Chapter 2. Current Trends, Mixing Ratios, and Emissions of Ozone-Depleting Substances and Their Substitutes (Including Appendix 2.A)

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KEY FINDINGS

Measures of production, consumption, emission, and atmospheric abundances of ozone-depleting substances 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 towards 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 States[1]:

- By 2005, the summed, global annual production and consumption of ozone-depleting substances to regulated uses had decreased 95% from peak amounts reported during the late 1980s owing to the Montreal Protocol[2]. Summed U.S. production and consumption of these substances to regulated uses declined by 97-98% over this same period[2].
- 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 replace[3].
- Declines in overall U.S. consumption of ozone-depleting substances and substitute chemicals through 2005 for regulated uses have been more rapid than total global declines. When ozone-depletion influences are considered[4], the fractional contribution of the U.S. to annual global consumption of ozone-

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[1] Global production and consumption amounts for regulated uses of ODSs were obtained from UNEP compilations of data reported to them (UNEP, 2007), and, for magnitudes of unregulated uses, from UNEP Technical Option committee reports (UNEP/MBTOC, 2007; UNEP/CTOC, 2007); global production data for HFCs was taken from IPCC-TEAP (2005); U.S. emissions of ODSs were taken from EPA's vintaging model analysis, which is a time-dependent analysis of the amount and type of ODS in applications throughout the U.S., loss rates of ODS from these applications, and how these quantities change over time (EPA, 2007).

[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 (nondispersive) applications. Consumption should equal production on a global scale averaged over time. In this Key Finding, production and consumption values 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, and emission data throughout this document to allow ozone influences or direct climate effects of a wide range of different chemicals to be considered on an equivalent basis and as sums. These weighting factors account for the wide range of influenced different chemicals have on ozone and climate. In the case of ozone, the weighting factors are ozone depletion potentials (ODPs). In the case of climate, the weighting factors are 100-year global warming potentials (GWPs). Additional descriptions of these weighting factors appear in the main chapter text.

depleting substances (ODSs) in data reported to UNEP[5] 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 CH_3Br relative to global consumption in recent years. When direct climate effects of these chemicals are considered, the contribution of the U.S. to total global consumption of ODSs for regulated, dispersive uses decreased somewhat less, from a mean of 26 (±2)% in 1989-1994 to 20 (±1)%, on average, during the 2001-2005 period.

- Declines in U.S. consumption for regulated uses 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, respectively) because of Critical Use Exemptions[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 by the Montreal Protocol. Nearly half (43%) of the global, industrially-derived emissions of CH_3Br during 2005 arose from QPS[6] consumption not regulated by the Montreal Protocol.

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[5] The United Nations Environment Programme (UNEP) compiles and publishes 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 CH_3Br. This use is not scheduled for regulation or phase-out in the Montreal Protocol and is not included in amounts reported to and published by UNEP. 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.

- U.S. consumption of CH_3Br for all fumigation uses declined 40% from 1997 to 2005 despite enhanced critical use exemptions[6] and QPS[6] consumption since 2001. Enhanced Critical Use Exemptions (CUEs) caused the annual U.S. contribution to global CH_3Br consumption for regulated uses in data reported to UNEP to increase from 23 (±4)% during 2000-2003 to 36 (±1)% during 2004-2005. In the U.S. during 2001-2006, the additional consumption of methyl bromide for fumigation not regulated by the protocol (QPS use) was, on average, 57 (±20)% of the amounts used and reported to UNEP[5] for regulated applications and had increased by 13%/yr, 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 for relevance to ozone depletion was dominated by chlorofluorocarbons, or CFCs, (50%), HCFCs (33%), and CH_3Br (11%); in the U.S. consumption was dominated by HCFCs (54%) and CH_3Br (34%). When weighted by climate influences, global production in 2005 was accounted for primarily by CFCs (24%), HCFCs (42%), and HFCs (34%); in the U.S., consumption was dominated by HFCs (63%) and HCFCs (36%). Current estimates of global HFC production have large uncertainties owing to restrictions on reporting production magnitudes when less than 3 manufacturers produce a given chemical.
- Future emission rates from banks[7] will play a substantial role in determining future mixing ratios for some ODSs. 2005 banks in the U.S. and throughout the

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[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. Owing to a lack of available data at this time, U.S. bank estimates presented here do not include stockpiles of halons.

globe are estimated to have been 12-16 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 U.S. and throughout the globe. The U.S. EPA has classified approximately one-quarter of U.S. banks in 2005 as being accessible (210 ODP-kilotons[8], and 1.5 Gigatons CO_2-equivalents)[8] and these accessible banks were comprised predominantly of halons and HCFCs. 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 of these chemicals starting in 1985. Though these emission estimates are recognized to have substantial uncertainties, they suggest that*:**

- Total emissions of ODSs and substitutes from the U.S. 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

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[8] Accessible banks are amounts of ODSs in use in fire extinguishers, refrigeration, and air conditioning sectors (not foams). Quantities (production, consumption, emission, or banks) weighted by ozone-depletion potentials have units of ODP-Tons or ODP-kiloton; 1 ODP-kiloton= 1 billion grams multiplied by the ODP of a given chemical. These quantities weighted for climate influence are multiplied by Global Warming Potentials (GWP), which are indices comparing the direct temperature impact of a pulse emission of a chemical to an identical pulse of CO_2 over a 100-year time horizon; hence, units for quantities weighted by 100-yr GWPs are expressed equivalently by, for example, GWP-Tons or CO_2-equivalent Tons.

ozone depletion. When weighted with factors relevant to climate, annual U.S. emissions of ODSs and substitutes including HFCs declined slightly less, or 74%, over this same period.

- The U.S. accounted for a substantial fraction of global atmospheric mixing ratios of individual ODSs and HFCs measured in 2005, though precise quantification of these contributions are 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 EECl[9] arising from these chemicals in that year.
- Changes in atmospheric chlorine and bromine inferred from U.S. emission 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 uses[6] and for QPS[6] uses of CH_3Br.
- Atmospheric changes derived from U.S. emissions of chlorinated and brominated ODSs indicate a decline in total reactive halogen (EECl)[9] arising from U.S.

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[9] Equivalent Effective Chlorine, or EECl, is an index to gauge the abundance of ozone-depleting halogens (chlorine and bromine atoms) from measurements of multiple ozone-depleting substances having different numbers of chlorine and bromine atoms. It accounts for the enhanced efficiency 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.

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 CH_3Br).

- 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. emissions is estimated as having been between 0.068 and 0.16 W per m^2 in 2005. This U.S. contribution amounted to between 19 and 49% of the total global direct climate influence of these chemicals (of 0.33 W per m^2).

***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 CH_3Br are now decreasing. Increases are still observed for H-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 QPS[6] applications, and substantial natural sources over which humans do not exert direct control.

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[10] Direct radiative forcing is an estimate of the direct climate influence of a chemical and is expressed as energy per area of surface (Watts/m^2). 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. Direct forcings do not include indirect radiative effects associated with feedbacks, such as those related to ozone depletion, for example.

- 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 UNEP[5] 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 CH_3Cl 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 CH_3Br. 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 CH_3Br. The remainder is from naturally produced CH_3Br 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 (EECl[9]) accounted for by the long-lived ODSs considered here has been 20% of what would be needed to return EECl values to those in 1980 (*i.e.*, before substantial ozone depletion was observed). The decline in the shorter-lived gases CH_3CCl_3 and CH_3Br have contributed most to the observed decline. Decreases in stratospheric, ozone-depleting halogen (as EESC[9]) have been smaller because of the time delay associated with mixing tropospheric air into the stratosphere.

- The combined 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 only slow declines in atmospheric abundances of CFC and continued increases in abundances of HCFCs and HFCs. The total contribution of anthropogenic ODSs and substitutes was 0.33 W per m^2 in 2005, compared to a contribution from CO_2, CH_4, and N_2O of 2.3 W per m^2.

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 how these atmospheric changes have altered the overall abundance of ozone-depleting gases and their direct influence on climate. Furthermore, because this is a national assessment this chapter provides estimates of these quantities for the United States in addition to global totals and a discussion of their changes over time.

********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 hydrofluorocarbons (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. 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 any resulting stratospheric ozone increases, which would have a small warming influence. Therefore, it is important to know:

- What are the contributions of the various ozone-depleting substances, 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 issues that fall within the purview of this document.

******end of box*******************************

This chapter is organized into 6 different 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 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 to uses not regulated 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 (Section 2.1.4-2.1.5).

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 global emissions magnitudes derived from sales data to different applications and time-dependent ODS leak rates from different applications are considered, the so-called "bottom-up" analysis (AFEAS, 2007; UNEP/TEAP, 2006). As was the case for production and consumption, compound-dependent weighting factors related to stratospheric ozone (Section 2.2.1) and climate (Section 2.2.2) are applied to emissions estimates to add relevance. 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 (see Box 2.4). The contribution of emissions from other, non-regulated influences is discussed subsequently (Section 2.2.5).

U.S. emissions of ODS and substitute chemicals are regularly estimated by EPA (2007) using a model analysis of sales and use within the U.S. (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 possible 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 proportional to 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 EPA (2007), and, for earlier years, a range of contributions of U.S. to global halocarbon emissions (Box 2.5).

Subsequently, the overall influences of the wide range 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 2.6) are calculated to assess the changing influences on stratospheric ozone (See Section 2.4). Radiative efficiencies are applied to observed atmospheric changes to assess the direct influence these forcings have on climate (Section 2.5).

Finally, though they are included throughout the document, findings related specifically to the U.S. 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 2.5). Additional topics with enhanced relevance to U.S. policy are highlighted throughout the text in additional boxes. These include a discussion of methyl bromide (Box 2.2) and HCFCs (Box 2.3).

Throughout the chapter different weighting factors are applied to quantities being discussed. These weighting factors are useful because different chemicals influence ozone and climate to different extents. 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). With regard to stratospheric ozone, the weighting factors applied to production, consumption, and emissions are generally Ozone Depletion Potentials (ODP), which 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). The ODPs are based on a unit mass emission and are normalized to an ODP for CFC-11 of 1.0. With regard to climate change, the weighting factors applied are 100-year Global Warming Potentials (GWPs), which take into account the infrared absorption spectrum of a chemical or its radiative efficiency, and its persistence in the atmosphere. The GWPs are also based on unit mass emissions, are normalized to a GWP for CO_2 of 1.0, and are generally referred to as CO_2-equivalents. The values for ODPs and GWPs presented in the 2006 WMO ozone assessment are those used in this document throughout (Appendix 2.A) (Daniel and Velders *et al*., 2007).

Slightly 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 the United Nations Environmental Programme (UNEP) and from different companies by the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS, 2007). The data provided by these organizations show how dramatically the use of ozone-depleting chemicals has changed over the past 20 years in response to the adjusted and amended 1987 Montreal Protocol on Substances that Deplete the Ozone Layer and 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 critical data for assessing global and national changes in production and consumption of all regulated ODSs including CFCs, halons, carbon tetrachloride (CCl_4), methyl chloroform (CH_3CCl_3), HCFCs, and methyl bromide (CH_3Br) particularly in recent years (UNEP, 2007). The data through 2005 indicate that annual total global production and consumption of ODSs and substitutes for ODSs has declined by $1.6\text{-}1.7\times10^6$ 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). The average total global production and consumption in 2004-2005 was approximately 1.1×10^5 ODP-Tons per year.

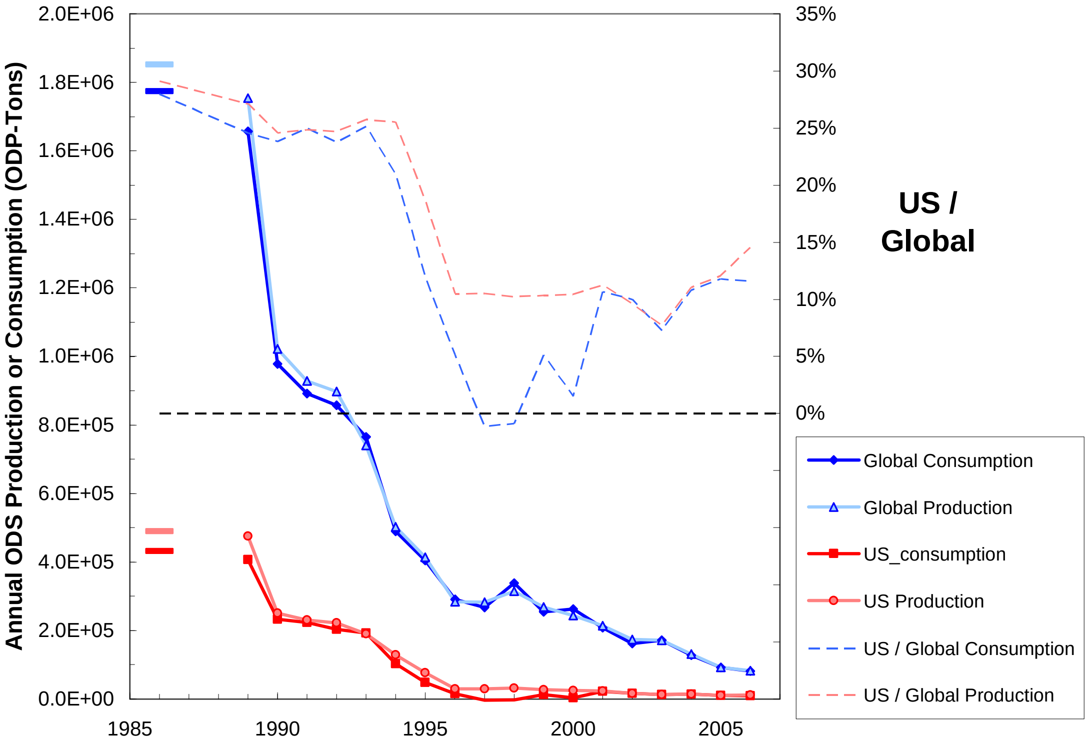


Figure 2.1 Annual global production and consumption of all regulated ODSs and substitutes (dark and light blue solid lines) compared to similar quantities for the U.S. (dark and light red solid lines), as derived from data reported to UNEP (UNEP, 2007). Baseline production and consumption quantities are shown as separate bars with corresponding colors in 1986. All of these data are weighted by ODP. Also shown are the contributions of U.S. consumption (blue dashed line) and production (red dashed line) to global totals (right axis). Negative consumption indicates exports being larger than the sum of imports plus production in a given year (see text)..

