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Fluorine in the Atmosphere

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Abstract

Scientific evidence, accumulated over more than two decades of study by the international research community, has shown that human-produced halocarbons are responsible for the observed depletions of the ozone layer. Fluorine-containing chlorofluorocarbons (CFCs) and halons are sufficiently long-lived so as to reach the stratosphere where they are photodissociated to release chlorine, bromine, and fluorine atoms. Although chlorine and bromine have been proven to be main responsible for the destruction of the ozone layer in the polar regions, fluorine by itself does not contribute to ozone depletion. Fluorine atoms released from the photodissociation of fluorine-bearing sources are quickly sequestered into carbonyl compounds and subsequently into the ultimate hydrogen fluoride, which is very stable in the stratosphere. The primary interest in monitoring inorganic fluorine (defined as F_y) in the atmosphere is as a surrogate of the amounts of its precursors, mainly the CFCs and hydrochlorofluorocarbons, involved in ozone depletion by chlorine. Fluorinated halocarbons and other gases such as perfluorocarbons or sulfur hexafluoride (SF_6) are also extremely potent greenhouse gases for which the current trends must be monitored and future scenarios of growth must be evaluated.

1. INTRODUCTION

Ozone levels in the atmosphere undergo normal seasonal variations, but recent levels of ozone loss over the poles and lower latitudes could not be explained by natural variability alone. Man-made chlorofluorocarbon (CFC) compounds were developed in the early 1930s for a variety of industrial and commercial applications, but it was not until the 1970s that these and other chlorine-containing substances were suspected of having the potential to destroy atmospheric ozone. In 1985, a team of British researchers first reported unusually low ozone levels over Halley Bay, Antarctica, which were caused by chemical reactions with chlorine and nitrogen compounds [1]. Research was initiated that found CFCs to be largely responsible for the anomalously low levels during the polar springtime. This polar ozone depletion at lower stratospheric altitudes is what has been termed as the “ozone hole.” The primary concern over ozone depletion is the potential impacts on human health and ecosystems due to increased UV exposure. Increase in skin cancer and cataracts in human populations are expected in a higher UV environment. Lower yields of certain cash crops may result owing to increased UV-B stress. Higher UV-B levels in the upper ocean layer may inhibit phytoplankton activities, which can impact the entire marine ecosystem. In addition to direct biological consequences, indirect effects may arise through changes in atmospheric chemistry. Increased UV-B will alter photochemical reaction rates in the lower atmosphere that are important in the production of surface layer ozone and urban smog.

Concern over these potential effects has prompted the international community to enact policies aimed at reducing the production of ozone-depleting chemicals. An important event in the history of international ozone policy was the Montreal Protocol on Substances That Deplete the Ozone Layer (1987), which called for the phase-out and reduction of certain substances over a multiyear time frame. Discoveries of more extensive ozone loss and rapid formulation of replacement substances for chlorine-containing compounds have led to refinements of the original protocol. Updates set forth at London (1990) and Copenhagen (1992) have called for accelerated phase-out and replacement schedules.

The Montreal Protocol on Substances That Deplete the Ozone Layer is a landmark international agreement designed to protect the stratospheric ozone layer. The treaty was originally signed in 1987 and substantially amended in 1990 and 1992. The Montreal Protocol stipulates that the production and consumption of compounds that deplete ozone in the stratosphere – CFCs, halons, carbon tetrachloride, and methyl chloroform – are to be phased out by 2000 (2005 for methyl chloroform). Methyl bromide, an ozone-depleting compound used extensively in agricultural applications, is set to be phased out internationally by 2010. In December 2005, it was decided at the Montreal Conference to extend the commitments of the Kyoto Protocol beyond 2012. The framework for the Montreal Protocol was based on the Vienna Convention for the Protection of the Ozone

Layer (1985), a non-binding agreement that outlined states' responsibilities for protecting human health and the environment against the adverse effects of ozone depletion.

The CFCs are entirely of anthropogenic origin, and have found use as foam-blowing agents, as refrigerants, and as solvents. These compounds are quite stable in the atmosphere and have lifetimes of between 50 and 500 years or even more. These long lifetimes, coupled with their strong infrared absorption capacity, also make the CFCs significant greenhouse gases. Although the CFCs make up the greatest fraction of the halogen burden in the atmosphere, a number of other compounds must also be considered when compiling an atmospheric halogen burden. Hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs) together with perfluorocarbons (PFCs) are currently being developed as replacements for the CFCs, and some of these compounds are already in use and have been detected in the atmosphere. Halons, which are fully halogenated compounds containing bromine, have been manufactured as fire suppressants. In addition, some natural sources of halogen exist in the form of partially halogenated methane and ethane. HCl is also an important contributor to the tropospheric chlorine budget, with a wide variety of natural and anthropogenic sources.

In parallel, the Kyoto Protocol (1997) is actually under discussion as an amendment to the United Nations Framework Convention on Climate Change (UNFCCC). Countries that ratify this protocol commit to reduce their emissions of carbon dioxide and five other greenhouse gases, among them CFCs and HCFCs, or engage in emission trading if they maintain or increase emissions of these gases. The objective of the protocol is the stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. Indeed, the Intergovernmental Panel on Climate Change (IPCC) has predicted an average global rise in temperature of 1.4 to 5.8°C between 1990 and 2100. Some current estimates indicate that even if successfully and completely implemented, the Kyoto Protocol will have some difficulties in providing a significant reduction in temperature.

The present chapter deals with atmospheric fluorine by studying sources and sinks of halogen compounds. It then presents the chemical and radiative impacts of these compounds on the Earth's atmosphere. Measurement networks and platforms are presented. Finally, present and future halogen trends are quantified based upon different emission scenarios.

