposphere.

Equivalent Effective Stratospheric Chlorine (EESC) is a closely related index used to estimate the time evolution of ozone-depleting halogen in the stratosphere. In most past formulations it has differed from EECI only in that it includes a time lag associated with transporting air from the troposphere, where ODS measurements are regularly made, to the stratosphere. EESC is often used to estimate when the cumulative effect of all ODSs on ozone will return to a level attained at some earlier time, often chosen to be 1980, assuming no changes in dynamical, climate, or other non-ODS-related influences (WMO, 2007). Quite different “recovery” times can be calculated for midlatitude EESC and Antarctic EESC in springtime when lag times of three years for midlatitudes and six years for Antarctica are assumed (see Chapter 5 for additional discussion of recovery times). Furthermore, EESC projections for different scenarios of ODS uses have been an important tool for assessing the potential influence of various policy choices on ozone.

Recently, EESC has also been used to improve our understanding of the extent to which changes in ozone abundances may be due to policy restrictions under the currently adjusted and amended Montreal Protocol. Specifically, attempts have been made to identify both a slowing of the declining ozone trends and even a reversal of the decline, and whether these recovery milestones can be attributed to ODS changes.

Despite its usefulness, EESC provides only a rough estimate of the effect of ODSs on stratospheric ozone because it incorporates simplified assumptions regarding mixing processes and degradation rates. Recent efforts to enhance the formulation perhaps provide a more realistic evolution of stratospheric reactive halogen over time and space (Newman *et al.*, 2006, 2007). Other differences in more recent work relating to the calculation of EESC suggest some rather large alterations to estimated ODS recovery times and are currently a source of uncertainty in this analysis.

(CHBr₃), derived in this way suggest no large long-term changes in atmospheric mixing ratios in polar regions during the past two decades (Law and Sturges *et al.*, 2007).

As was true for chlorine, the integrated influence of changes in the tropospheric abundance of brominated gases can be measured in the stratosphere from airborne, balloon-borne, and satellite instrumentation. These data have been important for quantifying the role non-regulated chemicals play in controlling the abundance of bromine in the stratosphere. They have also demonstrated that the total abundance of Br in the stratosphere has increased over time in a manner that can be explained by the tropospheric mixing ratio changes observed

for halons and CH₃Br, considering lag times associated with air transport (Law and Sturges *et al.*, 2007). A recent study published since WMO (2007) suggests that the accumulation rate of bromine in the stratosphere has slowed in a manner consistent with the trend observed in the troposphere, after considering the time it takes to transport air from the troposphere to the stratosphere (Dorf *et al.*, 2006).

Tropospheric bromine attributable to U.S. emissions of halons and CH₃Br also peaked in 1998-1999 and declined through 2003, as estimated by the U.S. EPA (U.S. EPA, 2007) (Figure 2.14). Since 2003, however, the increased emissions of CH₃Br from Critical Use Exemptions and QPS uses (Box 2.3) have

caused the tropospheric abundance of bromine attributable to U.S. emissions to increase. While the contribution of United States to total atmospheric bromine (the industrially derived emissions from regulated uses only) declined throughout the 1980s and early 1990s, it reversed course and actually increased by about 7% from 2000-2005; the U.S. contribution to atmospheric bromine is estimated at between 17 and 35% in 2005 (only halons and anthropogenic CH₃Br considered).

2.4.3 Equivalent Effective Stratospheric Chlorine and Equivalent Effective Chlorine

The combined influence of changes in chlorinated and brominated ODSs on reactive halogen abundances in the stratosphere and on stratospheric ozone can be assessed from aggregate quantities such as EESC and EECl (Box 2.7). These quantities are derived with weighting factors applied to tropospheric ODS abundances to provide a rough estimate of how total reactive halogen abundances are changing or will likely change in the stratosphere based upon observed trends in tropospheric mixing ratios of ODSs.

EECl from measured global surface mixing ratios of regulated ODSs, substitutes, and CH₃Cl peaked in 1994 and has since declined (Figure 2.15). By 2004, EECl had declined by 277 ppt, or 8-9% from the peak. This decline represents about 20% of the decline needed for EECl levels to return to their 1980 levels (Clerbaux and Cunnold *et al.*, 2007). Most of this decline resulted from changes in the atmospheric abundance of the shorter-lived ODSs: CH₃CCl₃ and CH₃Br.

In 2005 CFCs still contributed the most to the atmospheric burden of EECl (45%) from all long-lived chlorinated and brominated chemicals, including those with large natural sources (CH₃Cl and CH₃Br) (Table 2.2). Other chlorinated gases contributed 25%, brominated gases contributed 28%, and HCFCs contributed 2.5% to EECl in 2005 (Table 2.2). These percentages include natural contributions to the atmospheric abundance of CH₃Cl and CH₃Br. When only anthropogenic contributions to 2005 EECl are considered, the relative contribution of CFCs increases (to 59%), that for chlorocarbons