Table 2.1 Declines in the 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 (%)** [d]
	Weighted by Ozone Depletion Potential	
Globe	95 [b]	82
United States	97–98 [c]	81
	Weighted by 100-yr Global Warming Potential	
Globe	81 [b]	77
United States	87 [c]	74

[a] Considers production and consumption of ODSs to only dispersive uses regulated 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 Cunnold *et al.*, 2007).
[c] Derived from consumption of ODSs to regulated uses reported to UNEP (UNEP, 2007), and the EPA (2007) vintaging model estimates for HFCs.
[d] 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 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 UNEP/TEAP (2005).

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 CCl_4 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%), CH_3Br 11% (14%), and halons 6% (5%) (CH_3CCl_3 and CCl_4 accounted for <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 CFC weighted consumption in 2006.

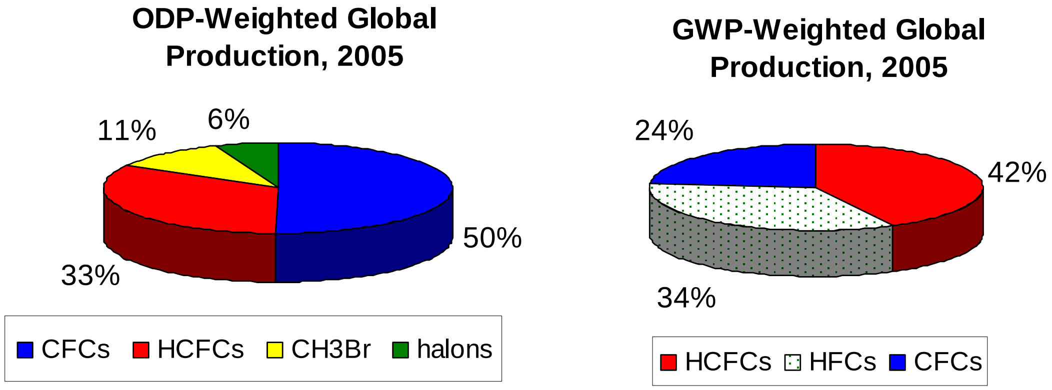


Figure 2.2 Relative contribution of different compound classes or compounds to total global, ODP-weighted production of ODS, substitutes, and HFCs reported to UNEP for regulated uses and by AFEAS for 2005 (left panel), and the global, GWP-weighted production of these chemicals in the same year (right panel) (UNEP, 2007; Personal communication, the UN Ozone Secretariat, 2007; AFEAS, 2007). HFC production includes only the portion of global HFC data reported by AFEAS (2007) for HFC-134a, HFC-125, and HFC-143a, and, 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 CCl_4 ODP-weighted production was -7% during 2005, though its contribution was not included in this Figure. See the text for additional discussion regarding negative consumption and production values.

Ozone-depleting substances also strongly absorb terrestrial radiation in the atmospheric window region (8-12 µm). This absorption leads to a change in the atmosphere's energy balance by causing some of the energy that would have escaped to space to be trapped in the Earth/atmosphere system. A net change of radiation at the tropopause caused by a unit change (*e.g.*, part per billion or ppb) in a greenhouse gas (GHG) is referred to as that gas' radiative efficiency. The global warming potential (GWP) of a GHG represents the cumulative radiative effect of a unit mass of that gas relative to the same quantity for a unit mass of CO_2 over some time horizon. Hence, the GWP provides an approximate measure of the relative integrated climate forcing of a GHG. If only the direct radiative effect of the GHG is considered, so that chemical and other feedback processes are neglected, the GWP is considered a direct GWP. Feedback processes can lead to an indirect GWP contribution. Consideration of these indirect influences is briefly discussed in Section 2.5.2 of this chapter.

Global production of ODSs and substitutes can be weighted by GWPs to estimate the potential effect that production could have on climate forcing. Weighting by 100-year, direct GWPs allows production or emission magnitudes and changes to be considered on a CO_2-equivalent basis. This weighting accounts for each chemical's infrared radiation absorption cross section and persistence relative to a 100-year period. Global production estimates of ODSs and substitutes that deplete ozone (*i.e.*, HCFCs) (data compiled by UNEP, 2007, weighted by GWPs) and substitutes that do not deplete ozone (HFCs) (IPCC/TEAP, 2005) are combined to provide an overall understanding of these influences (Figure 2.3). The results indicate that the annual production of ODSs and substitutes declined by 8040 GWP-megaton from 1989 to 2005 when weighted by 100-year, direct GWPs, which corresponds to a decline of 81% (Table 2.1). Increases in global HFC production have slowed this decline somewhat; production of HFCs in 2005 is estimated here at approximately 630 GWP megaton (includes 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).

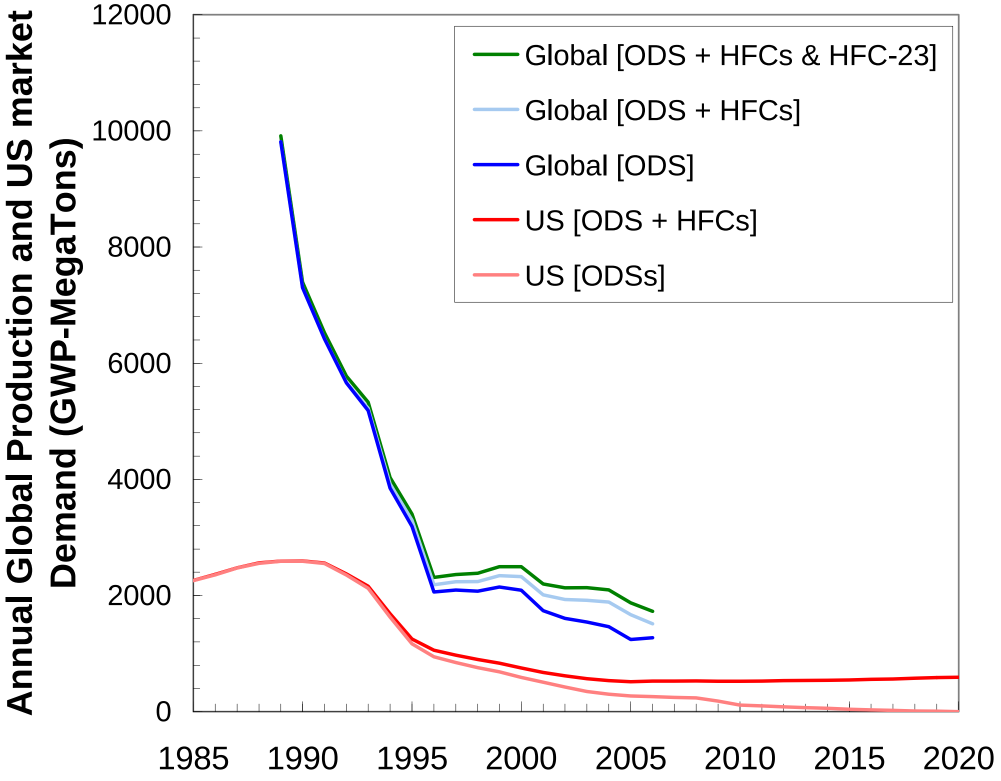


Figure 2.3 Global production of ODSs and HFCs compared to U.S. consumption estimates. All data are weighted by 100-year GWPs. Results are shown for subsets of different compound classes. Global ODS production derived from UNEP (2007) compilations (blue line) are compared to U.S. consumption data for 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 (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.

Based upon these production figures, CFCs accounted for 25%, HCFCs 45%, and HFCs 29% of the global, CO_2-equivalent production of all ODSs and their substitutes in 2005 (Figure 2.2). Global production of ODSs and substitutes including HFCs was approximately 1870 CO_2-equivalent megatons in 2005. The contribution of HFCs considered here is an underestimate because production data on HFCs other than -134a, -125, -143a, and -23 are not currently available. To provide an estimate of the magnitude of use of HFCs other than these, we note that these four gases accounted for 95% of 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 $0.1\ (\pm0.03)\times10^6$ 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 the 1995, the annual UNEP – AFEAS difference has been 80 ± 10%, on average, of the consumption reported by these Article 5 countries.

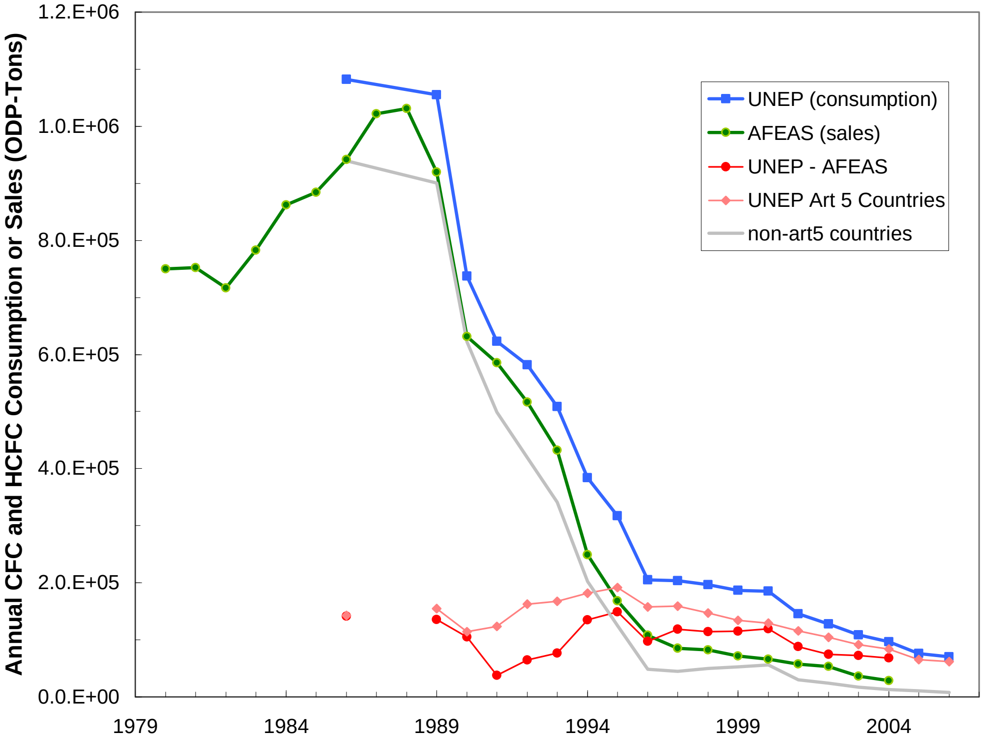


Figure 2.4 Comparison of annual AFEAS sales (green line) and annual UNEP consumption (blue line) totals for the aggregate of CFCs and HCFCs, weighted by ozone depletion potential. Also shown is the annual difference (UNEP consumption minus AFEAS sales), and the magnitude of global consumption in countries 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 covered by AFEAS.

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 (see 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 to dispersive, regulated uses 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 regulated 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 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 emissions during use. ODSs produced substantially as feedstocks include CFC-113, CCl_4, CH_3CCl_3, HCFC-22, HCFC-142b, CH_3Br, and H-1301.

In addition to feedstock applications, methyl bromide is sold for QPS applications that are not regulated 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/MBTOC, 2007). Based on data for CH_3Br use in QPS applications during 1999-2005, including this non-regulated 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 CH_3Br 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 maufacture were captured and destroyed. On national scales, HFC-23 production has been estimated from HCFC-22 production magnitudes (EPA, 2007).

2.1.4 Production and Consumption: U.S. Trends for ODSs and Substitutes

2.1.4.1 U.S. Production and Consumption Weighted by Ozone-Depletion Potential (ODP)

Production and consumption magnitudes of ODSs for regulated, dispersive uses in the U.S. 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 U.S. production and consumption of ozone-depleting substances for regulated, dispersive uses since the late 1980s was $0.4\text{-}0.5\times10^6$ ODP-Tons per year (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 1.2–1.3×10^4 ODP-Tons per year.

An analysis of data reported to UNEP reveals that the contribution of the U.S. to total global ODS production and consumption to 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 U.S. 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 U.S. accounted for <3% of global consumption of CFCs, CH_3CCl_3, and halons, between 20 and 39% of HCFC consumption, and between 17 and 37% of CH_3Br consumption (UNEP, 2007).

In data reported to UNEP (2007), both global and U.S. consumption of HCFCs remained relatively constant during 2003-2005. The U.S. accounted for 22±2% of global 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 U.S. 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 CH_3Br (34%) and CFCs (12%); other compounds contributed less than 1% (Figure 2.5).

Consumption of CH_3Br in the U.S. for dispersive and regulated uses decreased from 1999 to 2002 but then increased from 2003-2005 owing in part to critical use exemptions (UNEP/MBTOC, 2007). U.S. CH_3Br 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 CH_3Br consumption for regulated uses increased from 23 ± 4% during 2000-2003 to 36 ± 1% during 2004-2005. Since 2005, amounts approved for critical use exemptions (CUEs) in the U.S. have declined (UNEP/MBTOC, 2007).