2. SOURCES AND SINKS

Halogens are found in the atmosphere in two general forms, organic and inorganic. The organic species are often referred to as "source gases," since these species are released at the Earth's surface (from a variety of sources, some

natural and some man-made). Destruction of the source gases in the atmosphere leads to the release of halogens, which are then partitioned into a number of inorganic forms through chemical reactions. The CFC, HCFC, and HFC are manufactured for use as refrigerants, foam-blowing agents, and solvents. The manufacture of CFCs is now banned due to their impact on stratospheric ozone levels, and HCFCs will progressively also be phased out of production. HFCs have been shown to be “ozone friendly” and are replacing their chlorine-containing analogues in industrial applications. Halons, bromine- and fluorine-containing organic compounds, have been used as fire-extinguishing compounds in the past. Their production is now banned owing to their harmful effects on stratospheric ozone. Examples include Halon-1301 (CF_3Br) and Halon-1211 (CF_2ClBr).

Following the initial proposals of the potential impacts of CFCs on stratospheric ozone, measurement programs were established to monitor the concentrations of organic halogen source gases in the atmosphere and to determine temporal and spatial trends in their abundances (Figs. 1 and 2). Thus a global data network is now available from which the budget of these halogen source gases can be assessed (see Section 5). The atmospheric abundances, trends, and lifetimes of the primary organic fluorine-containing species are listed in Table 1. All CFCs, HCFCs, and halons have purely anthropogenic sources. Chlorine source gases such as CH_3CCl_3 and CCl_4 are also entirely man-made, while CH_3Cl is the major contributor to the natural halogen burden.

Approximately 85% of the total amount of organic chlorine comes from compounds with solely anthropogenic sources. These anthropogenic compounds are

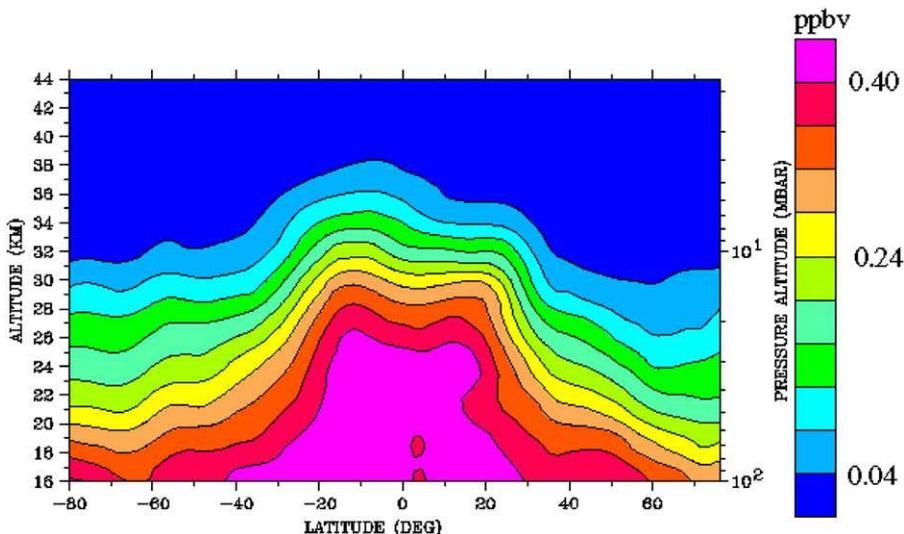


Fig. 1. Global latitude vs. height distribution of CCl_2F_2 (CFC-12), as measured by the CLAES instrument aboard the UARS satellite in March 1992.

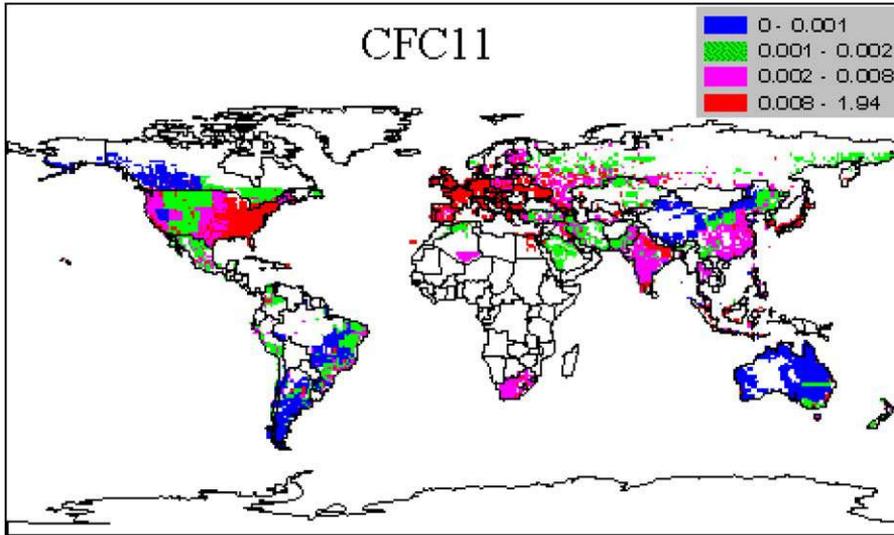


Fig. 2. Emission distribution of CCl_3F (CFC-11) based on McCulloch *et al.* [2]. Within countries in which the emissions have been distributed according to population figures. Data compiled by Jennifer Logan (Harvard University).

used primarily as refrigerants (CFCs-11, -12, and -114, HCFC-22), foam-blowing agents (HCFCs-142b, -141b, and -22, CFCs-11 and -12), solvents (CFC-113, HCFC-141b, methyl chloroform, carbon tetrachloride, chloroform, trichloroethylene, and perchloroethylene), and fire retardants (Halon-1211). Global production of CFC-11 and -12 began in the early 1960s (along with CCl_4) and increased rapidly through the mid-1970s. Maximum production happened in 1988 and decreased substantially since that time. Production of CFCs, methyl chloroform, carbon tetrachloride, and halons has been phased out and production of HCFC and HFC replacements has been phased in by developed countries as of 1996, as called for by the 1987 Montreal Protocol report and subsequent amendments on regulation of substances that deplete the ozone layer.

The main sources of atmospheric inorganic fluorine are the CFCs and HCFC-22 (Table 1). Therefore, the trends in atmospheric chlorine and fluorine levels are both tightly linked to the observed trends in these gases. Unlike chlorine, however, fluorine does not play a significant role in stratospheric ozone destruction because of the high stability of the reservoir species HF (see Section 3.1).