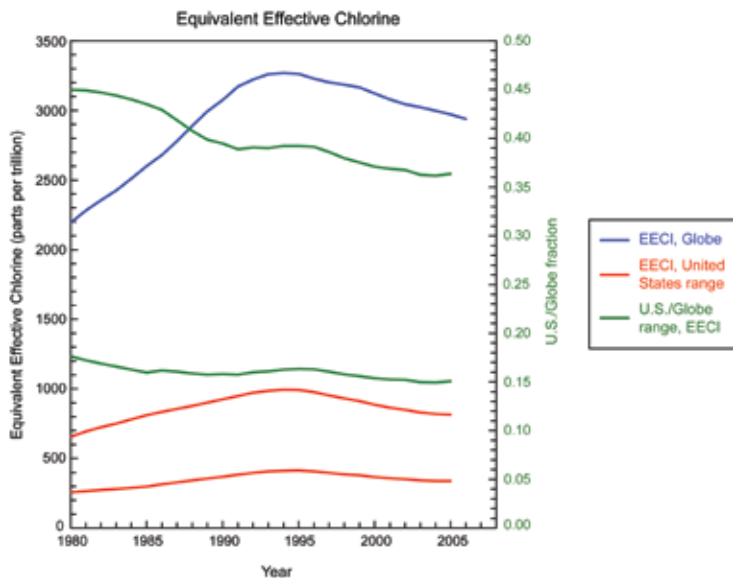


Figure 2.15 EECl from measured global mixing ratios of ODSs (blue line) and from estimates of ODS mixing ratios attributable to U.S. emissions (upper and lower ranges bounded by red lines; see Box 2.6 for discussion of U.S. emissions). While all long-lived ODSs, including CH₃Cl and the natural contribution of CH₃Br, are included in global EECl, natural contributions are not included in the United States/Global fraction or EECl calculated from U.S. emissions alone. Also shown are ranges for the fraction of EECl attributable to U.S. emissions (green lines, right-hand axis).

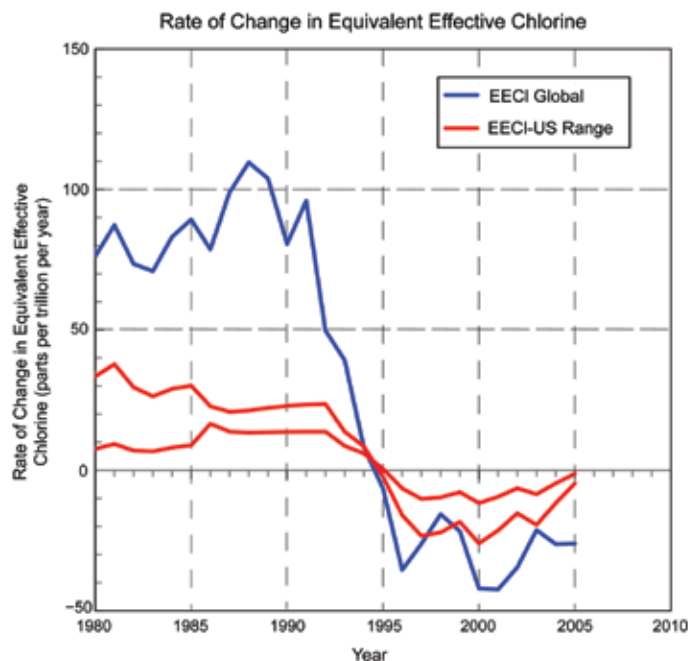


Figure 2.16 Rate of change in global EECl derived from measured global atmospheric mixing ratios of ODSs and substitute chemicals (blue line), and the rate of change in EECl derived from atmospheric mixing ratios calculated from upper and lower bounds on U.S. emissions of ODSs (bounded by red lines; see Box 2.6 for discussion of U.S. emissions). High and low U.S. EECl estimates express the influence of emission uncertainties on these rates (Box 2.6).

United States emissions of ozone-depleting substances have accounted for between 15 and 39% of total Equivalent Effective Chlorine, an index used to quantify overall changes in reactive halogen trends, from regulated chemicals from 1994 to 2004, and between 15 and 36% in 2005.



decreases (to 17%), that for bromocarbons decreases (to 20%), and that for CH₃Br alone becomes 3.1% (see footnote to Table 2.2 for grouping definitions).

Declines are also calculated for EECl attributable to U.S. emissions of ODSs for regulated uses during 1994-2004, though substantial uncertainty in atmospheric abundances derived from U.S. emissions prevents a precise determination of EECl from U.S. emissions alone. United States emissions of ODSs for regulated uses have accounted for between 15 and 39% of total EECl from regulated chemicals from 1994 to 2004, and between 15 and 36% in 2005.

Despite the added uncertainty U.S. emissions before 1985 add to estimates of the U.S. contribution to Cl, Br, and EECl in today's atmosphere, these uncertainties have a much smaller influence on our understanding of changes in these quantities (Figure 2.16). Global EECl declined fairly consistently since the mid-1990s. EECl from U.S. emissions followed global trends until about 2003, when declines in U.S. EECl slowed substantially. From 2004 to 2005, U.S. EECl declines were substantially smaller than in earlier years, primarily because of the increases in U.S. emissions of brominated gases during these years (primarily CH₃Br) (Figure 2.16).

On uncertainty in the U.S. contribution. Though estimates of the rate of change in EECl attributable to U.S. emissions of ODSs and substitutes are much less dependent upon pre-1985 emission rates, they do rely on the accuracy of emission algorithms of ODSs from in-use applications. Such algorithms are difficult to verify experimentally on national scales (Section 2.2.6).