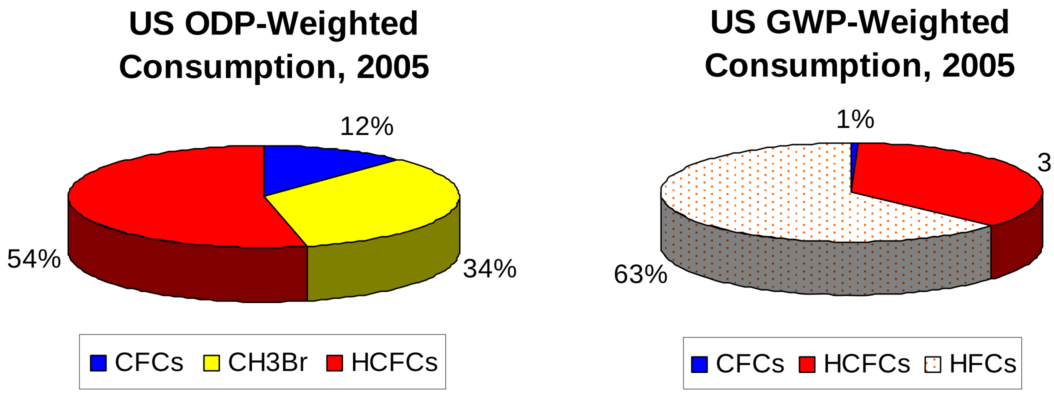


Figure 2.5 Relative contributions of different compound classes or compounds to total United States, ODP-weighted consumption or sales of ODS, substitutes, and HFCs reported to UNEP for regulated uses or estimated by the U.S. EPA (left panel), and total United States, GWP-weighted consumption or sales of these chemicals in the same year (right panel) (UNEP, 2007; EPA, 2007). Relative contributions of less than 1% are not included in these charts; note that the U.S. CCl_4 ODP-weighted consumption was -16% during 2005, though this contribution was not included in the total or shown in the pie chart.

2.1.4.2 U.S. Consumption Weighted by Global Warming Potential (GWP)

U.S. consumption data for ODSs and substitutes (UNEP, 2007) has been combined with the U.S. EPA vintaging model estimates of HFC demand (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 GWP-weighted consumption of ODSs and their substitutes (Figure 2.3). By 2005, the consumption of these chemicals had declined by approximately 2600 CO_2-equivalent megatons (87%, Table 2.1) from amounts reported and estimated for 1989. The total U.S. GWP-weighted consumption of ODSs and substitutes during 2004-2005 was nearly 400 CO_2-equivalent megatons. The decline in CO_2-equivalent consumption has decreased slightly faster in the U.S. than across the globe; the contribution of the U.S. to total global ODS production and consumption to regulated, dispersive uses decreased from a mean of 29 (±2)% in 1989-1994 to 21 (±1)%, on average, during 2001-2005 (Figure 2.1). Whereas in the late 1980s more than 90% of CO_2-equivalent U.S. consumption resulted from CFCs, in 2005 more than half of U.S. CO_2-equivalent consumption was of HFCs (63%) and nearly the rest was of HCFCs (36%) (Figure 2.5).

2.1.5 U.S. Production and Consumption of ODSs and Substitutes Not Included in Published UNEP Compilations

Production and consumption of ODSs for chemical feedstock purposes and of CH_3Br in QPS applications are not included in UNEP compilations because these uses are not regulated by the Montreal Protocol. While losses from feedstock applications are estimated to be small (0.5%, see Section 2.2.4), most CH_3Br used in QPS applications is emitted to the atmosphere (UNEP/MBTOC, 2007). Furthermore, amounts of CH_3Br used in QPS applications are substantial compared to amounts reported to UNEP for regulated uses and they have increased in recent years. For example, in the U.S., annual consumption of CH_3Br in QPS applications during 2001-2006 was 1.8-2.9 kilotons, or 57 (±20)% of annual consumption reported by the U.S. to UNEP for regulated uses; this QPS use had increased by about 13%/year, on average, over this period (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 (EPA, 2007). These estimates show how HFC use in the U.S. has increased by a factor of 3 over the past decade, when use is weighted by compound-dependent CO_2-equivalents. HFC use in the U.S. accounted for nearly 2/3^{rds} of the CO_2-equivalent consumption of ODSs and substitutes in 2005. This vintaging model projects a doubling of CO_2-equivalent HFC use in the U.S. during 2005-2015 (EPA, 2007).

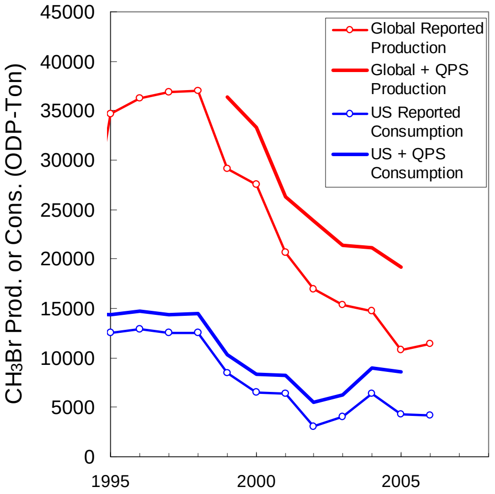
********BOX 2.2: Focus on Methyl Bromide*******************************

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 anthropogenically produced CH_3Br 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 Cunnold *et al*., 2007). Since 1998, anthropogenic production for all fumigant-related applications has declined by about 50%.

Second, a substantial fraction of industrial production is for dispersive applications not regulated by the Protocol. These non-regulated uses, primarily in quarantine and pre-shipment (QPS) applications, have increased recently and have led to a slower decline in total global CH_3Br 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 CH_3Br were from uses not regulated 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 (see Box Figure 2.2-1) (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%/yr, on average, during 2001-2006 (EPA, 2007), leading to an annual emission 30 to 80% higher than the annual amounts reported to UNEP during these years.

Third, declines in CH_3Br 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 U.S. have resulted in higher annual consumption of CH_3Br and an increased United States/Global consumption ratio during 2004-2005 compared to 2002-2003 (see Box Figure 2.2-1).



Box Figure 2.2-1 Global production and U.S. consumption magnitudes for restricted uses reported to UNEP (UNEP, 2007) (lines with circles) compared to these reported amounts plus use to QPS applications considered (solid lines) (UNEP/MBTOC, 2007; EPA, 2007)) (feedstock uses not included).

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Despite increases in QPS use and enhanced CUEs in recent years and variability in underlying natural emissions, global atmospheric mixing ratios of CH_3Br have declined continuously since 1998 (Clerbaux and Cunnold *et al.*, 2007). While the U.S. 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 CH_3Br in the U.S. (Figure 2.14).

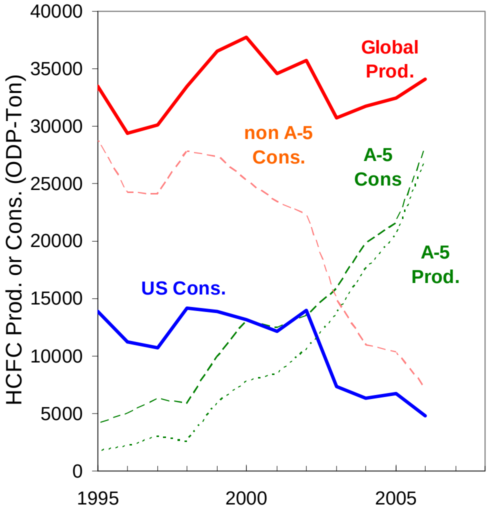
****************** **end of Box** ************************

BOX 2.3: Focus on HCFCs

HCFCs were attractive substitutes for CFCs because they have similar properties to CFCs in many applications, but shorter lifetimes, generally fewer chlorine atoms/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 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 2.3-1). Consumption has declined substantially in developed countries (non-Article 5) and in the U.S. 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) has increased dramatically.



Box Figure 2.3-1 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).

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 (see Box Figure 2.3-1). This apparent discrepancy likely arises from the large bank of HCFCs; while HCFC emissions were similar to HCFC consumption in 2005 (~6 ODP-kiloton) the HCFC bank was over 10 times larger (see Box 2.4). In the U.S. during 2005, HCFC-22, HCFC-142b and HCFC 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 is summarized in Chapter 5.

*********end of Box*******************

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 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 are 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) and model-derived parameters such as photolytic fluxes, OH abundances, and 3-D distributions of ODS atmospheric mixing ratios. This method 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 *vs.* 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 – 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.

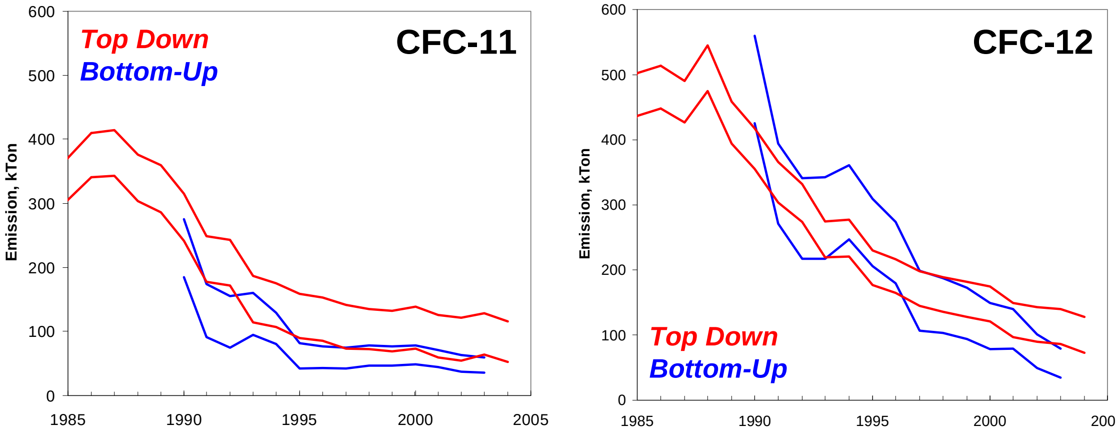


Figure 2.6 Comparison between global emissions derived from measured changes in the global atmospheric mixing ratio of CFCs (top down method; emissions bounded by red lines) and global emissions derived from an analysis of sales to different uses and estimates of releases from those uses over time (bottom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

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-megatons 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 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.

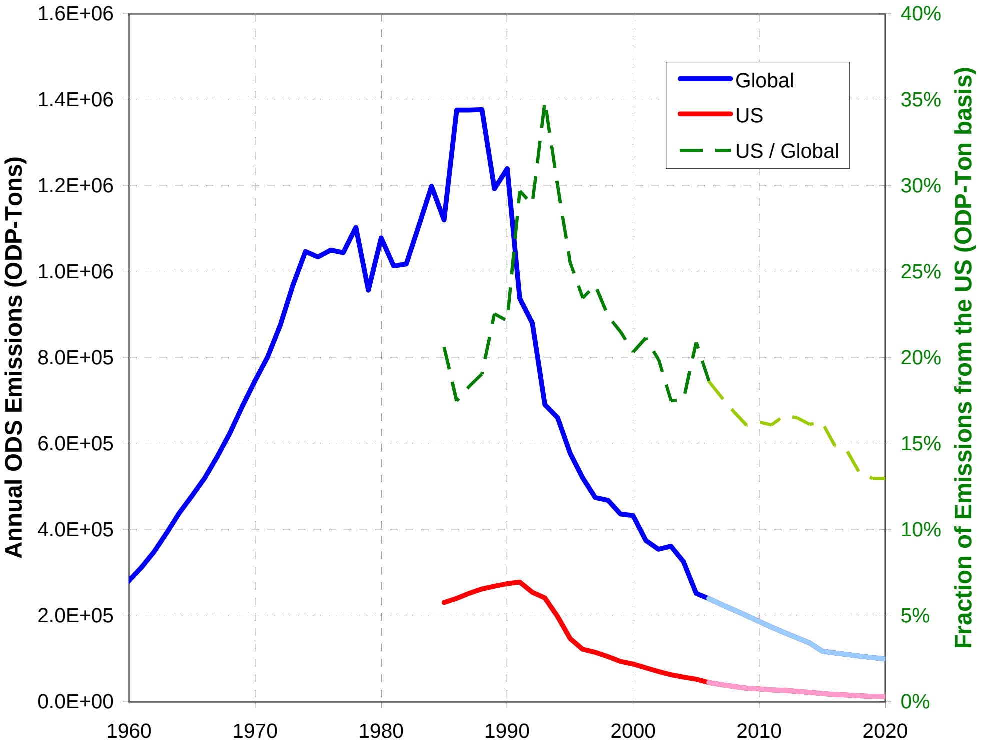


Figure 2.7 Aggregated emissions of ODSs derived for the entire globe (blue line; Clerbaux and Cunnold *et al.*, 2007; Daniel and Velders *et al.*, 2007) and for the U.S. (red line; U.S. EPA, 2007) over time, weighted by ODP. Lighter lines represent projections into the future. The United States/Global emission fraction weighted by ODP is shown relative to the right-hand axis (dashed green line). 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).

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

When the emission history compiled as the WMO scenario A1 (Daniel and Velders *et al.*, 2007) is combined with 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 (Figure 2.8). The overall annual decline amounted to 7270 GWP-megatons per year by 2005, which corresponds to a 77% decrease from peak global GWP-weighted emissions in 1988 (Table 2.1). The decline integrated between 1988 and 2005 amounts to a decrease of over 90 Gigaton CO_2 equivalents compared to constant emissions at 1988 levels. Declines in CFC emissions accounted for a decrease of 7900 GWP-megatons per year by 2005, but this decline was partially offset by increases in HCFCs and HFC emissions from 1990 to 2005 of 210 and 530 GWP-megatons per year, respectively.

In 2005, total global emissions of ODSs and substitutes are estimated to have been 2150 GWP-megatons, with 38% of this being accounted for by emissions of CFCs, 27% by HCFCs and 29% by HFCs (HFC global emissions for 2005 interpolated from 2002 estimates and 2015 business as usual scenario (UNEP/TEAP, 2005).