Ozone-depleting halogens in the troposphere continue to decrease. As of mid-2000, equivalent organic chlorine in the troposphere was nearly 5% below the peak value in 1992–1994. The recent rate of decrease is slightly less than in mid-1990s due to the reduced influence of methyl chloroform on this decline. In 2000, tropospheric mixing ratios of CFC-11 (Fig. 3) and -113 were decreasing faster than in 1996, and mixing ratios of CFC-12 were still increasing, but more slowly.

Table 1. Main organic sources for stratospheric fluorine chemistry and their associated lifetime, mixing ratio, and growth rate, as for 2000

Chemical formula	Common or industrial name	Mixing ratio (ppt)	Lifetime (year)	Growth rate (% per year)
<i>Major sources</i>				
CCl ₂ F ₂	CFC-12	543	100	0.42
CCl ₃ F	CFC-11	260	45	-0.41
CCl ₂ FCClF ₂	CFC-113	82	85	-0.43
CHClF ₂	HCFC-22	143	12	3.8
<i>Minor sources</i>				
CH ₂ FCF ₃	HFC-134a	14.6	14	27
CH ₃ CCl ₂ F	HCFC-141b	13	9.3	15
CH ₃ CClF ₂	HCFC-142b	12.5	17.9	9.4
CHF ₃	HFC-23	15.5	270	5.8
CHF ₂ CF ₃	HFC-125	1.4	29	22
CClF ₂ CClF ₂	CFC-114	17.2	300	-0.58
CBrClF ₂	H-1211	4.1	16	3.2
CBrF ₃	H-1301	2.9	65	2.8
CBrF ₂ CBrF ₂	H-2402	0.43	20	0.2
<i>Inert</i>				
CF ₄	FC-14	76	50,000	1
SF ₆	Sulfur hexafluoride	4.6	3200	4.5
CClF ₂ CF ₃	CFC-115	8.1	1700	0.20

Non-anthropogenic sources of CFCs, halons, carbon tetrachloride, methyl chloroform, and HCFCs are insignificant.

The substantial reduction in emissions of ozone-depleting substances during the 1990s that are inferred from measured atmospheric trends are consistent with controls on production and consumption in the fully amended and adjusted Montreal Protocol. The year 1999 is the first in which production and consumption of a class of ozone-depleting substances (CFCs) were restricted by all Parties to the Montreal Protocol. Atmospheric measurements are consistent with emissions derived from reported global production data for CFCs. Indeed, combined chlorine and bromine in the lower stratosphere (10–25 km), where most ozone loss occurs, leveled off around 1999. Bromine is included as an ozone-depleting chemical because although it is not as abundant as chlorine, it is 45 times more effective per atom in destroying stratospheric ozone. Earlier measurements showed that the peak of equivalent chlorine (chlorine plus 45 times bromine) had already occurred at the surface between mid-1992 and mid-1994 (Fig. 3).

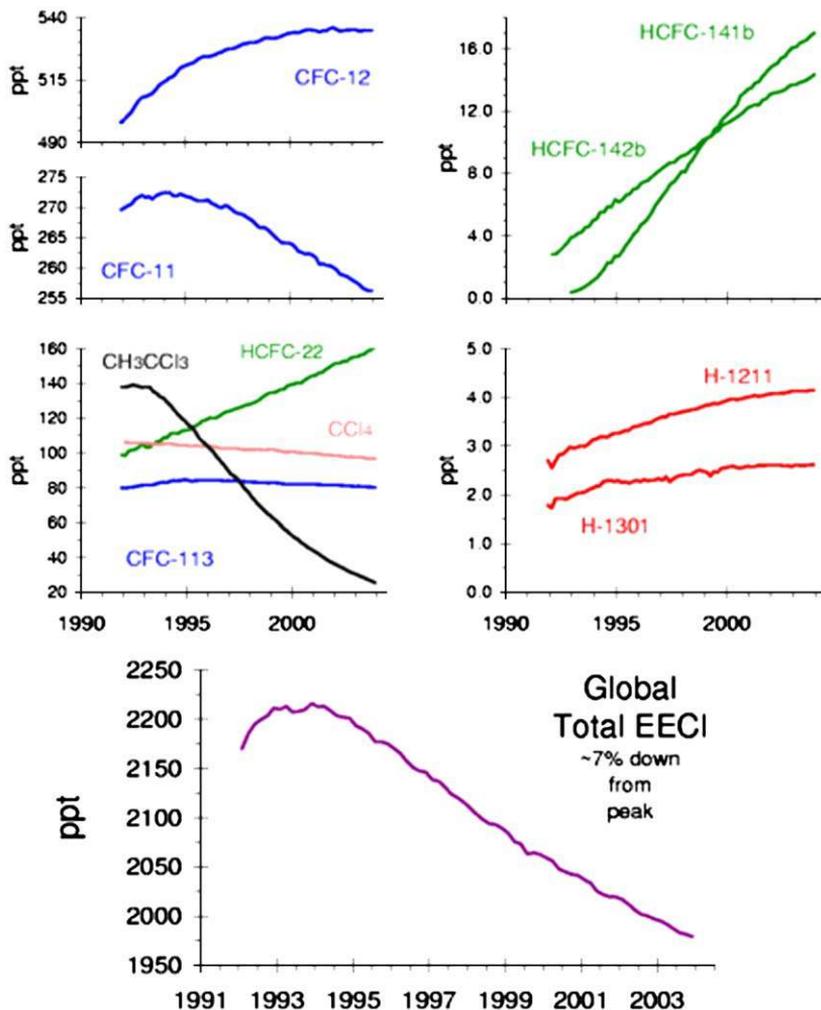


Fig. 3. Global trends in anthropogenic halocarbons (upper panels) and in equivalent chlorine (EECI = chlorine plus 45 times bromine).