2.4.3.1 ESTIMATING REACTIVE HALOGEN TRENDS FOR THE MIDLATITUDE STRATOSPHERE

Changes in stratospheric halogen abundance are delayed from those observed in the troposphere because of the time it takes for air to be transported from the troposphere to stratosphere. In addition to this time lag, mixing processes also influence how tropospheric composition changes propagate to the stratosphere. Estimates

of stratospheric halogen trends in the midlatitude stratosphere have been roughly derived with a lag of three years on EECl. The EESC calculated for the midlatitude stratosphere suggests that by 2004, the midlatitude stratospheric halogen burden had declined by approximately 7% from its peak.

2.4.3.2 ESTIMATING REACTIVE HALOGEN TRENDS USING EESC FOR THE ANTARCTIC STRATOSPHERE

Measurements suggest that air found in the lower Antarctic stratosphere during the early springtime has resided in the stratosphere for about six years, or approximately twice as long as it takes to transport air from the troposphere to the midlatitude stratosphere. This influence, combined with the expected slow decline in EESC during the twenty-first century compared to the relatively fast buildup around 1980, suggests that it will take 15-20 years longer for EESC in Antarctica to fall below the 1980s levels than it will for midlatitude EESC to drop similarly (Daniel and Velders *et al.*, 2007) (see also Chapter 5). By 2004, EESC over Antarctica is estimated to have declined from peak levels by only 3%, when estimated simply as a six-year lag of EECl. More detailed analyses of these projections are currently being refined to include mixing effects and a better representation of decomposition rates for individual ODSs and substitute chemicals (*e.g.*, Newman *et al.*, 2006).

2.5 CHANGES IN RADIATIVE FORCING ARISING FROM OZONE-DEPLETING CHEMICALS AND SUBSTITUTES

2.5.1 Changes in Direct Radiative Forcing

As previously noted in this chapter, weighting emissions by 100-year GWPs allows one to compare the integrated radiative forcing from various greenhouse gases, including ODSs, with the intent to gain insight into the resulting climate effects (see Box 2.2). Instantaneous radiative forcing is generally calculated by multiplying the atmospheric mixing ratios of the various GHGs by their radiative efficiencies (Section 2.1.1). While the relationship between changes in radiative forcing and global average temperature vary somewhat among models,

radiative forcing remains arguably the best simple metric available to compare the direct climate effect of greenhouse gas abundances. As with “direct” GWPs (Box 2.2), direct radiative forcing represents the forcing of GHGs due to their own absorption of infrared energy and neglects any potential chemical or other feedbacks.

The direct, global radiative forcing due to ODSs and substitutes reached about 0.34 W per m² in 2005 and was still increasing slowly (Figure 2.17). Due to compliance with the Montreal Protocol, however, the recent increase in radiative forcing was much slower than measured in the early 1990s. HFCs contributed a noticeable amount to this increase on a global scale. Radiative forcing from non-HFC ODSs and substitutes changed less than 0.001 W per m² from 2001-2005. For the purpose of putting this total direct forcing into perspective, the amount of radiative forcing due to CO₂, CH₄,

and N₂O in 2005 was approximately 1.66 W per m², 0.48 W per m², and 0.16 W per m², respectively (Forster *et al.*, 2007). While the increase in forcing from ODSs has occurred relatively rapidly, the decrease will be largely limited by the global ODS lifetimes, and will occur more slowly. These future projections will be further discussed in Chapter 5.

The relative direct forcing contributions of classes of ODS chemicals and their replacements are shown in Figure 2.18. The CFCs have contributed between 79 and 86% of the total direct forcing from ODSs since 1980. However, over the last decade the fractional contribution of the CFCs has declined, as have the fractional contributions of CH₃CCl₃ and CCl₄. Increases in HCFC abundances, primarily HCFC-22, and in HFC abundances are counteracting the decline of these other gases. Consideration of the indirect forcing due to ODS-induced ozone depletion alters this figure somewhat, though

The direct, global radiative forcing due to ODSs and substitutes reached about 0.34 W per m² in 2005 and was still increasing slowly. Putting this total direct forcing into perspective, the amount of radiative forcing due to CO₂, CH₄, and N₂O in 2005 was approximately 1.66 W per m², 0.48 W per m², and 0.16 W per m², respectively.