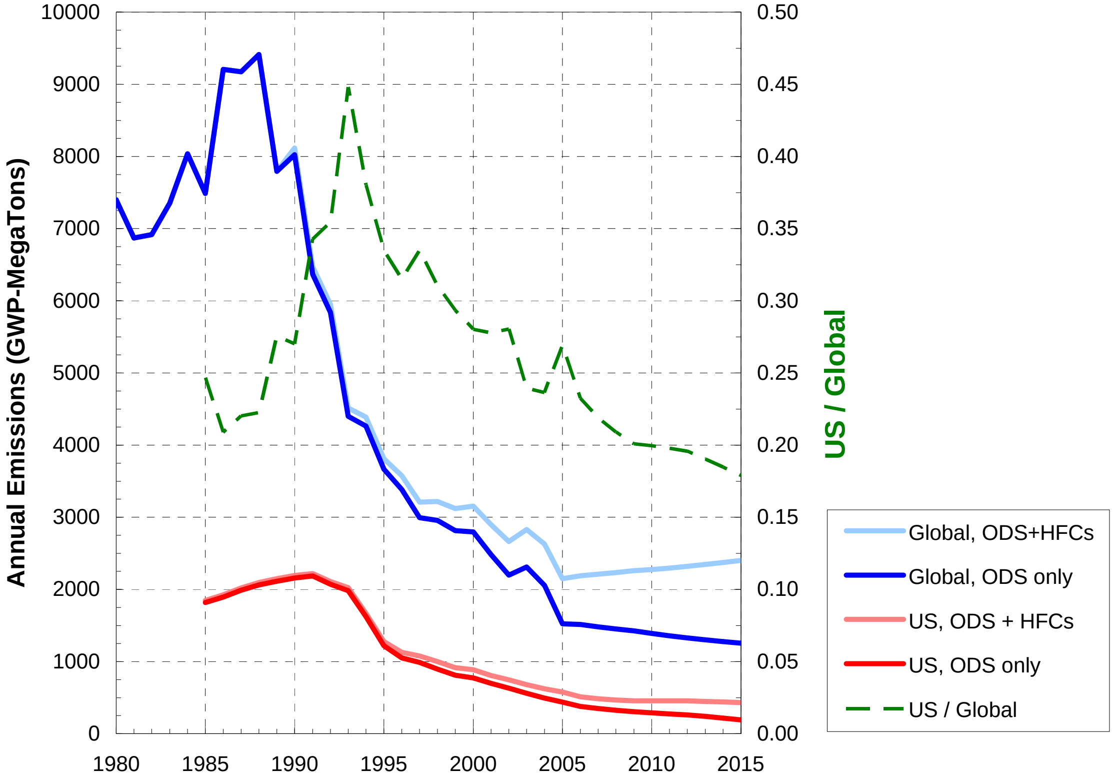


Figure 2.8 Aggregated, GWP-weighted emissions of ODSs derived for the entire globe (blue line; Clerbaux and Cunnold *et al*., 2007; Daniel and Velders *et al*., 2007) and for the U.S. (red line; EPA, 2007). Lighter lines represent the contribution from emissions of HFCs, which were derived on the global scale from Campbell and Shende *et al*., (2005) and for the U.S. (EPA, 2007). The United States/Global GWP-weighted emission fraction is shown relative to the right-hand axis (dashed green line). 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. (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.

2.2.3 Global Emissions: The Contribution of Banks and Bank Sizes

"Banks" of ODSs exist where there are reserves of ODSs that could be potentially released at a later date due to legacy processes or equipment. The release of these banks has become the most important factor in determining 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, 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 2.4). 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 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.

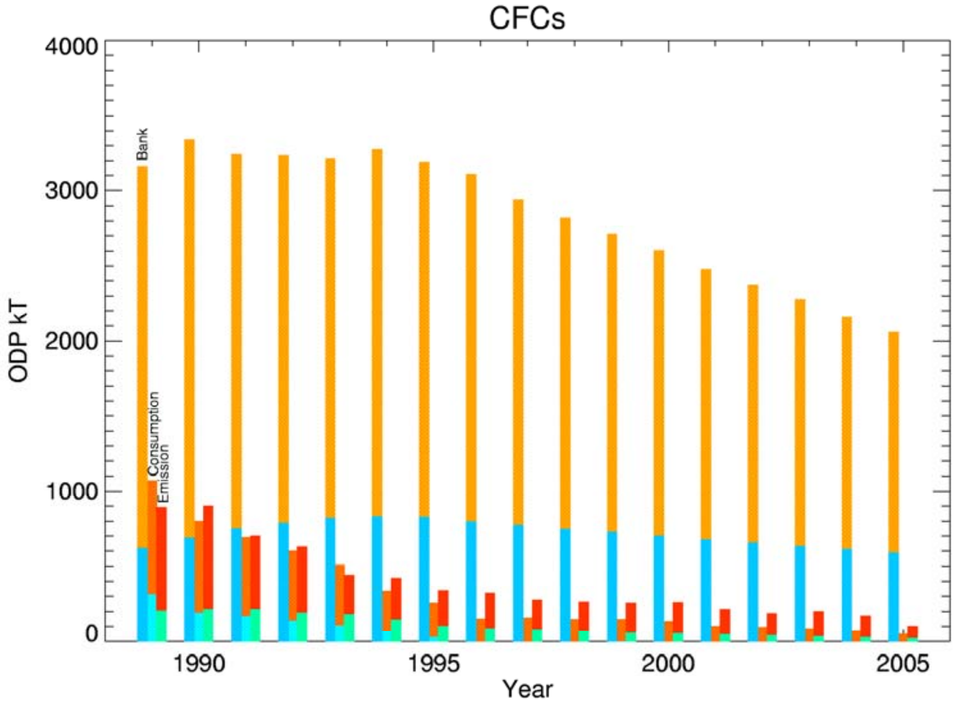


Figure 2.9 Time evolution of CFC banks, annual consumption, and annual emission, weighted by compound-dependent ODPs. The total height of the bars represents global values, while the lower blue/green portions represent the U.S. portions. Global banks are taken from WMO (Clerbaux and Cunnold *et al*., 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 EPA vintaging model analysis of CFCs in the United States.

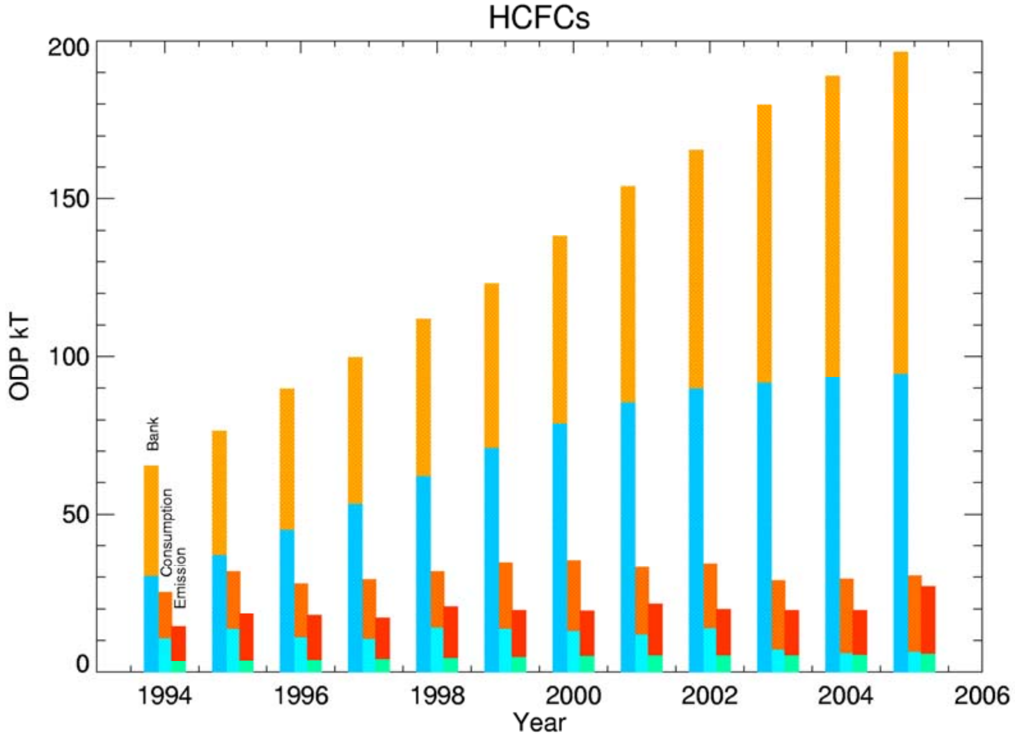


Figure 2.10 Same as Figure 2.9, but for HCFCs.

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 (see also Box 2.4).

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

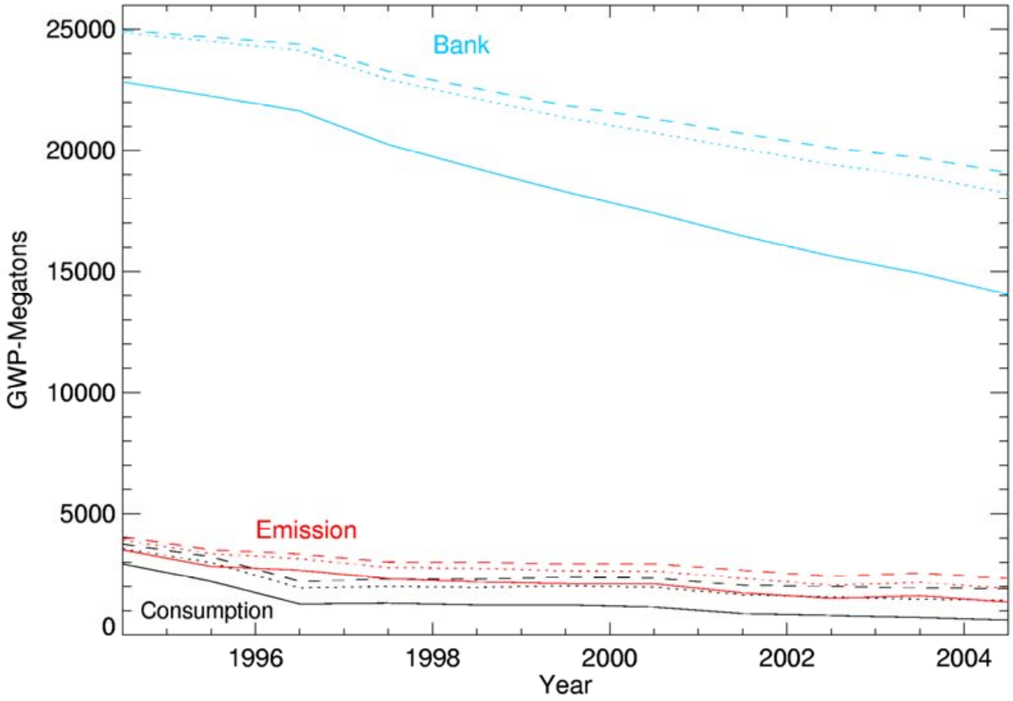


Figure 2.11 Comparison of GWP-weighted annual global consumption and emission with total bank sizes. Solid lines represent contributions of CFCs, dotted lines also include HCFCs, and dashed lines further add the HFC-134a contribution to the bank.

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 GWP-weighted sense. Although global banks for HFC-134a was still a small fraction of total GWP-weighted banks in 2005, banks of HCFCs have continued to increase over time and accounted for almost 25% of the total GWP-weighted bank in 2005. The 2005 global banks continue to represent an important reservoir in terms of climate forcing, equivalent to 19,000 megatons of CO_2-equivalent emissions (Figure 2.11). When compared to the reductions in emissions that already have resulted from compliance with the Montreal Protocol (>90 Giga Tons integrated through 2005), 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).

********BOX 2.4: Banks of ODSs 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.

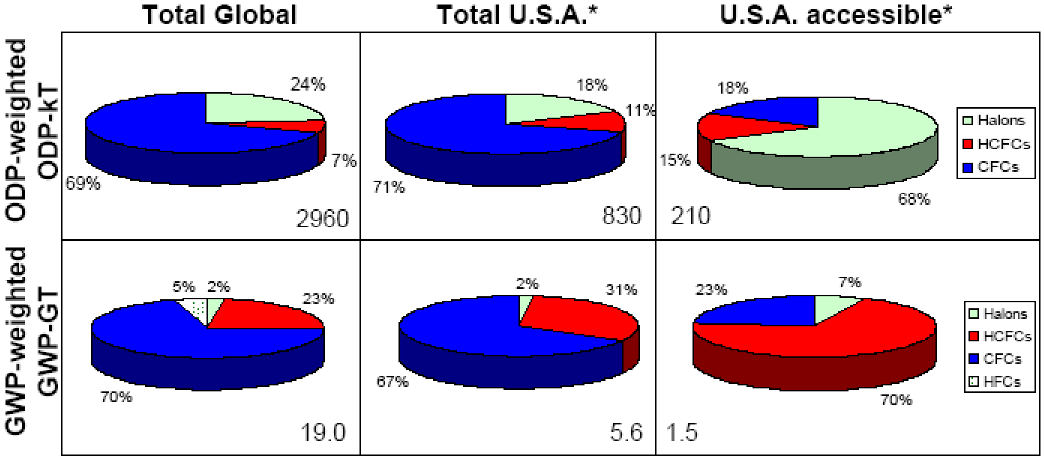
Today the situation is far different. Most ODSs are used in slow-release applications, many of which contain a significant quantity of a halocarbon compared to its current atmospheric abundance; this quantity is in some cases much larger than the amount of halocarbon emitted annually. Accurate knowledge 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. 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 annual change in bank size is often characterized by small differences between large numbers and systematic errors can accumulate over time. A second method, which was discussed in IPCC/TEAP (2005) and is used in the 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 don't 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 estimated to likely be more accurate than the top-down estimate and was used to project future halocarbon abundances.

The current bank sizes have important scientific and policy implications. Because banks that are not captured will eventually make it 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 to be 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 are displayed below (Box Figure 2.4-1):



* US HFC bank data is currently unavailable; global pie charts include bank estimates for HFC-134a.

Box Figure 2.4-1 The size and relative contribution of different compound classes to 2005 banks estimated for the globe, for the United States, and for the U.S. but classified as accessible (Daniel and Velders *et al*., 2007; EPA, 2007). Top row includes bank estimates weighted by compound-dependent ODPs; banks in the bottom row have been weighted by GWPs. Pie charts show relative percentages; units refer to weighted total bank sizes, which are given in the lower corners of each box. Note that halon stockpiles are not included in any of the U.S.A. bank estimates from the U.S. EPA owing to lack of available data at this time.

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 12 to 14-16 times larger, respectively (weighting by ODP or GWP). 2005 accessible banks in the U.S. were about 4 times larger than U.S. annual emissions in that year (either weighting). For comparison, CO_2 global emissions from fossil fuel and cement production have been estimated at 27-30 Gigaton CO_2 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 (67-71%), they account for only 18-23% of 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 (HFCs were excluded from this analysis owing to a lack of data). The halon contributions to U.S. banks calculated here should be considered underestimates because stockpiles were likely non-zero in 2005.