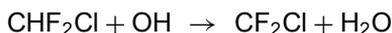
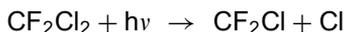
3. CHEMICAL IMPACTS

3.1. Chemistry of stratospheric fluorine

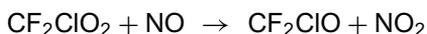
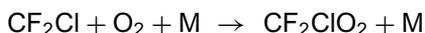
The release of fluorine from CFCs, HCFCs, and other fluorine-containing gases is believed to be analogous to the better-known CH_4 oxidation scheme. An important assumption made is that when CFCs break down in the stratosphere, the first bond that is broken is a carbon–chlorine bond, and the remaining C–Cl bonds

break before any C–F bonds do (based on consideration of the thermodynamics of the dissociation of halogen-substituted analogues of methyl radical [3,4]). In the case of HCFCs, the C–H bonds break first.

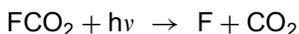
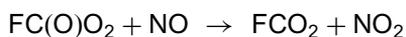
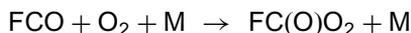
From this assumption, CFCs and HCFCs containing two fluorine atoms are first broken down to CF_2Cl . This is the case for the two most abundant fluorine-containing source gases, CF_2Cl_2 (CFC-12) and CHF_2Cl (HCFC-22):



CF_2Cl then undergoes the following chain of reactions:



Thus each molecule of CFC-12 breaks down to form one molecule of carbonyl fluoride, COF_2 . This species (Fig. 4) has a relatively long lifetime and is only slowly photolyzed. It is therefore an important fluorine temporary reservoir in the middle stratosphere. Measurements of COF_2 are still relatively sparse. Rinsland *et al.* [5] were the first to report a mixing ratio profile from the ATMOS space shuttle experiment. A recent update of the ATMOS spectra analysis is given by Irion *et al.* [6]. These measurements indicate that COF_2 forms relatively high in the stratosphere following the photolysis of CF_2Cl_2 . The general morphology of the vertical profile shows a peak of COF_2 at about 30 km at mid-latitudes, with a mixing ratio larger than 200 parts per trillion volume (pptv) in 1994, in good agreement with the balloon observations reported by Sen *et al.* [7]. In the tropics, the maximum abundance of COF_2 is found at a higher altitude, at about 40 km [8]. This may be simply understood in terms of stratospheric dynamics and the chemistry of the precursor CF_2Cl_2 . CFCs enter the stratosphere largely through upward motion in the tropics, where they are photolyzed weakly in the lower stratosphere because of the large overlying column of ozone. As altitude increases, the CFCs photodissociate and various breakdown products are formed. In the upper stratosphere, COF_2 is photolyzed more rapidly and releases two fluorine atoms F as follows:



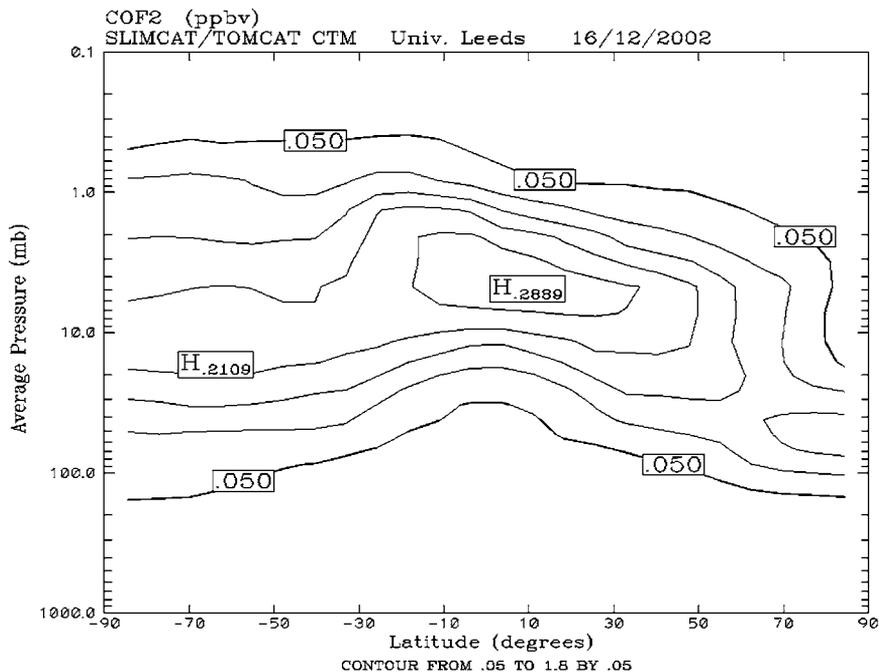


Fig. 4. Latitude vs. pressure distribution of COF₂ (ppbv) as calculated by the SLIMCAT 3D chemical-transport model for the December 2002 period (Courtesy M. Chipperfield, University of Leeds). Contour from 0.05 to 1.80 by 0.05 ppbv. H_{0.2889} means local high value of 0.2889 ppbv.

These processes explain the slow decrease in COF₂ observed above 30 km at mid-latitudes and above 40 km in the tropics. Numerical models indicate that mixing ratios larger than 50 pptv should persist into the mesosphere [4,9]. Note that the absolute abundance of COF₂ shows a time evolution that reflects the trend in man-made fluorine-bearing compounds. Zander *et al.* [8] report for instance a 67% increase in the burden of COF₂ in the middle and upper stratosphere between 1985 and 1992. The long-term monitoring of COF₂ at Jungfraujoch (46°N) also allowed Melen *et al.* [10] to identify a 4% per year increase in the COF₂ vertical column abundance between 1985 and 1995 (Fig. 5).

Because of its relatively long lifetime in the lower and middle stratosphere, COF₂ is an important temporary fluorine reservoir and contributes significantly to the column abundance of total inorganic fluorine (defined as $F_y = [\text{HF}] + 2[\text{COF}_2] + [\text{COFCl}]$) at all latitudes: long-term measurements performed from the ground at Jungfraujoch show that about 30% of F_y is in the form of COF₂ [12], whereas the model simulations performed by Chipperfield *et al.* [9] predict that over 50% may still be in this form in the tropics (Fig. 6).