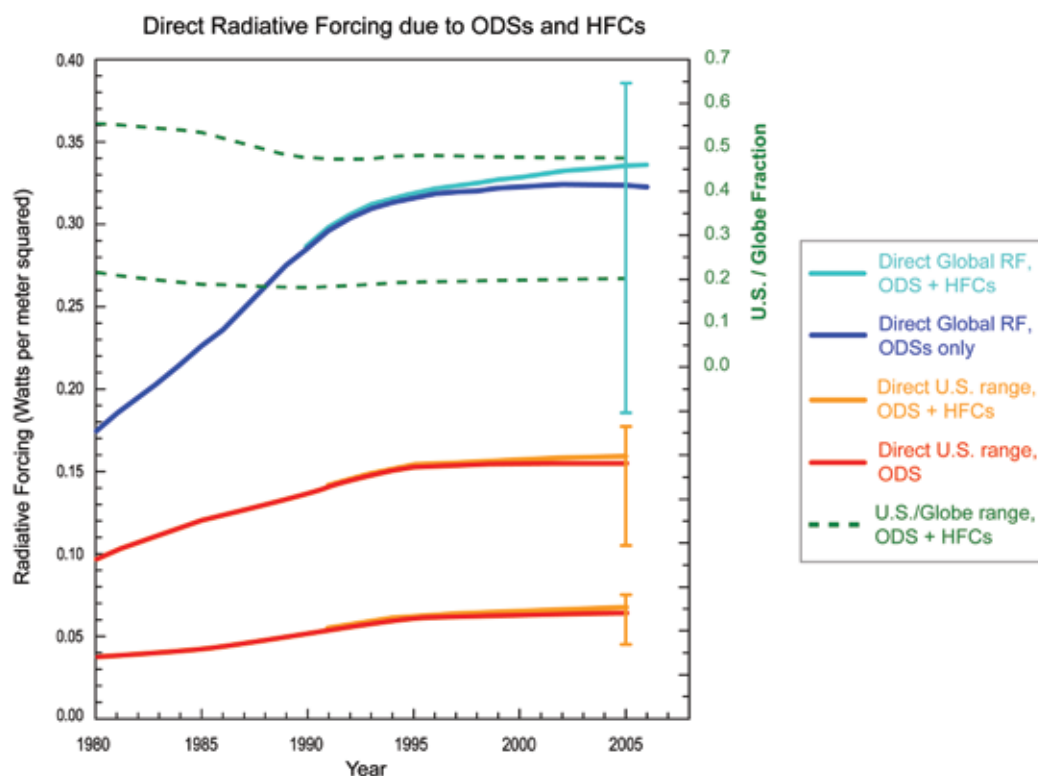


Figure 2.17 Radiative forcing time series arising from changing atmospheric mixing ratios of ODSs and their substitutes. Direct radiative forcing is calculated by weighting global atmospheric mixing ratios of ODSs or a range of ODS mixing ratios attributable to the U.S. (see Box 2.6) by compound-dependent radiative efficiencies for the years 1980-2005. The additional forcing contribution of HFCs to global or U.S. radiative forcing is indicated by the lighter-colored lines. The uncertainties indicated for 2005 include the range of influences (and uncertainty) of the indirect forcing associated with stratospheric ozone depletion. This indirect influence was estimated for the U.S. by considering the range of EECL attributable to the U.S. relative to total global EECL in 2005 (see Box 2.2).

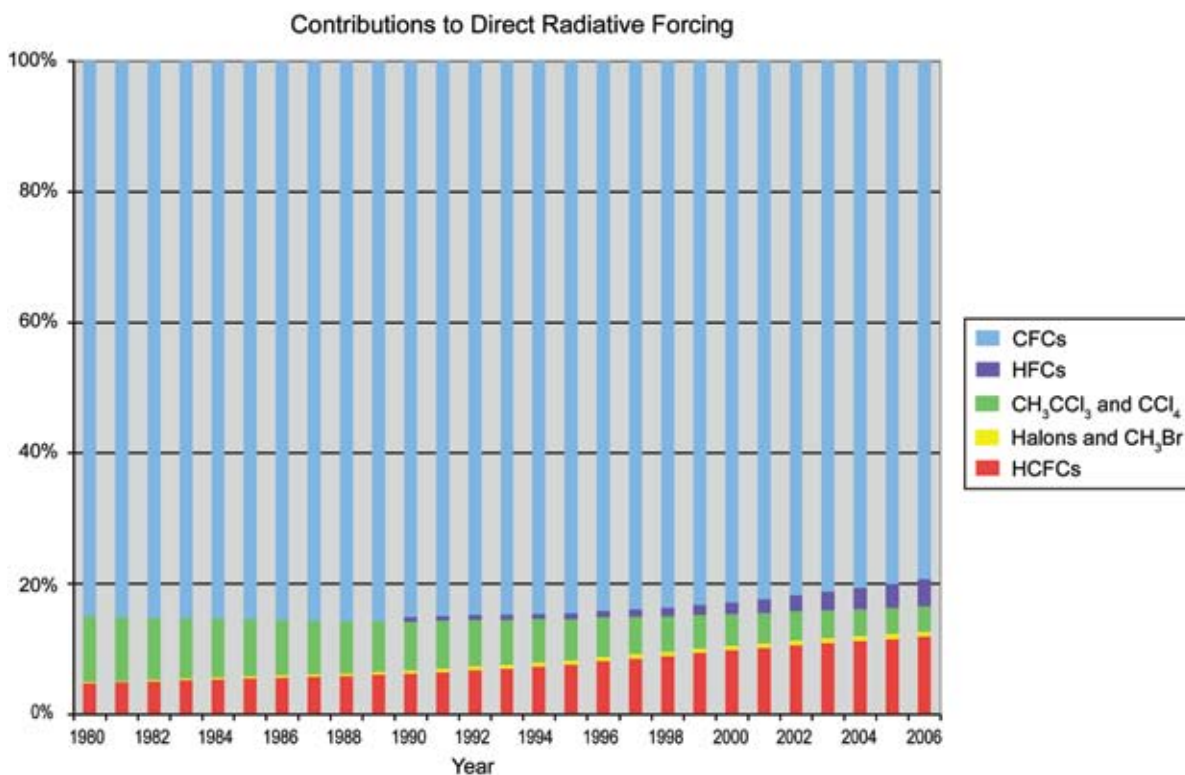


Figure 2.18 Relative contributions of ODS compound classes to global direct radiative forcing. Percentages in 2005 are CFCs=80%, HCFCs = 12%, other ODSs = 5%, HFCs = 4%.

in 2005, for example, the percent contribution of each compound class changes by less than 4% when a mean radiative ozone influence of -0.05 W per m^2 is considered (derived by scaling ozone radiative forcing of -0.05 W per m^2 by the fraction of EEC1 contributed by each compound class).