********** **End of box** ****************

2.2.4 Global Emissions: The Influence of Non-regulated 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 <1% of total ODP-weighted emission in 2002.

All production of HCFC-22 including feedstock-related production not regulated by the Montreal Protocol has an added influence on the atmosphere that arises from HFC-23 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 Cunnold *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; UNEP/TEAP, 2006). In a “business-as-usual” scenario regarding HCFC-production for regulated and feedstock purposes, HFC-23 emissions were projected to increase 60% from 2005 to 2015.

Production of CH_3Br for QPS purposes is also not regulated by the Montreal Protocol (see Box 2.2). This global production was similar in magnitude to that used for regulated purposes in 2005. The emission rate for CH_3Br in QPS uses is estimated to be 78-90% of the amount produced (UNEP/MBTOC, 2007). Based upon 2005 production to regulated and non-regulated (feedstock and QPS) uses of CH_3Br, we estimate that global emissions from non-regulated applications accounted for nearly half (43 (36-49)%) of all anthropogenic CH_3Br emission during this year. Most of this non-regulated emission (>99%) is estimated to arise from QPS uses.

Unlike other regulated ODSs, a substantial amount of CH_3Br 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 CH_3Br 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 Cunnold *et al.*, 2007).

The magnitude of variability in non-industrial emissions of CH_3Br 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 Cunnold *et al.*, 2007) suggest that global emissions of CH_3Br have declined each year since industrial production was first reduced (1999).

2.2.5 U.S. Emissions and Banks: Estimates Derived by 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 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 (see 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 2.5 for further description of the vintaging model). With this method the U.S. EPA has estimated annual, U.S. emissions of ozone-depleting substances and their replacements since 1985 (EPA, 2007). The data compiled by the EPA covers industrial production for uses regulated by the Montreal Protocol and for non-regulated 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 a 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-kiloton 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. U.S. emissions of ODSs and substitutes are estimated to have been 52.7 ODP-kiloton in 2005. Emissions for the substitute HCFCs have increased over this period; U.S. HCFC emissions in 2005 were nearly 6 ODP-kiloton, which represents an increase of 3.5 ODP-kiloton 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 CH_3Br, and 11% were from HCFCs.

The contribution of the U.S. 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-yr GWP values, the U.S. emissions estimated by EPA suggest a reduction of 1640 GWP-megatons in annual emissions of ODSs and substitute chemicals including HFCs by 2005 compared to 1991 when they were at their peak. This corresponds to a decrease of 74% (Figure 2.8; Table 2.1). The largest decline was for CFCs emissions, which accounted for, on average, 91% of the GWP-weighted total annual U.S. emissions in 1985-1995 and only 43% of these emissions in 2005. By 2005, GWP-weighted emissions of HCFCs accounted for one-third and HFCs one-quarter of total annual U.S. emissions of ODSs and substitutes.

Independent assessments of ODS emissions in the U.S. 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 EPA for CFC-12, CFC-113, CFC-114, and CFC-115, but a factor of 3 higher for CFC-11. This discrepancy likely arises because the 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 of ±50% is applied to U.S. emission estimates 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 U.S. are estimated with the 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 loss rate of ODS from these applications, and estimates of how these variables change over time with input from industry. Considering ODS alone, the 2005 banks amounted to over 10 years worth of emissions at rates estimated for 2005, or 803 ODP-kiloton and 5.6 gigaton CO_2-equivalents (see Box 2.4) (halon stockpiles not included).

The 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 EPA could be recovered and destroyed with the proper incentives or certain technological advances, halocarbons that are not recovered and destroyed will eventually escape into the atmosphere. Banks in the U.S. classified by the EPA as being accessible amount to approximately 25% of the total U.S. bank (ODP or 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 GWP-weighted bank. Less than 10% of the total U.S. CFC bank in 2005 is considered accessible (~9.5% when GWP-weighted; ~6% when ODP-weighted) compared to over 30% of the U.S. HCFC bank (60% when GWP-weighted and 37% when ODP-weighted) (see Box 2.4).

Comparing these EPA vintaging model bank size estimates in 2005 with the global banks from WMO (Daniel and Velders *et al.*, 2007), the U.S. contributed 21 and 26% to the global ODP- and GWP-weighted banks, respectively. In this year the U.S. accessible banks accounted for about 5 and 7% of the ODP- and 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 GWP-weighted bank. Similarly, the U.S. accessible bank is projected to decrease to 2 and 4% of the ODP- and 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 accounted. These estimates are specific to the region most directly influencing the air reaching a measurement site. Unfortunately, U.S. emissions have been derived with 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 (EPA, 2007). Estimates of U.S. emissions have been made for selected CFCs, CH_3CCl_3, and CCl_4 over 1996-2003 based on individual studies in California and in the north-east. The results point to a clear decline in U.S. emissions of CFC-12 over this period (Clerbaux and Cunnold *et al.*, 2007). Although U.S. emissions derived for CFCs from these estimates are generally lower than from the 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 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 EPA (2007).

2.3 CHANGES IN THE ATMOSPERIC 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 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 atmospheric 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 (<10) 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

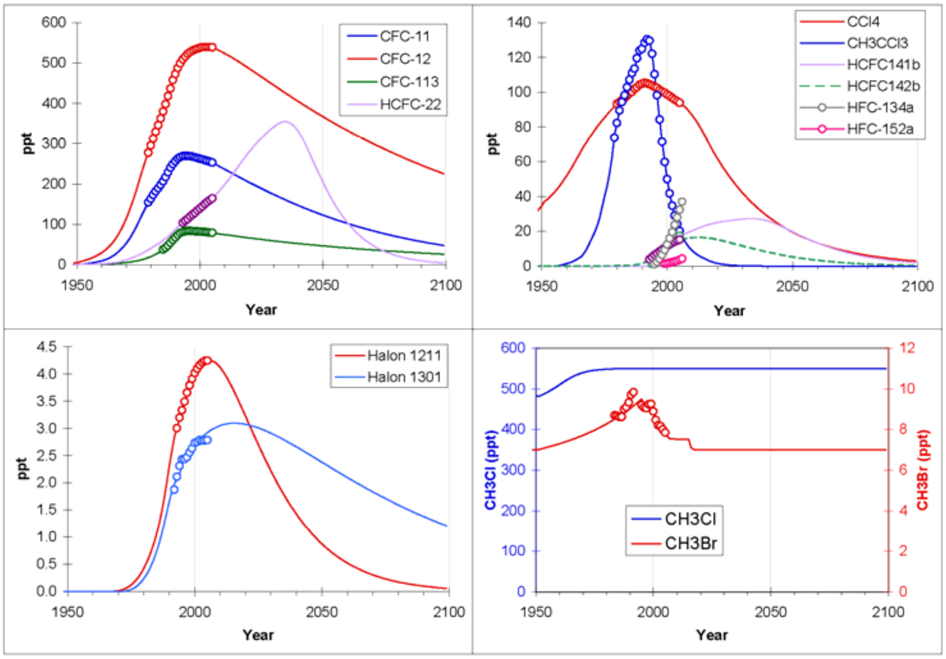


Figure 2.12 Global surface mixing ratios of ODSs and substitute chemicals observed from surface sampling networks (open circles), and as estimated for the past and future in WMO scenario A1 (Clerbaux and Cunnold *et al*., 2007; Daniel and Velders *et al*., 2007). Past projections are based on histories derived from the analysis of archived air samples, the analysis and modeling of firn-air samples, and historic industrial production data.

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 infra-red 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 concentrations 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 <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* discreet 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 toten 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 H-1211 and H-1301 estimated by 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 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 order 0.06 ppt in 2004, its mixing ratio increased at ~6%/yr 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 global atmosphere at mixing ratios of a few ppt. After HFC-134a and HFC-23, the ones 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 in release rates from the applications in which the chemicals were used, and the persistence of the chemical 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 ~5 yrs 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 atmospheric over decades. This, combined with atmospheric lifetimes of 50 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.

Table 2.2 The most abundant ODSs and substitute chemicals.

Compound	Lifetime (years)	Tropospheric Chlorine or Bromine Contribution (ppt)			EECl Contrib. (%)[c]	ODS	ODS Substitute	Regulation [a]
		1985	1995	2005	2005			
CFCs					**45%**			
CFC-11	45	622	808	759	21%	X		M
CFC-12	100	763	1046	1078	18%	X		M
CFC-113	85	114	252	237	5%	X		M
CFC-114	300	25	34	34	0.3%	X		M
CFC-115	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_3CCl_3	5	324	330	60	1.8%	X		M
CCl_4	26	398	412	376	11%	X		M
CH_3Cl	1	550	550	550	12% [c]	X		
Bromocarbons					**28%**			
CH_3Br	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 CH_3Br production and consumption is regulated. Lifetimes are from WMO (Clerbaux and Cunnold *et al.*, 2007) and halogen abundances are from 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 (Clearbaux 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 anthropogenic components. If only anthropogenic emissions of CH_3Cl and CH_3Br were included (*i.e.*, assuming 2005 abundances of 0 ppt for CH_3Cl and 1.25 ppt (7.9 − 9.5*0.7) for CH_3Br), the percentages calculated for 2005 abundances would be CFCs: 59%; HCFCs: 3.3%; Other Chlorocarbons: 17%; Other Bromocarbons: 20%; CH_3Br: 3.1%.

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 H-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 yrs. 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 (~26 yr; 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 inter-annual variability in non-industrial 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 2 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 ODS 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-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 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 are temperature sensitive; increases in reaction rates of ~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 trace gases abundances and would likely also shorten lifetimes for ODSs where stratospheric losses are relatively important (see 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 (see Box 2.5). 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 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 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).

*********BOX 2.5: 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 (UNEP/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 (EPA, 2007) (see **Box Table 2.5-1**). The 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, however, 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 (see **Box Table 2.5-1**).

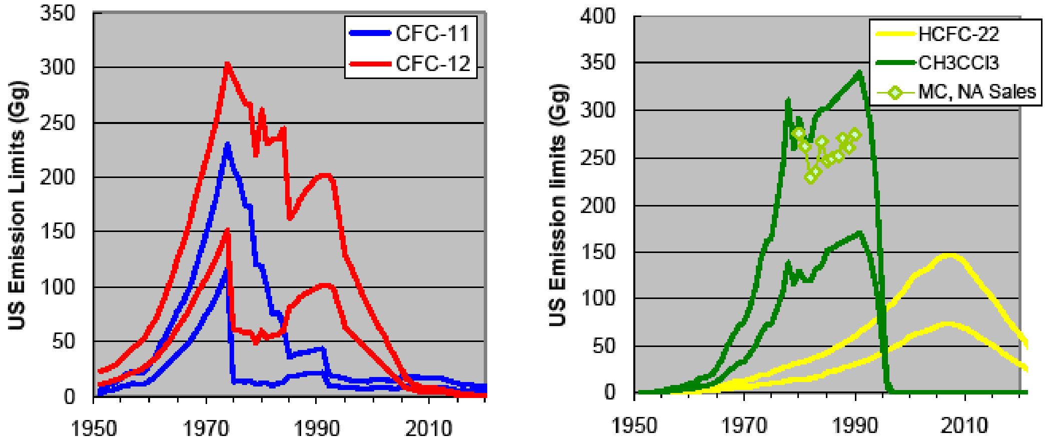
Box Table 2.5-1 Methodology for Deriving Limits to Compound-Specific, Annual U.S. Emissions*:

	Upper range	Lower range
Pre 1975		
CFCs	[GE]*0.67	[GE]*0.33
Non-CFCs	GEF$_{\text{US/Global(1985-1990)}}$ *1.5	GEF $_{\text{US/Global(1985-1990)}}$ ÷1.5
HFC-23	GPF$_{\text{(HCFC-22)US/Global(1985-1990)}}$ *1.2	GPF$_{\text{(HCFC-22)US/Global(1985-1990)}}$ *0.9
1975-1984		
CFCs	interpolate [GE]*0.67 in 1975 to GEF$_{\text{US/Global(1985-1990)}}$ *2 in 1984	GEF$_{\text{US/Global(1985-1990)}}$ ÷2
Non-CFCs	GEF$_{\text{US/Global(1985-1990)}}$ *1.5	GEF $_{\text{US/Global(1985-1990)}}$ ÷1.5
HFC-23	HCFC-22 Prod.$_{\text{US/Global(1985-1990)}}$ *1.2	HCFC-22 Prod.$_{\text{US/Global(1985-1990)}}$ *0.9
1985-2005		
All HFCs	EPA (2007) + 20%	EPA (2007) - 10%
All others	EPA (2007) + 50%	EPA (2007) - 25%

* where GE = global annual emissions; GEF$_{\text{US/Global(1985-1990)}}$ refers to the mean US/global emission over the period 1985 to 1990 determined from a ratio of compound-specific emissions from the EPA (2007) vintaging model and WMO scenario Ab global emissions (Daniel and Velders *et al.*, 2007); and GPF$_{\text{(HCFC-22)US/Global(1985-1990)}}$ refers to the mean US/global production ratio for HCFC-22 during 1985 to 1990 in data reported by AFEAS (2007) and by the EPA (2007) and the assumption that HFC-23 emissions were proportional to HCFC-22 production during those years.

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 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 EPA, an uncertainty analysis has been performed on 2005 emissions derived by the EPA vintaging 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. Given these considerations, we have augmented the uncertainties derived for the high-GWP ODS substitutes by a factor of approximately 2.5 to derive 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.

These approaches have yielded estimates to expected upper and lower ranges to U.S. emissions of ODSs and substitute chemicals (Box Figure 2.5-1).



Box Figure 2.5-1 Ranges estimated for U.S. emissions derived from the analysis presented in **Box Table 2.5-1**; 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.

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 or much longer than atmospheric mixing times (see, for example, UNEP/TEAP, 2006; Clerbaux and Cunnold *et al*., 2007).