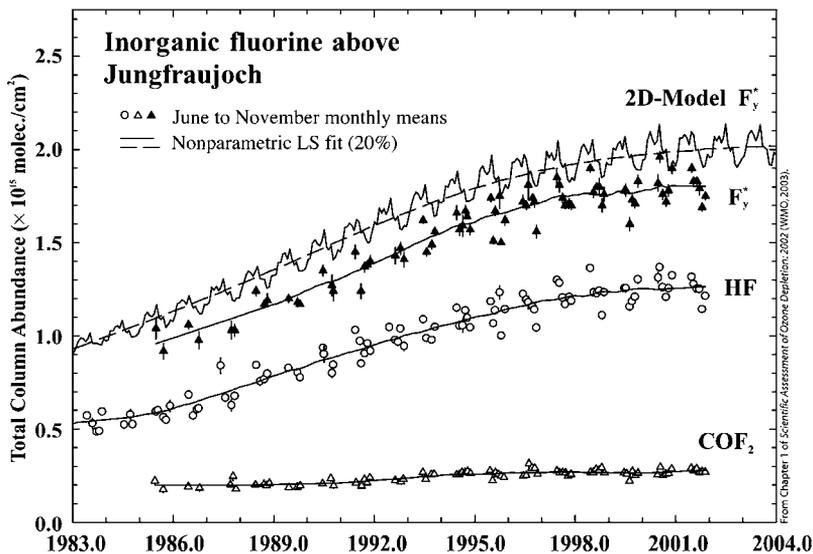
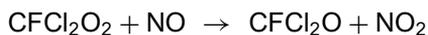
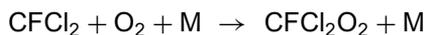
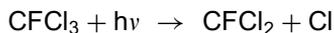
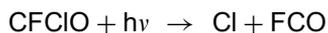


Fig. 5. Time series of monthly mean vertical column abundances of HF (open circles: update from Mahieu *et al.* [11]); COF₂ (open triangles: update from Melen *et al.* [10]); and their weighted sum, F^{*_y} (filled triangles; where F^{*_y} = [HF] + 2[COF₂]) derived from observations at the Jungfraujoch (46.5°N) between 1983 and 2001. The thick lines through the individual datasets represent nonparametric least-squares fits with 20% weighting. Also shown is column F^{*_y} above the Jungfraujoch calculated with a two-dimensional (2D) model [9]. The 10–12% high bias in the model calculations compared with the summer/fall observations is believed to arise in part from systematic uncertainties in the meridional transport of the 2D model. Taken from WMO [12].

CFCs with a single fluorine atom such as CFC₁₁ (CFC-11), an important contributor to the fluorine input in the atmosphere, are initially broken down to CFC₁₂, which then undergoes a chain of reactions:



Thus, the photolysis of CFC-11 here leads to the formation of chlorofluoroformaldehyde, CFCIO. This temporary reservoir is photolyzed more rapidly than COF₂ and produces FCO:



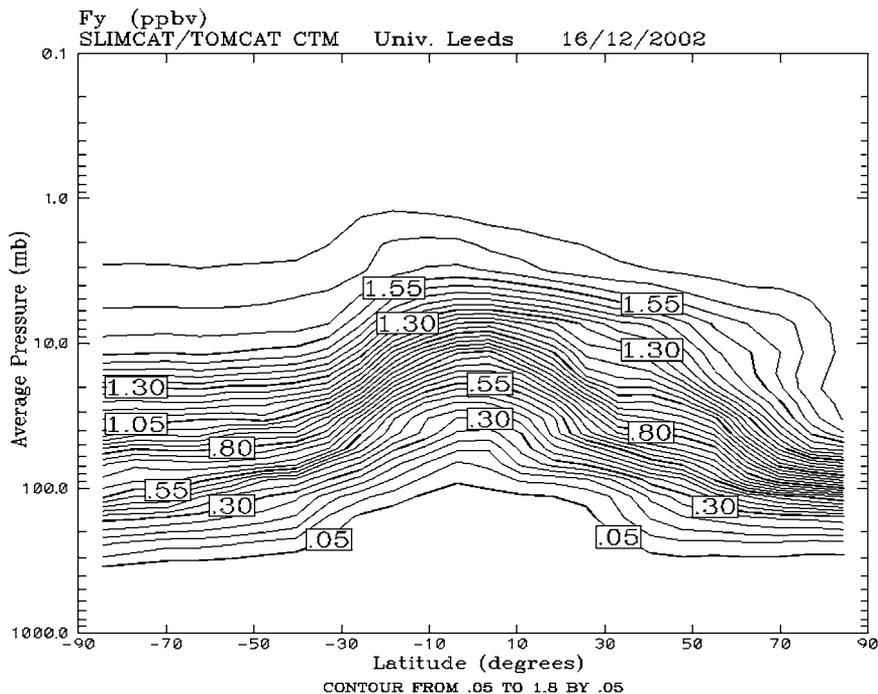


Fig. 6. Latitude vs. pressure distribution of total inorganic fluorine F_y (ppbv) as calculated by the SLIMCAT 3D chemical-transport model for the December 2002 period (Courtesy M. Chipperfield, University of Leeds). Contour from 0.05 to 1.80 by 0.05 ppbv.

which in turn releases fluorine atoms by the process already mentioned above. Because of its shorter lifetime, CFCIO is much less efficient than CF₂O for sequestering fluorine in the stratosphere. CFCIO has not been measured yet in the stratosphere but model calculations indicate that it is formed at a lower altitude than CF₂O, following the photolysis of CFCI₃, the CFC being photolyzed lower in the atmosphere. The peak mixing ratio is found at about 25 km at mid-latitudes. Models predict a slightly higher maximum in the tropics, at about 30 km [9], with a maximum mixing ratio on the order of 160 pptv in 2002 (see Fig. 7). Since CFCIO is also the most easily photolyzed fluorine-containing breakdown product, its abundance falls off rapidly with increasing altitude above the peak: CFCIO becomes more than one order of magnitude smaller than COF₂ 5 km above its peak, at 30 km. From model calculations [9], the contribution of CFCIO to the column abundance of total inorganic chlorine is of the order of 10% at mid-latitudes.