2.5.1.1 ESTIMATING THE U.S. CONTRIBUTION TO DIRECT RADIATIVE FORCING CHANGES

Using estimates of atmospheric mixing ratios of ODSs arising solely from U.S. emissions (Section 2.3), the U.S. contribution to the direct global radiative forcing from ODSs and substitutes is calculated to have been between 0.068 and 0.16 W per m^2 in 2005 (Figure 2.17). The error bars are calculated by summing the individual high and low direct forcing estimates for each of the ODSs. Since 1990, the U.S. contribution has accounted for between 19 and 49% of the global direct forcing from ODSs and substitute chemicals. The contributions of the various ODS classes to radiative forcing show the same qualitative behavior for U.S. emissions as for the global emissions that are apparent in Figure 2.18; HCFC contributions are increasing while CFC, CH_3CCl_3 , and CCl_4 contributions

are decreasing. We estimate that the United States accounted for about 45% of the increase in direct radiative forcing arising from HCFCs during 2000 to 2006.

2.5.2 Changes in Net Radiative Forcing

As stated in Box 2.2, the direct quantities represent the effect of the ODSs themselves on radiative forcing through their absorption of infrared energy. Their destruction of stratospheric ozone leads to an additional radiative effect, referred to as an “indirect” effect of the ODSs.

In the past, it had been thought that the indirect forcing might have offset as much as 50% of total direct halocarbon radiative forcing, but estimates from different studies varied widely (Ramaswamy *et al.*, 2001). More recently, now that ozone trends are thought to be better quantified, particularly in the radiatively important region near the tropopause, the magnitude of the ozone forcing has been revised to $-0.05 \pm 0.05 \text{ W per m}^2$ for the changes in stratospheric ozone between 1979 and 1998 and $-0.05 \pm 0.10 \text{ W per m}^2$ for the changes in stratospheric ozone from preindustrial times to 2005 (Forster *et al.*, 2007). Although revised

Since 1990, the U.S. contribution has accounted for between 19 and 49% of the global direct forcing from ozone-depleting substances and substitute chemicals.

to a smaller value, the ozone forcing remains potentially significant relative to the direct forcing and continues to be highly uncertain, with even the sign in doubt (Figure 2.17; see Box 2.2). However, it is known that this indirect forcing will gradually become negligible as ozone recovers from depletion due to ODSs (Daniel *et al.*, 1995; see Chapter 5).

The IPCC (2007) estimate for the magnitude of the ozone forcing through 2005 (-0.05 ± 0.10 W per m^2) is added to the global direct ODS forcing in Figure 2.17. As discussed in Box 2.2, there are potential problems related to adding these direct and indirect forcing quantities; nevertheless, such an addition does permit a comparison of the sizes of these globally averaged forcings. Estimates for the U.S. contribution to the indirect forcing are also added to the U.S. direct ODS forcing curves. The U.S. indirect forcing has been calculated by scaling the global ozone forcing range by the U.S. contribution to global EECL. For both the global and U.S. cases, the indirect forcing remains potentially significant but quite uncertain compared to the direct radiative forcing estimates.

2.6 SUMMARY OF FINDINGS RELATED TO THE ROLE OF THE UNITED STATES IN INFLUENCING PAST CHANGES IN PRODUCTION, CONSUMPTION, EMISSIONS, AND MIXING RATIOS OF OZONE-DEPLETING SUBSTANCES AND THEIR SUBSTITUTES

Stratospheric ozone depletion is a global issue because the amount of ozone depletion above the United States, or any other location, results from the global emission of ODSs. A reduction in U.S. ODS emissions leads to reduced ozone depletion above the United States only to the extent to which it reduces global ODS emissions.

In response to restrictions put into place under the Montreal Protocol, U.S. consumption of ODSs for regulated dispersive uses, considered in sum, have declined substantially from peak levels. By 2005, ODP-weighted consumption in the United States had declined by 97-98%,

or nearly 400 ODP-Kt since the late 1980s (UNEP, 2007). These data indicate that the United States accounted for 24 (± 2)% of total global production of ODSs during the years of substantial production (1986-1994), and 10 (± 2)%, on average, during 2001-2005 (when weighted by ODPs).

United States consumption declines have been slightly faster than phase-out schedules for all developed countries in the adjusted and amended Montreal Protocol for most ODSs. Critical Use Exemptions have resulted in ODS consumption for CH_3Br and CFCs above these scheduled allotments in recent years. For example, though CH_3Br consumption in developed countries was to have been zero in 2005 and thereafter, U.S. consumption for critical uses was 28% of 1986 baseline consumption during this year (4.4 ODP-Kt) and, in 2006, was 27% of 1986 baseline consumption (4.1 ODP-Kt) (UNEP/MBTOC, 2007). Authorized CUEs for CH_3Br consumption in the United States for 2007 were reduced compared to 2005 and 2006 (17% of the U.S. 1986 baseline consumption). U.S. consumption also has continued for critical uses of CFCs despite the 1996 phase-out, though this consumption has been comparably small (less than 1% of 1986 United States baseline CFC consumption in all years since 1996).