***********End of box 2.5 ************

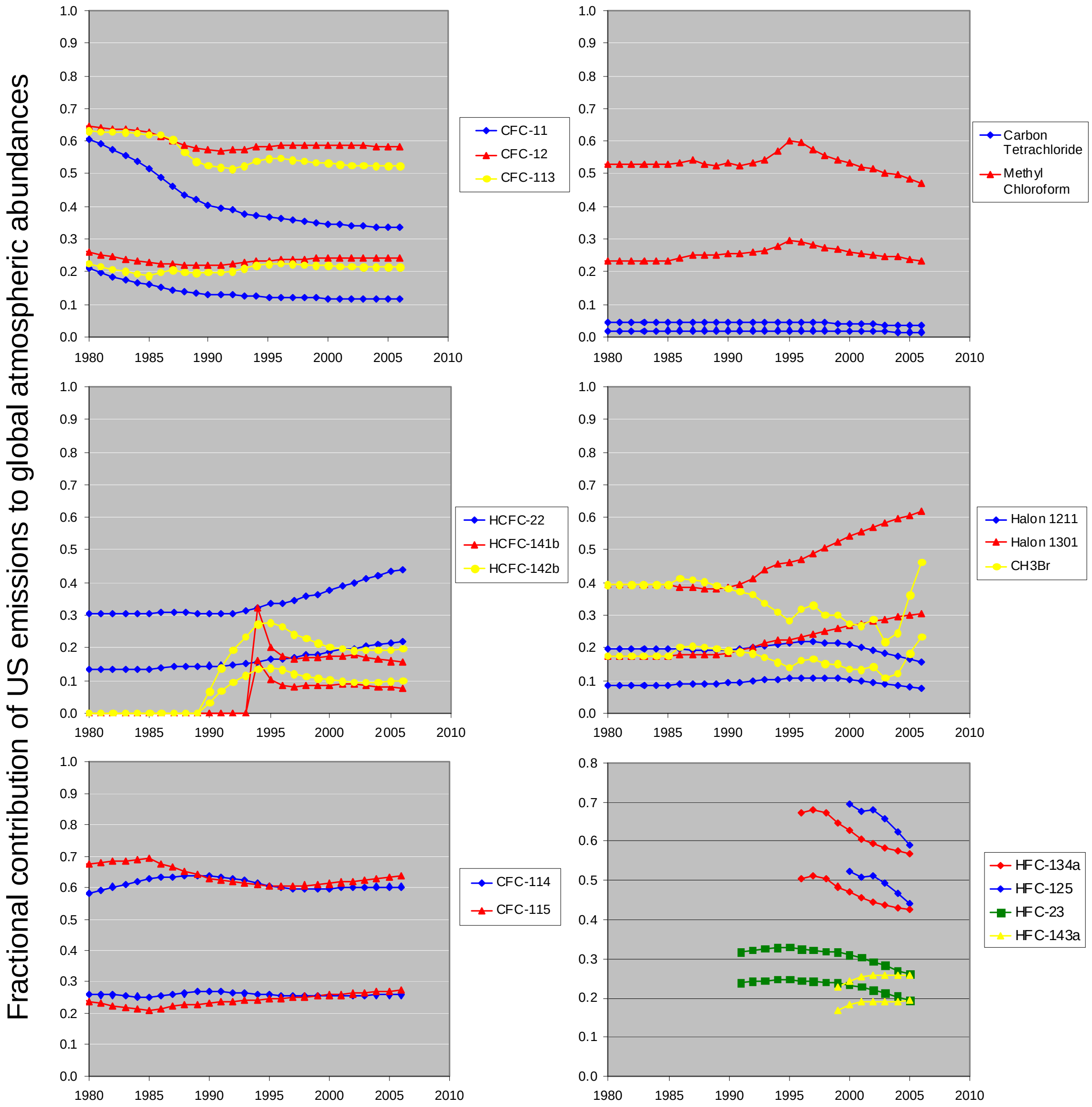


Figure 2.13 Upper and lower ranges to the fractional contributions of U.S. industrial emissions to global atmospheric abundances of ODSs and substitutes chemicals over time (see Box 2.5 for the derivation of

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 > 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)

The smallest contributions of U.S. emissions to present-day mixing ratios are calculated for CCl_4, CFC-11, HCFC-142b, HCFC-141b, and H-1211. Larger contributions are estimated for some other CFCs, CH_3CCl_3, HCFC-22, H-1301, CH_3Br, and some HFCs (Figure 2.13).

The largest increases in recent years are calculated for CH_3Br, HCFC-22, and Halon 1301. The increased contribution of U.S. CH_3Br emissions to its atmospheric abundance arises from increases in U.S. consumption compared to global consumption since 2002 (see Section 2.1.4 of this chapter and Box 2.2). The U.S. contribution to atmospheric mixing ratios of H-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, HCFCs, *etc*. Only those with fairly long lifetimes and low water solubilities escape scavenging by aerosols and rain, however, and become 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 if 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 (HCl and $ClONO_2$, and 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 4 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 H-1211). The remaining 15% (or 550 ppt Cl) is accounted for by methyl chloride, a chemical having predominantly (>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 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 concentrations peaked in mid-to-late 1990s and have since declined. These 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 (HALOE), and relatively short data records for other instruments that offer higher precision (ACE and MLS).

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 the 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. Declines in CFC abundances accounted for about half of the decline in total tropospheric Cl in 2004 (-9 ppt Cl per year). CH_3CCl_3 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 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.

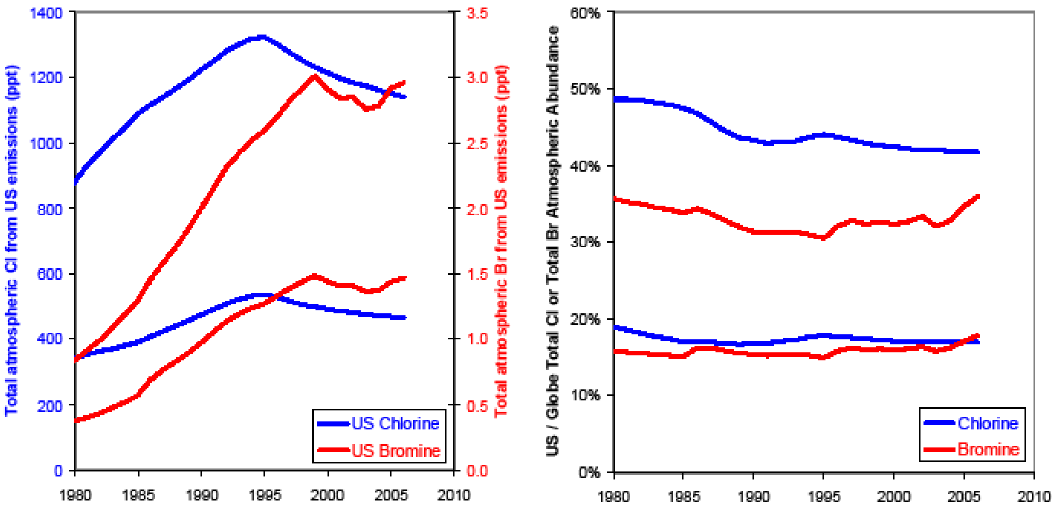


Figure 2.14 A) Estimated ranges of the tropospheric abundance of Cl and Br from U.S. emissions of all regulated ODSs. These ranges from upper and lower estimates of U.S. emissions (see Box 2.5 for additional information). B) Estimated ranges in the fractional contribution of U.S. emissions to global atmospheric mixing ratios arising from industrial production of ODSs. In both panels, only emissions arising from industrial production of ODSs to regulated uses plus QPS uses of CH_3Br was 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 H-1211; and of total Br include: CH_3Br, H-1211, H-1301, and H-2402.

2.4.2 Atmospheric Bromine

Bromine in the stratosphere catalyzes the destruction of ozone with an efficiency that is approximately 60 times that of chlorine (WMO, 2007). As a result, small concentrations 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. Together, 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 <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 CH_2Br_2 and $CHBr_3$ derived in this way suggest no large long-term changes in atmospheric mixing ratios in polar-regions during the past 2 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. This data has 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 CH_3Br, 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 CH_3Br also peaked in 1998-1999 and declined through 2003, as estimated by the U.S. EPA (EPA, 2007) (Figure 2.14). Since 2003, however, the increased emissions of CH_3Br from critical use exemptions and QPS uses (see Box 2.2) have caused the tropospheric abundance of bromine attributable to U.S. emissions to increase. While the contribution of U.S. to total atmospheric bromine (industrially-derived emissions to 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 CH_3Br 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 (See Box 2.6). 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.

*********BOX 2.6: Equivalent Effective Chlorine (EECl) and Equivalent Effective Stratospheric Chlorine (EESC)**********

The threat posed to the ozone layer from ODSs is not directly proportional to the summed concentrations 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 the evolution of reactive stratospheric halogen in a simple manner based on observed changes in tropospheric abundances of ODSs.

Effective Equivalent Chlorine (EECl) 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 EECl changes correspond to the dates those changes were measured in the troposphere.

Effective Equivalent 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 EECl only as 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 mid-latitude EESC and Antarctic EESC in springtime when lag times of 3 yrs for mid-latitudes and 6 yrs 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 changes in stratospheric inorganic halogen abundances because it incorporates simplified assumptions regarding mixing processes and degradation rates. Recent efforts to improve the formulation provide a more realistic evolution of stratospheric reactive halogen over time (Newman *et al.*, 2006; 2007). Other differences in these recent formulations of EESC suggest some rather large alterations to estimated ODS recovery times and are currently a source of uncertainty in this analysis.

******end of box**

EECl from measured global surface mixing ratios of regulated ODSs, substitutes, and CH_3Cl 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 CH_3CCl_3 and CH_3Br.

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 (CH_3Cl and CH_3Br) (Table 2.2). Chlorinated and brominated gases each, as a group, contributed 25 and 28%, respectively, while HCFCs contributed 2.5% to EECl in 2005. These percentages include natural contributions to the atmospheric abundance of CH_3Cl and CH_3Br. When only anthropogenic contributions to 2005 EECl are considered, the relative contribution of CFCs increases (to 59%), that for chlorocarbons decreases (to 17%), that for bromocarbons decreases (to 20%), and that for CH_3Br becomes 3.1% (see footnote to Table 2.2).

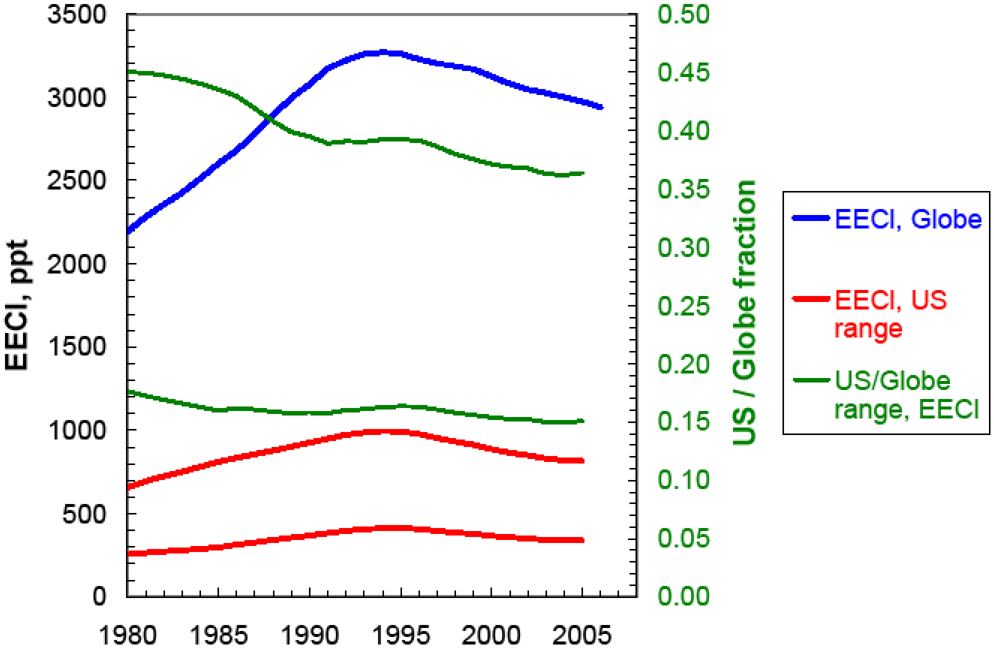


Figure 2.15 EECl from measured global mixing ratios of ODSs (blue line) and from estimates of ODS mixing ratios attributable to U.S. emissions (upper and lower ranges bounded by red lines; see Box 2.5 for discussion of U.S. emissions). While all long-lived ODSs, including CH_3Cl and the natural contribution of CH_3Br, 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).

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. U.S. emissions of ODSs for regulated uses have accounted for between 15 and 39% of total EECl from regulated chemicals during the past decade, 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 2004-2005 U.S. EECl declines were substantially smaller than in earlier years, primarily because of the increases in U.S. emission of brominated gases during these years (primarily CH_3Br) (Figure 2.16).

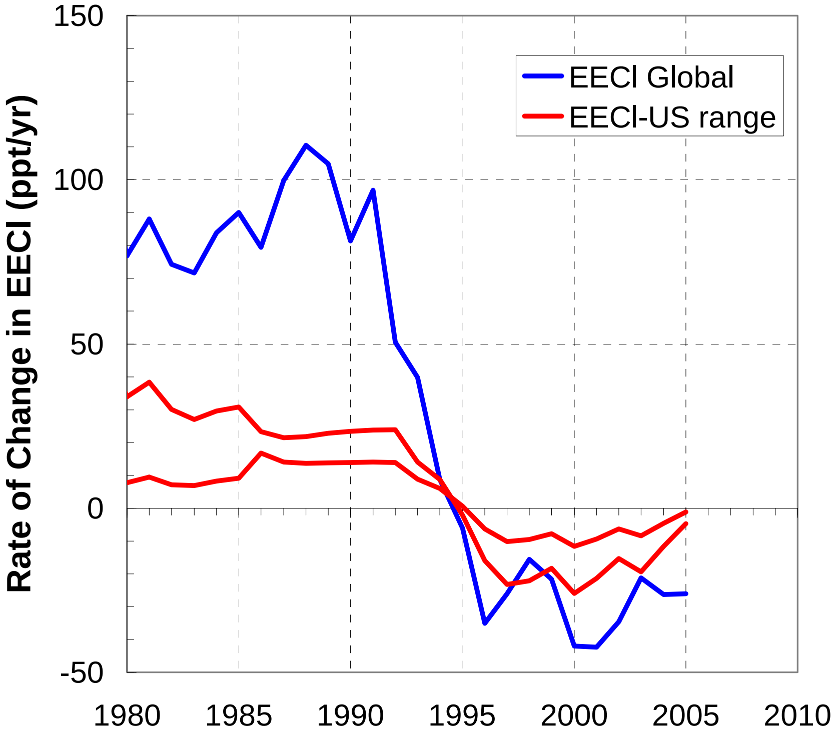


Figure 2.16 Rate of change in global EECl derived from measured global atmospheric mixing ratios of ODSs and substitute chemicals (blue line), and the rate of change in EECl derived from atmospheric mixing ratios calculated from upper and lower bounds on U.S. emissions of ODSs (bounded by red lines; see Box 2.5 for discussion of U.S. emissions). High and low U.S. EECl estimates express the influence of emission uncertainties have on these rates (see Box 2.5).