In the middle and upper stratosphere, the free F atoms produced by the dissociation of the intermediate reservoirs COF₂ and CFCIO mostly react with O₂

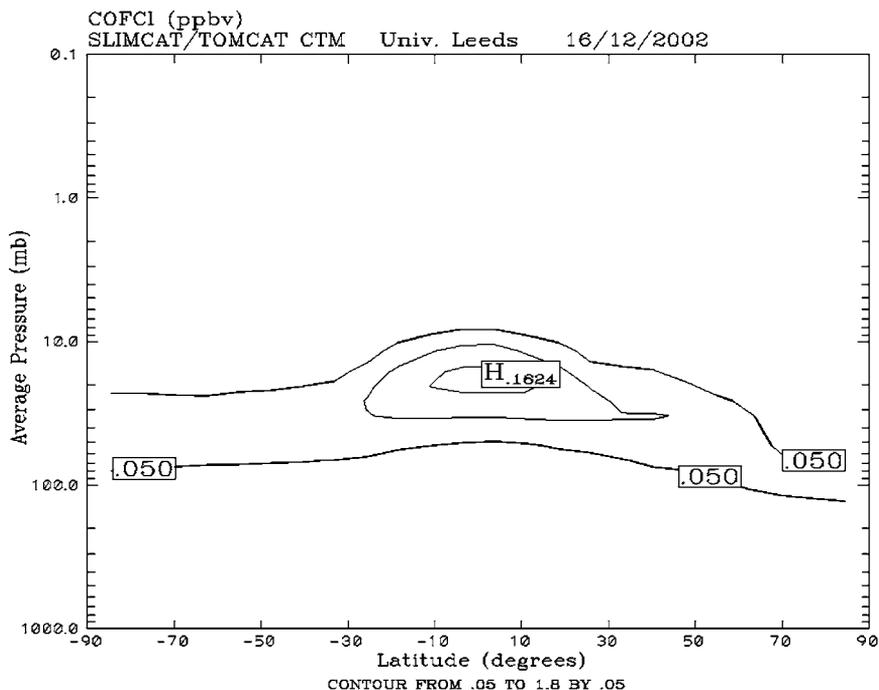
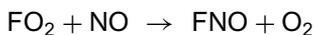
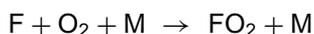
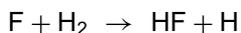
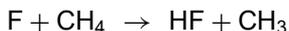


Fig. 7. Latitude vs. pressure distribution of COFCl (ppbv) as calculated by the SLIMCAT 3D chemical-transport model for the December 2002 period (Courtesy M. Chipperfield, University of Leeds). Contour from 0.05 to 1.80 by 0.05 ppbv. $H_{0.1624}$ means local high value of 0.1624 ppbv.

and participate in the following null cycle:

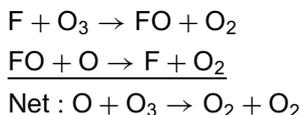


The F atoms eventually react with methane, water vapor, or molecular hydrogen to form hydrogen fluoride (HF):



This set of reactions is similar to that of forming HCl from Cl atoms. Unlike HCl however, HF cannot react with OH, as the reaction is endothermic. In addition,

photolysis cannot occur to any appreciable extent in the stratosphere, making HF an essentially permanent reservoir of stratospheric fluorine. Because of this strong stability, the atmospheric densities of F and FO are very small and prevent the 'classical' odd oxygen-destroying catalytic cycle from being efficient:



Thus, fluorine chemistry does not represent a significant sink for stratospheric ozone. All fluorine released from the source gases ends up in the form of HF, which accumulates in the stratosphere (Fig. 8). It is ultimately removed either by slow diffusion and rainout in the troposphere or by upward transport to the mesosphere where its mixing ratio remains constant up to high altitudes.

The high stability of HF makes it an effective tracer of fluorine input in the stratosphere arising from fluorinated anthropogenic gases. It is also a useful tracer of stratospheric motion and is often used as a reference for chemically more active tracers. Column HF is routinely measured by infrared spectroscopy

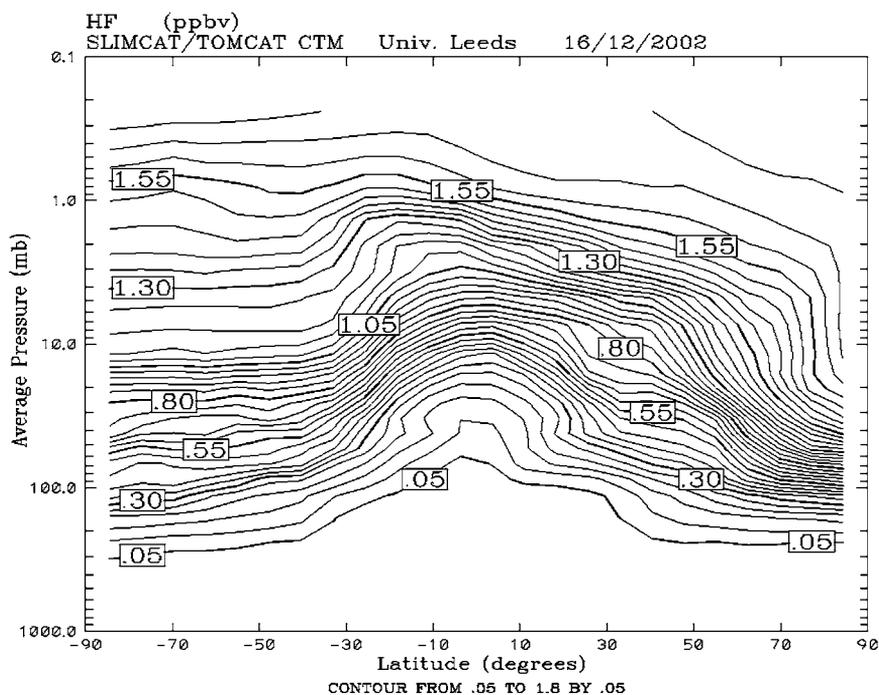


Fig. 8. Latitude vs. pressure distribution of HF (ppbv) as calculated by the SLIMCAT 3D chemical-transport model for the December 2002 period (Courtesy M. Chipperfield, University of Leeds). Contour from 0.05 to 1.80 by 0.05 ppbv.