The decreases in global and U.S. production and consumption have led to substantial reductions in emissions of most ODSs to the atmosphere. But while global emissions can be derived from observed global atmospheric changes and knowledge of ODS atmospheric lifetimes, U.S. emissions and their changes are more uncertain, as they were derived from vintaging model analyses of sales, use, and release patterns of ODSs (a “bottom-up” analysis; U.S. EPA, 2007). The results suggest that both global and U.S. emissions of ODSs declined overall by 81-82% since the late 1980s when weighted by ODPs (Table 2.1). Furthermore, this analysis suggests that the United States accounted for a decreasing amount of global ODS emissions, from a peak of 35% in 1993 to 20 (± 2)% during 2000-2005 (Figure 2.7).

Similar relative contributions of U.S. emissions in 2005 to global atmospheric abundances are calculated for the atmospheric abundance



of chlorine (17-42%), bromine (17-35%), and EECI (15-36%) during 2000-2005. EECI arising from U.S. emissions declined every year from 1994 through 2004, but did so much more slowly during 2004 to 2005, largely due to the recent increase in U.S. CH₃Br emissions. U.S. emissions have also resulted in the U.S. accounting for 19-49% of global direct radiative forcing from ODSs in the 2000s.

Weighting ODS emissions by 100-year, direct GWPs allows the magnitude of these emissions to be compared to those of CO₂ to approximate their direct climate effects. Declines of 77 (77-84)% and 74 (71-75)% are calculated for annual global and U.S. GWP-weighted emissions of ODS and substitute chemicals through 2004, or a decline in annual emissions on a global scale of 7270 (3600-8500) Mt CO₂-equivalents and a decline in annual emissions in the United States of 1640 (900-1880) Mt CO₂-equivalents (quantities in parenthesis are calculated with consideration of net GWPs that include radiative forcing and uncertainty associated with stratospheric ozone changes;

see Box 2.2). The U.S. decline alone is likely a large fraction of the global benefit anticipated as a result of adherence the Kyoto Protocol (~2000 Mt CO₂-equivalent emissions; Velders *et al.*, 2007).



APPENDIX 2A

Table 2A.1 Lifetimes, relative fractional halogen release factor, and Ozone Depletion Potentials for halocarbons. Reproduced from Daniel and Velders *et al.* (2007).

Halocarbon	Lifetime (years)	Relative Fractional Release Factor ^a	Semi-Empirical ODP	ODP in Montreal Protocol
Annex A-I				
CFC-11	45	1	1.0	1.0
CFC-12	100	0.60	1.0	1.0
CFC-113	85	0.75	1.0	0.8
CFC-114	300	0.28±0.02 ^b	1.0	1.0
CFC-115	1700		0.44 [†]	0.6
Annex A-II				
Halon-1301	65	0.62	16	10.0
Halon-1211	16	1.18	7.1 ^c	3.0
Halon-2402	20	1.22	11.5	6.0
Annex B-II				
Carbon tetrachloride	26	1.06	0.73	1.1
Annex B-III				
Methyl chloroform	5.0	1.08	0.12	0.1
Annex C-I				
HCFC-22	12.0	0.35	0.05	0.055
HCFC-123	1.3	1.11	0.02	0.02
HCFC-124	5.8	0.52	0.02	0.022
HCFC-141b	9.3	0.72	0.12	0.11
HCFC-142b	17.9	0.36	0.07	0.065
HCFC-225ca	1.9	1.1	0.02	0.025
HCFC-225cb	5.8	0.5	0.03	0.033
Annex E				
Methyl bromide	0.7	1.12	0.51	0.6
Others				
Halon-1202	2.9		1.7 ^d	
Methyl chloride	1.0	0.80	0.02	

[†] Model-derived values, WMO (2003).

^a From WMO (2003), Table I-4, except for the value for CFC-114. For the EESC calculations in Section 1.8 of WMO (2003), slightly different relative fractional release factors were used by mistake for the halons.

^b From Schauffler *et al.*, 2003.

^c The ODP of halon-1211 should have been reported as 5.3 in the previous Assessment (WMO, 2003), but was incorrectly reported as 6.0 due to a calculation error.

^d WMO (2003), with adjustment for updated α value.



Table 2A.2 Direct Global Warming Potentials for selected gases. Reproduced from Daniel and Velders et al. (2007).