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, though the few independent assessments of regional emissions conducted during the early 2000s that are available suggest that actual emissions may be lower than estimated by the EPA (see Section 2.2.5 of this chapter).

2.4.3.1 Estimating Reactive Halogen Trends in the Mid-latitude Stratosphere

Changes in stratospheric halogen abundance are delayed from 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 mid-latitude stratospheric have been roughly derived with a lag of 3 years on EECl. The EESC calculated for the mid-latitude stratosphere suggests that by 2004 the mid-latitude stratospheric halogen burden had declined by approximately 7% from its peak, when estimated simply as a 3 year lag of EECl.

2.4.3.2 Estimating Reactive Halogen Trends using EESC in the Antarctic Stratosphere

Measurements suggest that air found in the lower Antarctic stratosphere during the early springtime has resided in the stratosphere for about 6 years, or approximately twice as long as it takes to transport air from the troposphere to the mid-latitude stratosphere. This influence, combined with the slow decline in EESC during the 21st 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 mid-latitude 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 6-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 climate effects of emissions from different greenhouse gases. This provides a simple approximation relating the emission of a given compound to an equivalent CO_2 emission. The alteration of the radiative balance by the atmospheric abundance of a greenhouse gas is a measure of the direct influence this gas has on climate. As more energy is trapped in the Earth/atmosphere system, which occurs from higher atmospheric concentrations of greenhouse gases, the global average temperature will tend to increase. Radiative forcing is calculated by multiplying the atmospheric concentrations of the various GHGs by their radiative efficiencies (see Section 2.1.1 of this chapter). 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 (see Section 2.1.1 of this chapter), direct radiative forcing represents the forcing of GHGs due to their own absorption of infrared light energy and neglects any potential chemical or other feedbacks.

The direct, global radiative forcing due to ODSs and substitutes reached about 0.33 W per m^2 in 2006 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 m^2 from 2001-2005. For the purpose of putting this total direct forcing into perspective, the amount of radiative forcing due to CO_2, CH_4, and N_2O in 2005 was approximately 1.66 W per m^2, 0.48 W per m^2, and 0.16 W per m^2, 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.

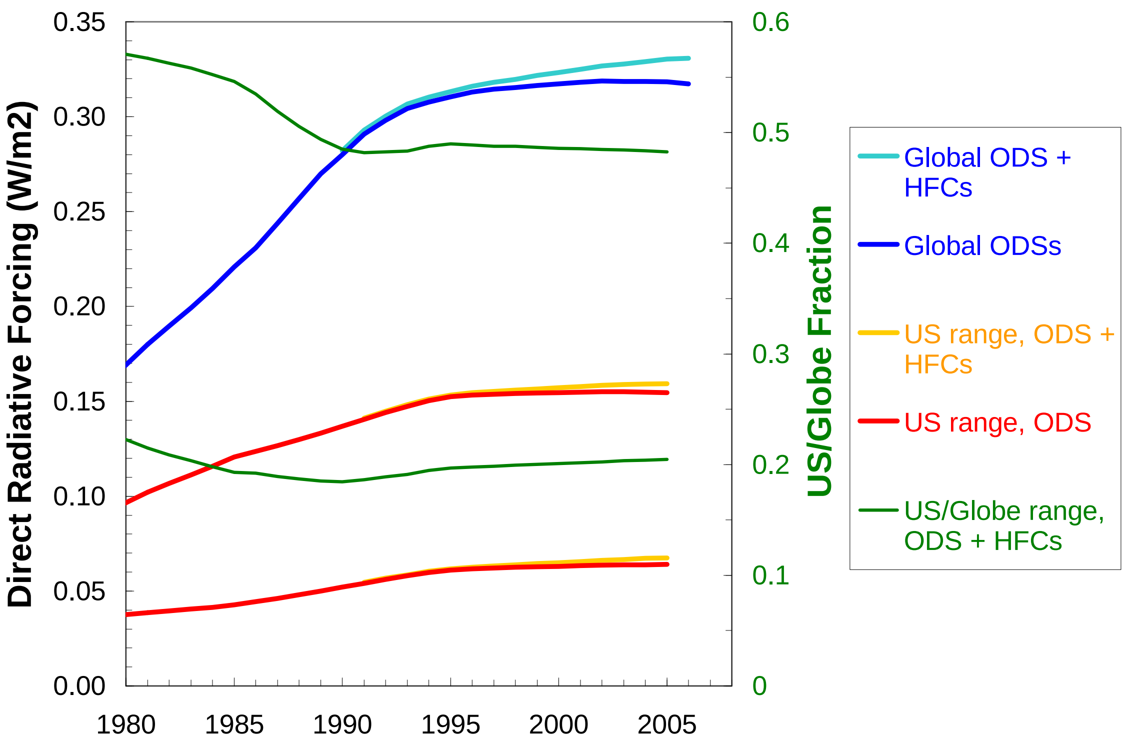


Figure 2.17 Direct radiative forcing time series arising from changing atmospheric concentrations of ODSs and their substitutes. Radiative forcing is calculated by weighting global atmospheric mixing ratios of ODSs and substitutes (blue lines) and by weighting atmospheric mixing ratios derived from a range of U.S. emissions (bounded by red lines; see Box 2.5 for discussion of U.S. emissions). Radiative forcing is shown with and without the contribution of HFCs.

———

The relative contributions of classes of ODS chemicals and their replacements are shown in Figure 2.18. The CFCs have contributed 79 to 86% of the total forcing from ODSs since 1980. However, over the last decade the fractional contribution of the CFCs has declined, as have the fractional contributions of CH_3CCl_3 and CCl_4. Increases in HCFC abundances, primarily HCFC-22, and in HFC abundances are counteracting the decline of these other gases.

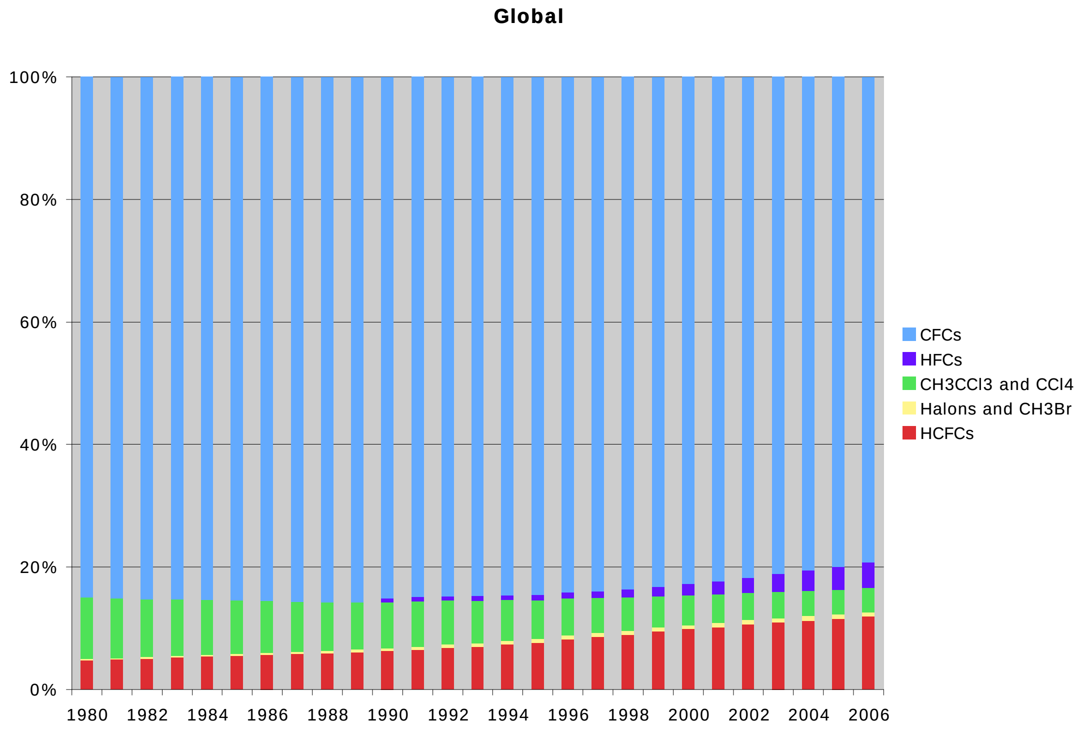


Figure 2.18 Relative contributions of ODS compound classes to global radiative forcing.

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 can be calculated to be 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 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 U.S. 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

So far in this chapter, we have only discussed the direct GWPs and the direct radiative forcing of the ODSs. As stated in section 2.1.1, the direct quantities represent the effect of the ODSs themselves on radiative forcing through their absorption of infrared energy. An additional complication to precisely quantifying the ODSs overall influence on climate forcing arises from their destruction of stratospheric ozone, itself a greenhouse gas. It has been recognized that destruction of this ozone likely will lead to a negative radiative forcing that will counteract the enhanced absorption of IR energy by ODSs themselves. This radiative effect of ozone destruction is thus labeled an “indirect effect”. Indirect GWPs have been calculated that include this influence (*e.g.*, Daniel and Velders *et al*., 2007) and an indirect radiative forcing can be estimated. The indirect offset depends strongly on the particular ODS, with the halons and CH_3Br leading to significant indirect effects that result in relatively large negative GWPs. For these chemicals, this particularly large offset results from bromine being so much more potent for ozone destruction compared to chlorine.

In the past, it had been thought that the ozone offset to total direct halocarbon radiative forcing could be even larger than 50%, but estimates from different studies varied widely (Ramaswamy *et al.*, 2001). More recently, now that ozone trends have been better quantified particularly in the radiatively important region near the tropopause, the magnitude of this effect is estimated to be -0.05±0.05 W per m^2 for the changes in ozone between 1979 and 1998 caused by ODS increases (Forster *et al.*, 2007). This still uncertain negative forcing is thus currently thought to represent an offset of less than 20% to the total direct ODS radiative forcing in 1998 (Figure 2.9).

This indirect forcing effect will gradually become negligible as ozone recovers to background levels (Daniel *et al.*, 1995). However, the ozone "recovery" and evolution of the future associated radiative forcing is complicated by the effects of, in particular, greenhouse gases, because they will alter the sensitivity of ozone and the magnitude of these indirect influences to the halogens. In addition to the discussed uncertainties in the magnitude of the indirect effect arising from measurements of historical ozone trends near the tropopause, there is substantial uncertainty concerning the precise spatial (vertical and horizontal) response of stratospheric ozone and its forcing to future changes in ODSs. For example, one important issue concerns the cessation of the roughly linear response of ozone inside the polar vortex to changing ODSs due to saturation effects. Also the significance of polar ozone depletion to the global radiative balance remains in question. Hence, here we make no further effort to quantify this indirect effect other than the approximate approach taken in Chapter 5 of this report, but emphasize that it remains an uncertain offset that must continue to receive attention when the radiative forcing of ODSs is concerned.

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 U.S. 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 to regulated dispersive uses, considered in sum, have declined substantially from peak levels. By 2005, ODP-weighted consumption in the U.S. had declined by 97-98%, or nearly 400 ODP-kilotons since the late 1980s (UNEP, 2007). These data indicate that the U.S. 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 methyl bromide consumption in developed countries was to have been zero in 2005 and thereafter, U.S. consumption to critical uses was 28% of 1986 baseline consumption during this year (4.4 ODP-kilotons), and, in 2006, was 27% of 1986 baseline consumption (4.1 ODP-kilotons) (UNEP/MBTOC, 2007). Authorized CUEs for CH_3Br consumption in the U.S. for 2007 were slightly reduced compared to 2005 and 2006 (17% of the U.S. 1986 baseline consumption). U.S. consumption also has continued for CFCs despite the 1996 phase out, though this consumption has been comparably small (<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 were derived from a vintaging model analyses of sales, use, and release patterns of ODSs ("a bottom-up" analysis; 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 U.S. 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 EECl (15-36%) during 2000-2005. EECl 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. CH_3Br 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 CO_2. Declines of 77 and 74% are calculated for global and U.S. GWP-weighted emissions of ODS and substitute chemicals through 2004, or an emissions decline on a global scale of 7270 megatons CO_2-equivalents and an emissions decline in the U.S. of 1640 megatons CO_2-equivalents. The U.S. decline alone is a large fraction of the global benefit anticipated as a result of adherence the Kyoto Protocol (~2000 megatons CO_2–equivalent emissions; Velders *et al*., 2007).

CHAPTER 2 REFERENCES

AFEAS, 2007: data tables accessible at http://www.afeas.org/.

Campbell, N., and R. Shende (Lead Authors), M. Bennett, O. Blinova, R. Derwent, A. McCulloch, M. Yamabe, J. Shevlin, and T. Vink, 2005: HFCs and PFCs: Current and Future Supply, Demand and Emissions, plus Emissions of CFCs, HCFCs and Halons, Chapter 11 in *IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbon and Perfluorocarbons*, Working Group I and II of the Intergovernmental Panel on Climate Change and the Technology and Economic Assessment Panel, Cambridge University Press, Cambridge, U.K. and N.Y., USA, 488 pp.