from the ground [11,13], and numerous observations have been obtained with air-borne, balloon-borne, and space-based instruments. Near global satellite measurements of HF have also been recorded since October 1991 by the HALOE instrument onboard the UARS satellite [14]. At all latitudes, the general morphology of the vertical distribution of the HF abundance shows a continuous increase from the tropopause to the mesosphere (Fig. 9): as altitude increases, organic fluorine compounds decompose due to photolysis and chemistry, forming the intermediate reservoirs COF_2 and CFCIO which dissociate to produce HF. Since HF is not photolyzed or otherwise lost by chemical reaction, its mixing ratio will continue to increase in the stratosphere and mesosphere until all the COF_2 has been photolyzed (Fig. 10). At 55 km, HF is estimated to represent about 90% of the total inorganic fluorine [14]. Based on model calculations, the remaining 10% are believed to be in the form of COF_2 at this altitude [4,9]. In 2004, the total inorganic fluorine burden was estimated to be 1.8 parts per billion volume (ppbv).

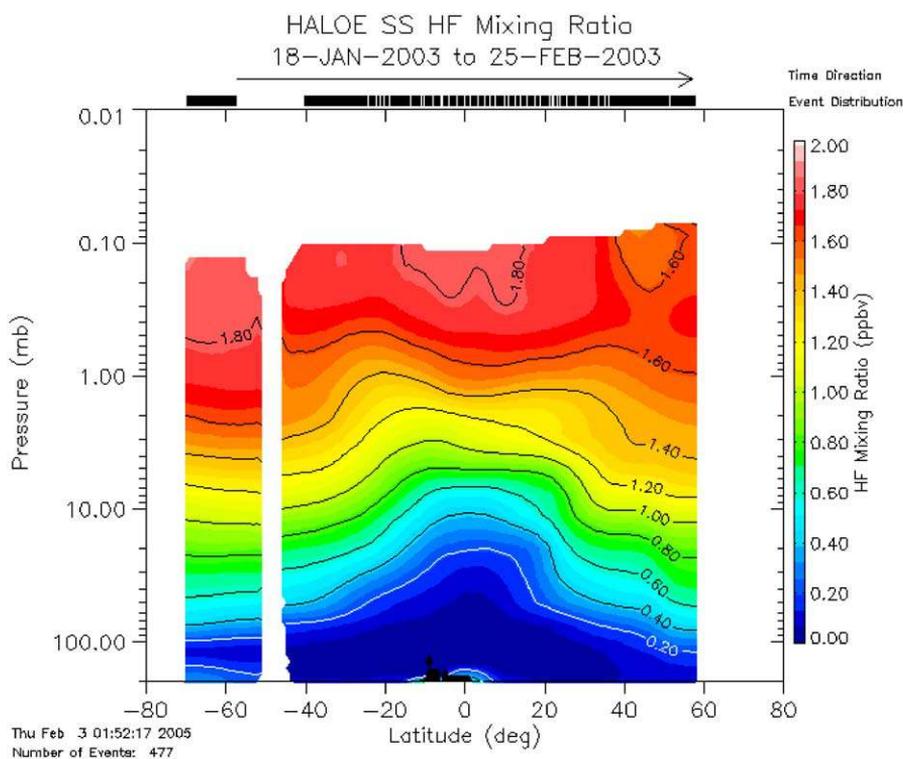


Fig. 9. Latitude vs. pressure cross-section of HF mixing ratio (ppbv) measured by the HALOE instrument on board the UARS satellite between 18 January 2003 and 25 February 2003.

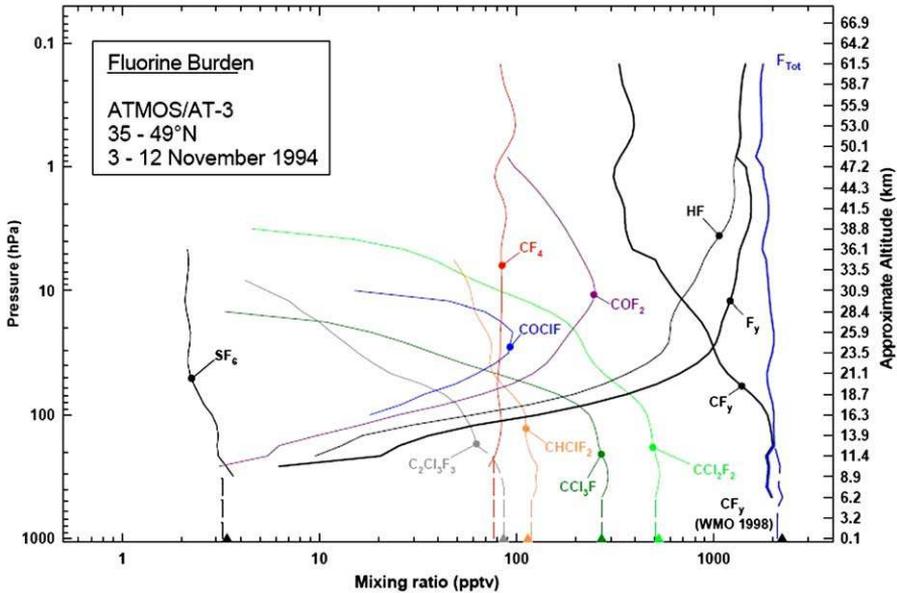
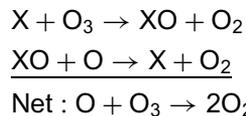


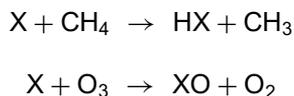
Fig. 10. Fluorine burden estimated from space-borne measurements during the ATMOS mission from Irion *et al.* [6].