Industrial Designation(s) or Common Name	Chemical Formula	Radiative Efficiency ^b (W per square m per ppbv)	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
Carbon dioxide	CO ₂	1.41 × 10 ^{-5 c}		1	1	1
Nitrous oxide	N ₂ O	3.03 × 10 ⁻³	114 ^d	289	298	153
Chlorofluorocarbons						
CFC-11	CCl ₃ F	0.25	45	6,730	4,750	1,620
CFC-12	CCl ₂ F ₂	0.32	100	10,990	10,890	5,200
CFC-13	CCIF ₃	0.25	640	10,800	14,420	16,430
CFC-113	CCl ₂ FCCIF ₂	0.30	85	6,540	6,130	2,690
CFC-114	CCIF ₂ CCIF ₂	0.31	300	8,040	10,040	8,730
CFC-115	CCIF ₂ CF ₃	0.18	1700	5,310	7,370	9,990
Hydrochlorofluorocarbons						
HCFC-21	CHCl ₂ F	0.14	1.7	530	151	46
HCFC-22	CHClF ₂	0.20	12.0	5,160	1,810	549
HCFC-123	CHCl ₂ CF ₃	0.14	1.3	273	77	24
HCFC-124	CHClFCF ₃	0.22	5.8	2,070	609	185
HCFC-141b	CH ₃ CCl ₂ F	0.14	9.3	2,250	725	220
HCFC-142b	CH ₃ CCIF ₂	0.20	17.9	5,490	2,310	705
HCFC-225ca	CHCl ₂ CF ₂ CF ₃	0.20	1.9	429	122	37
HCFC-225cb	CHClFCF ₂ CCIF ₂	0.32	5.8	2,030	595	181
Hydrofluorocarbons						
HFC-23	CHF ₃	0.19 ^e	270	11,990	14,760	12,230
HFC-32	CH ₂ F ₂	0.11 ^e	4.9	2,330	675	205
HFC-41	CH ₃ F	0.02	2.4	323	92	28
HFC-125	CHF ₂ CF ₃	0.23	29	6,340	3,500	1,100
HFC-134	CHF ₂ CHF ₂	0.18	9.6	3,400	1,100	335
HFC-134a	CH ₂ FCF ₃	0.16 ^e	14.0	3,830	1,430	435
HFC-143	CH ₂ FCHF ₂	0.13	3.5	1,240	353	107
HFC-143a	CH ₃ CF ₃	0.13	52	5,890	4,470	1,590
HFC-152	CH ₂ FCH ₂ F	0.09	0.60	187	53	16
HFC-152a	CH ₃ CHF ₂	0.09	1.4	437	124	38
HFC-227ea	CF ₃ CHFCF ₃	0.26 ^e	34.2	5,310	3,220	1,040
HFC-236cb	CH ₂ FCF ₂ CF ₃	0.23	13.6	3,630	1,340	407
HFC-236ea	CHF ₂ CHFCF ₃	0.30	10.7	4,090	1,370	418
HFC-236fa	CF ₃ CH ₂ CF ₃	0.28	240	8,100	9,810	7,660
HFC-245ca	CH ₂ FCF ₂ CHF ₂	0.23	6.2	2,340	693	211
HFC-245fa	CHF ₂ CH ₂ CF ₃	0.28	7.6	3,380	1,030	314
HFC-365mfc	CH ₃ CF ₂ CH ₂ CF ₃	0.21	8.6	2,520	794	241
HFC-43-10mee	CF ₃ CHFCF ₂ CF ₃	0.40	15.9	4,140	1,640	499

Industrial Designation(s) or Common Name	Chemical Formula	Radiative Efficiency ^b (W per square m per ppbv)	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
Chlorocarbons						
Methyl chloroform	CH ₃ CCl ₃	0.06	5.0	506	146	45
Carbon tetrachloride	CCl ₄	0.13	26	2,700	1,400	435
Methyl chloride	CH ₃ Cl	0.01	1.0	45	13	4
Bromocarbons						
Methyl bromide	CH ₃ Br	0.01	0.7	17	5	1
Halon-1201	CHBrF ₂	0.14	5.8	1,380	404	123
Halon-1211	CBrClF ₂	0.30	16	4,750	1,890	574
Halon-1301	CBrF ₃	0.32	65	8,480	7,140	2,760
Halon-2402	CBrF ₂ CBrF ₂	0.33	20	3,680	1,640	503
Fully fluorinated species						
Sulfur hexafluoride	SF ₆	0.52	3200	16,260	22,810	32,600
Trifluoromethylsulfur-pentafluoride	SF ₅ CF ₃	0.57	650-950	13,120-13,180	17,540-17,960	20,060-22,360
Perfluoromethane	CF ₄	0.10 ^e	50000	5,210	7,390	11,190
Perfluoroethane	C ₂ F ₆	0.26	10000	8,620	12,200	18,180
Perfluoropropane	C ₃ F ₈	0.26	2600	6,310	8,830	12,450
Perfluorobutane	C ₄ F ₁₀	0.33	2600	6,330	8,850	12,480
Perfluorocyclobutane	c-C ₄ F ₈	0.32	3200	7,310	10,250	14,660
Perfluoropentane	C ₅ F ₁₂	0.41	4100	6,510	9,150	13,260
Perfluorohexane	C ₆ F ₁₄	0.49	3200	6,620	9,290	13,280
Perfluorodecalin	C ₁₀ F ₁₈	0.56 ^f	1000	5,500	7,510	9,440
Halogenated alcohols and ethers						
HFE-125	CHF ₂ OCF ₃	0.44	136	13,790	14,910	8,490
HFE-134	CHF ₂ OCHF ₂	0.45	26	12,190	6,320	1,960
HFE-143a	CH ₃ OCF ₃	0.27	4.3	2,630	756	230
HCFE-235da2	CHF ₂ OCHClCF ₃	0.38	2.6	1,230	349	106
HFE-245fa2	CHF ₂ OCH ₂ CF ₃	0.31	4.9	2,280	659	200
HFE-254cb2	CH ₃ OCF ₂ CHF ₂	0.28	2.6	1,260	359	109
HFE-7100 (HFE-44-9)	CH ₃ OC ₄ F ₉	0.31	5.0	1,390	404	123
HFE-7200 (HFE-56-9)	C ₂ H ₅ OC ₄ F ₉	0.30	0.77	200	57	17
HFE-245cb2	CH ₃ OCF ₂ CF ₃	0.32	5.1	2,440	708	215
HFE-347mcc3	CH ₃ OCF ₂ CF ₂ CF ₃	0.34	5.2	1,980	575	175
HFE-356pcc3	CH ₃ OCF ₂ CF ₂ CHF ₂	0.33	0.93	386	110	33
HFE-374pc2	CH ₃ CH ₂ OCF ₂ CHF ₂	0.25	5.0	1,930	557	169
	CH ₃ OCF(CF ₃) ₂	0.31	3.4	1,200	343	104