Clerbaux, C., and D.M. Cunnold (Lead Authors), J. Anderson, A. Engel, P.J. Fraser, E. Mahieu, A. Manning, S.A. Montzka, R. Nassar, R. Prinn, S. Reimann, C.P. Rinsland, P. Simmonds, D. Verdonik, R. Weiss, D. Wuebbles, and Y. Yokouchi, 2007: Long-Lived Compounds, Chapter 1 in *Scientific Assessment of Ozone Depletion: 2006*, Global Ozone Research and Monitoring Project—Report No. 50, 572 pp., World Meteorological Organization, Geneva, Switzerland.

Daniel, J.S, and G.J.M. Velders, (Lead Authors), A.R. Douglass, P.M.D. Forster, D. A. Hauglustaine, I.S.A. Isaksen, L.J.M. Kuijpers, A. McCulloch, and T.J. Wallington, 2007: Halocarbon Scenarios, Ozone Depletion Potentials, and Global Warming Potentials, Chapter 8 in *Scientific Assessment of Ozone Depletion: 2006*, Global Ozone Research and Monitoring Project—Report No. 50, 572 pp., World Meteorological Organization, Geneva, Switzerland.

Daniel, J.S., S. Solomon, and D.L. Albritton, 1995: On the evaluation of halocarbon radiative forcing and global warming potentials, *Journal of Geophysical Research,* **100**, 1271-1285.

Dorf, M., J.H. Butler, A. Butz, C. Camy-Peyret, M.P. Chipperfield, L. Kritten, S. A. Montzka, B. Simmes, F. Weidner and K. Pfeilsticker, 2006: Long-term observations of stratospheric bromine reveal slow down in growth, *Geophysical Research Letters,* **33**, L24803, doi:10.1029/2006GL027714.

EPA, 2007: Inventory of U.S. Greenhouse Gas Emissions and Sinks, 1990-2005, U.S. EPA #430-R-07-002, April, 2007, Washington.

Forster, P., and V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D.W. Fahey, J. Haywood, J. Lean, D.C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz, and R. Van Dorland, 2007: Changes in Atmospheric Constituents and in Radiative Forcing. In: *Climate Change 2007: The Physical Science Basis. Contributions of Working Group 1 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.J. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

IPCC, 2001: Climate Change; the Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change (Cambridge Univ. Press, Cambridge, UK)..

IPCC/TEAP, 2005: *IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbon and Perfluorocarbons*, Working Group I and II of the Intergovernmental Panel on Climate Change and the Technology and Economic Assessment Panel, Cambridge University Press, Cambridge, U.K. and N.Y., USA, 488 pp., 2005.

Law, K.S., and W.T. Sturges, (Lead Authors), D.R. Blake, N.J. Blake, J.B. Burkholder, J.H. Butler, R.A. Cox, P.H. Haynes, K. Kreher, C. Mari, K. Pfeilsticker, J.M.C. Plane, R.J Salawitch, C. Schiller, B.-M. Sinnhuber, R. von Glasow, N.J. Warwick, D.J. Wuebbles, S.A. Yvon-Lewis, Halogenated and Very Short-Lived Substances, Chapter 2 in *Scientific Assessment of Ozone Depletion: 2006*, Global Ozone Research and Monitoring Project—Report No. 50, 572 pp., World Meteorological Organization, Geneva, Switzerland, 2007.

McCulloch, A., P.M. Midgley, D.A. Fisher, 1994: Distribution of emissions of chlorofluorocarbons (CFCs) 11, 12, 113, 114, and 115 among reporting and non-reporting countries in 1986, *Atmospheric Environment*, **28**, 2567-2582.

Midgley, P.M., and A. McCulloch, Chapter 5 Properties and applications of Industrial Halocarbons, in *The Handbook of Environmental Chemistry Vol. 4. Part E, Reactive Halogen Compounds in the Atmosphere*, (P. Fabian and O.N. Singh, eds.), Pringer-Verlag, Berlin, 1999.

Newman, P.A., E.R. Nash, S.R. Kawa, S.A. Montzka, and S.M. Schauffler, 2006: When will the Antarctic ozone hole recover? *Geophysical Research Letters,* **33**, L12814, doi:10.1029/2005GL025232.

Newman, P.A., J.S. Daniel, D.W. Waugh, and E.R. Nash, 2007: A new formulation of equivalent effective stratospheric chlorine (EESC), *Atmospheric Chemistry and Physics*, 7, 4537-45552.

Ramaswamy, V., O. Boucher, J. Haigh, D. Hauglustaine, J. Haywood, G. Myhre, T. Nakajima, G.Y. Shi, S. Solomon, 2001: Radiative Forcing of Climate Change. In *Climate Change 2001: The Scientific Basis. Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change* [Houghton, J.T., Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linded, X. Dai, K. Maskell, and C.A. Johnson (eds.)] Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 881 pp.

Rand, S., and M. Yamabe (Lead Authors), N. Campbell, J. Hu, P. Lapin, A. McCulloch, A. Merchant, K. Mizuno, J. Owens, and P. Rollet, 2005: Non-Medical Aerosols, Solvents, and HFC-23, Chapter 10 in *IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbon and Perfluorocarbons*, Working Group I and II of the Intergovernmental Panel on Climate Change and the Technology and Economic Assessment Panel, Cambridge University Press, Cambridge, U.K. and New York, N.Y., USA, 488 pp.

UNEP, 2007: Ozone Secretariat ODS production and consumption data tables on the web at http://ozone.unep.org/Data_Reporting/.

UNEP/CTOC, 2007: UNEP 2006 Report of the Chemical Technical Options Committee, 2006 Assessment, Nairobi.

UNEP/MBTOC, 2007**:** *The 2006 Report of the Methyl Bromide Technical Options Committee*, United Nations Environment Programme, Nairobi, Kenya, March.

UNEP/TEAP, 2006: *Technology and Economic Assessment Panel Task Force on Emissions Discrepancies Report*.

Velders, G.J.M., S.O. Andersen, J.S. Daniel, D.W. Fahey, M. McFarland, 2007: The importance of the Montreal Protocol in protecting climate. *Proceedings of the National Acadademy of Sciences,* **104(12)**, 4814-4819.

WMO (World Meteorological Organization), 2003: *Scientific Assessment of Ozone Depletion: 2002*, Global Ozone Research and Monitoring Project – Report No. 47, 498 pp., Geneva, Switzerland.

WMO (World Meteorological Organization), 2007: *Scientific Assessment of Ozone Depletion: 2006*, Global Ozone Research and Monitoring Project – Report No. 50, 572 pp., Geneva, Switzerland.

Appendix 2.A

Table 2.A.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 1-4, 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, S.M., E.L. Atlas, S.G. Donnelly, A. Andrews, S.A. Montzka, J.W. Elkins, D.F. Hurst, P.A. Romashkin, G.S. Dutton, and V. Stroud, Chlorine budget and partitioning during SOLVE, *J. Geophys. Res., 108* (D5), doi: 10.1029/2001JD002040, 4173, 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 2.A.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] ($W\ m^{-2}\ ppbv^{-1}$)	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_2O	3.03×10^{-3}	114 [d]	289	298	153
Chlorofluorocarbons						
CFC-11	CCl_3F	0.25	45	6,730	4,750	1,620
CFC-12	CCl_2F_2	0.32	100	10,990	10,890	5,200
CFC-13	$CClF_3$	0.25	640	10,800	14,420	16,430
CFC-113	CCl_2FCClF_2	0.30	85	6,540	6,130	2,690
CFC-114	$CClF_2CClF_2$	0.31	300	8,040	10,040	8,730
CFC-115	$CClF_2CF_3$	0.18	1700	5,310	7,370	9,990
Hydrochlorofluorocarbons						
HCFC-21	$CHCl_2F$	0.14	1.7	530	151	46
HCFC-22	$CHClF_2$	0.20	12.0	5,160	1,810	549
HCFC-123	$CHCl_2CF_3$	0.14	1.3	273	77	24
HCFC-124	$CHClFCF_3$	0.22	5.8	2,070	609	185
HCFC-141b	CH_3CCl_2F	0.14	9.3	2,250	725	220
HCFC-142b	CH_3CClF_2	0.20	17.9	5,490	2,310	705
HCFC-225ca	$CHCl_2CF_2CF_3$	0.20	1.9	429	122	37
HCFC-225cb	$CHClFCF_2CClF_2$	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_2F_2	0.11[e]	4.9	2,330	675	205
HFC-41	CH_3F	0.02	2.4	323	92	28
HFC-125	CHF_2CF_3	0.23	29	6,340	3,500	1,100
HFC-134	CHF_2CHF_2	0.18	9.6	3,400	1,100	335
HFC-134a	CH_2FCF_3	0.16[e]	14.0	3,830	1,430	435
HFC-143	CH_2FCHF_2	0.13	3.5	1,240	353	107
HFC-143a	CH_3CF_3	0.13	52	5,890	4,470	1,590
HFC-152	CH_2FCH_2F	0.09	0.60	187	53	16
HFC-152a	CH_3CHF_2	0.09	1.4	437	124	38
HFC-227ea	CF_3CHFCF_3	0.26[e]	34.2	5,310	3,220	1,040
HFC-236cb	$CH_2FCF_2CF_3$	0.23	13.6	3,630	1,340	407
HFC-236ea	CHF_2CHFCF_3	0.30	10.7	4,090	1,370	418
HFC-236fa	$CF_3CH_2CF_3$	0.28	240	8,100	9,810	7,660
HFC-245ca	$CH_2FCF_2CHF_2$	0.23	6.2	2,340	693	211
HFC-245fa	$CHF_2CH_2CF_3$	0.28	7.6	3,380	1,030	314
HFC-365mfc	$CH_3CF_2CH_2CF_3$	0.21	8.6	2,520	794	241
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	0.40	15.9	4,140	1,640	499
Chlorocarbons						
Methyl chloroform	CH_3CCl_3	0.06	5.0	506	146	45
Carbon tetrachloride	CCl_4	0.13	26	2,700	1,400	435
Methyl chloride	CH_3Cl	0.01	1.0	45	13	4
Bromocarbons						
Methyl bromide	CH_3Br	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	$CBrF_2CBrF_2$	0.33	20	3,680	1,640	503
Fully fluorinated species						
Sulfur hexafluoride	SF_6	0.52	3200	16,260	22,810	32,600
Trifluoromethylsulfurpentafluoroide	SF_5CF_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_2F_6	0.26	10000	8,620	12,200	18,180
Perfluoropropane	C_3F_8	0.26	2600	6,310	8,830	12,450
Perfluorobutane	C_4F_{10}	0.33	2600	6,330	8,850	12,480
Perfluorocyclobutane	$c\text{-}C_4F_8$	0.32	3200	7,310	10,250	14,660
Perfluoropentane	C_5F_{12}	0.41	4100	6,510	9,150	13,260
Perfluorohexane	C_6F_{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_2OCF_3	0.44	136	13,790	14,910	8,490
HFE-134	CHF_2OCHF_2	0.45	26	12,190	6,320	1,960
HFE-143a	CH_3OCF_3	0.27	4.3	2,630	756	230
HCFE-235da2	$CHF_2OCHClCF_3$	0.38	2.6	1,230	349	106
HFE-245fa2	$CHF_2OCH_2CF_3$	0.31	4.9	2,280	659	200
HFE-254cb2	$CH_3OCF_2CHF_2$	0.28	2.6	1,260	359	109
HFE-7100 (HFE-44-9)	$CH_3OC_4F_9$	0.31	5.0	1,390	404	123
HFE-7200 (HFE-56-9)	$C_2H_5OC_4F_9$	0.30	0.77	200	57	17
HFE-245cb2	$CH_3OCF_2CF_3$	0.32	5.1	2,440	708	215
HFE-347mcc3	$CH_3OCF_2CF_2CF_3$	0.34	5.2	1,980	575	175
HFE-356pcc3	$CH_3OCF_2CF_2CHF_2$	0.33	0.93	386	110	33
HFE-374pc2	$CH_3CH_2OCF_2CHF_2$	0.25	5.0	1,930	557	169
	$CH_3OCF(CF_3)_2$	0.31	3.4	1,200	343	104
HFE-43-10pccc124 [a]	$CHF_2OCF_2OC_2F_4OCHF_2$	1.37	6.3	6,320	1,870	569
	$(CF_3)_2CHOH$	0.28	2.0	764	217	66
HFE-236ca12	$CHF_2OCF_2OCHF_2$	0.66	12.1	8,040	2,820	859
HFE-338pcc13	$CHF_2OCF_2CF_2OCHF_2$	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	$c\text{-}C_3F_6$	0.42	>1000	>12,700	>17,340	>21,800
HFE-227ea	$CF_3CHFOCF_3$	0.40	11	4,540	1,540	468
HFE-236ea2	$CHF_2OCHFCF_3$	0.44	5.8	3,370	989	301
HFE-236fa	$CF_3CH_2OCF_3$	0.34	3.7	1,710	487	148
HFE-245fa1	$CHF_2CH_2OCF_3$	0.30	2.2	1,010	286	87
HFE-329mcc2	$CHF_2CF_2OCF_2CF_3$	0.49	6.8	3,060	919	279
HFE-338mcf2	$CF_3CH_2OCF_2CF_3$	0.43	4.3	1,920	552	168
HFE-347mcf2	$CHF_2CH_2OCF_2CF_3$	0.41	2.8	1,310	374	114
HFE-356mec3	$CH_3OCF_2CHFCF_3$	0.30	0.94	355	101	31
HFE-356pcf2	$CHF_2CH_2OCF_2CHF_2$	0.37	2.0	931	265	80
HFE-356pcf3	$CHF_2OCH_2CF_2CHF_2$	0.39	3.6	1,760	502	153
	$CHF_2OCH(CF_3)_2$	0.41	3.1	1,330	379	115
	$\text{-}(CF_2)_4CH(OH)\text{-}$	0.30	0.85	254	72	22

Note: Values are calculated for a CO_2 mixing ratio of 378 ppm, compared with 370 ppm in IPCC/TEAP (2005) and WMO (2003), which tends to increase all GWPs.

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[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, K.P., L.K. Gohar, M.D. Hurley, G. Marston, D. Martin, P.G. Simmonds, T.J. Wallington, and M. Watkins, Perfluorodecalin: Global warming potential and first detection in the atmosphere, *Atmos. Environ.*, *39* (9), 1759-1763, 2005.