Industrial Designation(s) or Common Name	Chemical Formula	Radiative Efficiency ^b (W per square m per ppbv)	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
HFE-43-10pccc124 ^a	CHF ₂ OCF ₂ OC ₂ F ₄ O-CHF ₂	1.37	6.3	6,320	1,870	569
	(CF ₃) ₂ CHOH	0.28	2.0	764	217	66
HFE-236ca12	CHF ₂ OCF ₂ OCHF ₂	0.66	12.1	8,040	2,820	859
HFE-338pcc13	CHF ₂ OCF ₂ CF ₂ O-CHF ₂	0.87	6.2	5,070	1,500	456
Species whose lifetimes have a high uncertainty						
Nitrogen trifluoride	NF ₃	0.21 ^e	740	13,370	18,000	21,270
Perfluorocyclopropane	c-C ₃ F ₆	0.42	>1000	>12,700	>17,340	>21,800
HFE-227ea	CF ₃ CHFOCF ₃	0.40	11	4,540	1,540	468
HFE-236ea2	CHF ₂ OCHFCF ₃	0.44	5.8	3,370	989	301
HFE-236fa	CF ₃ CH ₂ OCF ₃	0.34	3.7	1,710	487	148
HFE-245fa1	CHF ₂ CH ₂ OCF ₃	0.30	2.2	1,010	286	87
HFE-329mcc2	CHF ₂ CF ₂ OCF ₂ CF ₃	0.49	6.8	3,060	919	279
HFE-338mcf2	CF ₃ CH ₂ OCF ₂ CF ₃	0.43	4.3	1,920	552	168
HFE-347mcf2	CHF ₂ CH ₂ OCF ₂ CF ₃	0.41	2.8	1,310	374	114
HFE-356mec3	CH ₃ OCF ₂ CHFCF ₃	0.30	0.94	355	101	31
HFE-356pcf2	CHF ₂ CH ₂ OCF ₂ CHF ₂	0.37	2.0	931	265	80
HFE-356pcf3	CHF ₂ OCH ₂ CF ₂ CHF ₂	0.39	3.6	1,760	502	153
	CHF ₂ OCH(CF ₃) ₂	0.41	3.1	1,330	379	115
	-(CF ₂) ₄ CH(OH)-	0.30	0.85	254	72	22

Note: Values are calculated for a CO₂ mixing ratio of 378 ppm, compared with 370 ppm in IPCC/TEAP (2005) and WMO (2003), which tends to increase all GWPs.

^a Referred to as H-Galden 1040x in WMO/UNEP ozone assessments prior to WMO (2007).

^b All values not otherwise noted from IPCC/TEAP (2005).

^c See Section 8.2.3 of Daniel and Velders *et al.*, 2007.

^d This value is an adjustment time that includes feedbacks of emissions on the lifetime.

^e See Table 8-3 of Daniel and Velders *et al.*, 2007.

^f From Shine *et al.*, 2005.

Table 2A.3 Direct and indirect GWPs for a 100-year time horizon

Gas	Direct GWP ^a	Indirect GWP ^b	
		Low	High
CFC-11	4,750	-3,790	1,263
CFC-12	10,890	-2,160	720
CFC-113	6,130	-2,530	843
CH ₃ CCl ₃	146	-643	214
CCl ₄	1,400	-3,630	1,210
HCFC-22	1,810	-286	95
HCFC-123	77	-83	28
HCFC-124	609	-120	40
HCFC-141b	725	-667	222
HCFC-142b	2,310	-362	121
HCFC-225ca	122	-93	31
HCFC-225cb	595	-156	52
CH ₃ Br	5	-2,150	717
Halon 1211	1,890	-40,280	13,430
Halon 1301	7,140	-49,090	16,360
Halon 2402	1,640	-62,000	20,670

^a Uncertainties associated with direct GWPs are estimated to be 35% at the 2 σ level.

^b Indirect GWPs are affected by numerous uncertainties as discussed in the text. Here, the only contribution to the indirect GWP range considered is uncertainty in the ozone forcing through 2005 (-0.05 \pm 0.1 W per m²; IPCC, 2007). The 'Low' GWP assumes an ozone forcing of -0.15 W per m², while the 'High' is calculated for +0.05 W per m². Both indirect values are calculated by scaling the indirect GWPs in WMO (2007) by the ratio of the appropriate ozone forcing used here to the forcing assumed in WMO (2007), which was -0.15 W per m².