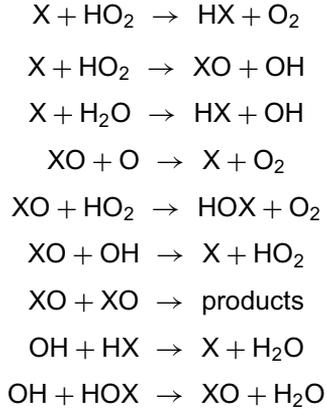
3.2. Chemistry of stratospheric chlorine

Once halogenated compounds are photolyzed or combine with other molecules in the atmosphere, they lead to a rapid release of free halogen atoms which give, after several reactions, inorganic species (see, e.g., Brasseur *et al.* [15]). This latter species belongs to several families (chlorine, fluorine, bromine, iodine) within which they can partition and, for some of them, directly destroy the ozone molecule (active molecules). If not, they are named reservoir molecules. They can indeed destroy O₃ through a catalytic cycle via the reaction:

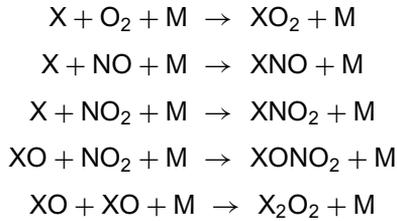


where X can be fluorine (F), bromine (Br), iodine (I), or chlorine (Cl) compounds. The ability of the family to destroy O₃ depends on the thermodynamics and reaction kinetics. Indeed, inorganic halogen species interact with various other molecules and families through bimolecular reactions:

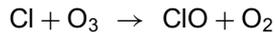




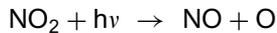
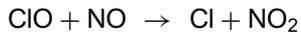
and termolecular reactions:



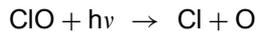
For the reasons given in Section 3.1, fluorine atoms are essentially sequestered in the form of HF in the stratosphere, and thus do not play any significant role in the ozone-destroying catalytic cycles presented here. However, this is not the case for chlorine and bromine atoms. Once a chlorine atom is formed, it rapidly reacts with O_3



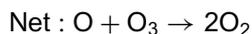
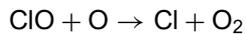
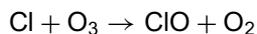
and ClO, once formed, is transformed back into Cl through different pathways



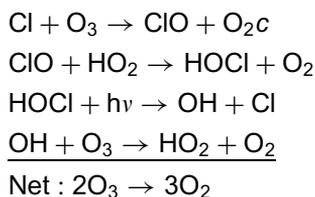
and



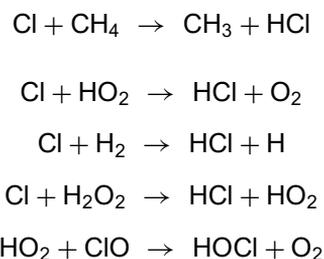
with no change in chemical composition. This is different in the catalytic cycle involving odd oxygen family $O_x = O + O_3$



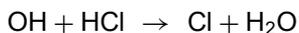
and $\text{HO}_x = (\text{OH} + \text{HO}_2)$ family



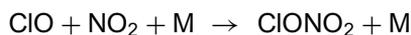
Other reactions can convert active chlorine ($\text{Cl} + \text{ClO}$) into reservoir species (essentially HCl , the most abundant chlorine reservoir, but also HOCl):



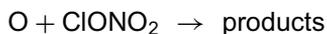
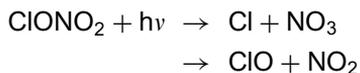
HCl comes back to Cl via the reaction:



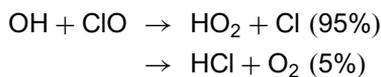
ClO can also react with ClONO_2 via the termolecular reaction:



while ClONO_2 is photolyzed or reacts with the oxygen atom:



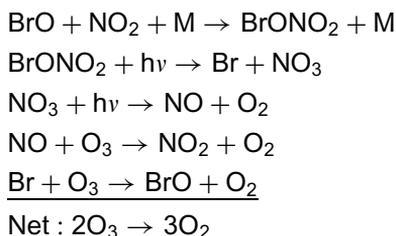
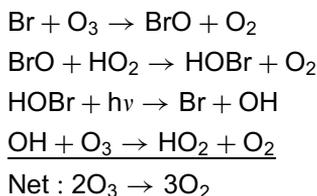
We can also note another pathway converting Cl from active species to reservoir ones:



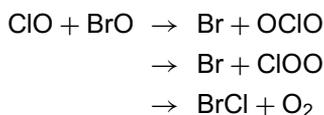
3.3. Links with stratospheric bromine chemistry

As already mentioned in Section 2, bromine, although not as abundant as chlorine, is 45 times more effective per atom in destroying stratospheric ozone. Indeed, bromine family plays a key role in the catalytic ozone destruction cycle

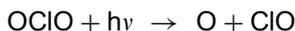
via the two following cycles:



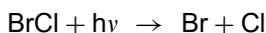
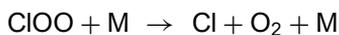
Furthermore, there is a cycle that couples the chemistry of chlorine and bromine through the reaction of ClO with BrO:



Production of OCIO in this reaction results in a null cycle:



but halogen atoms can be regenerated via the reactions:



3.4. Chlorine–bromine reactions in an “Ozone Hole” configuration

At high northern and southern winter latitudes (Fig. 11), the destruction of the ozone layer is governed by reactions that are far different from the ones listed above. Indeed, heterogeneous reactions can occur on the surface of polar stratospheric clouds (PSCs formed of liquid or solid particles composed of HNO_3 and H_2O). This leads to ozone loss, depending upon the occurrence of sunlight combined with gas-phase reactions involving bromine and chlorine chemical reactions [15].

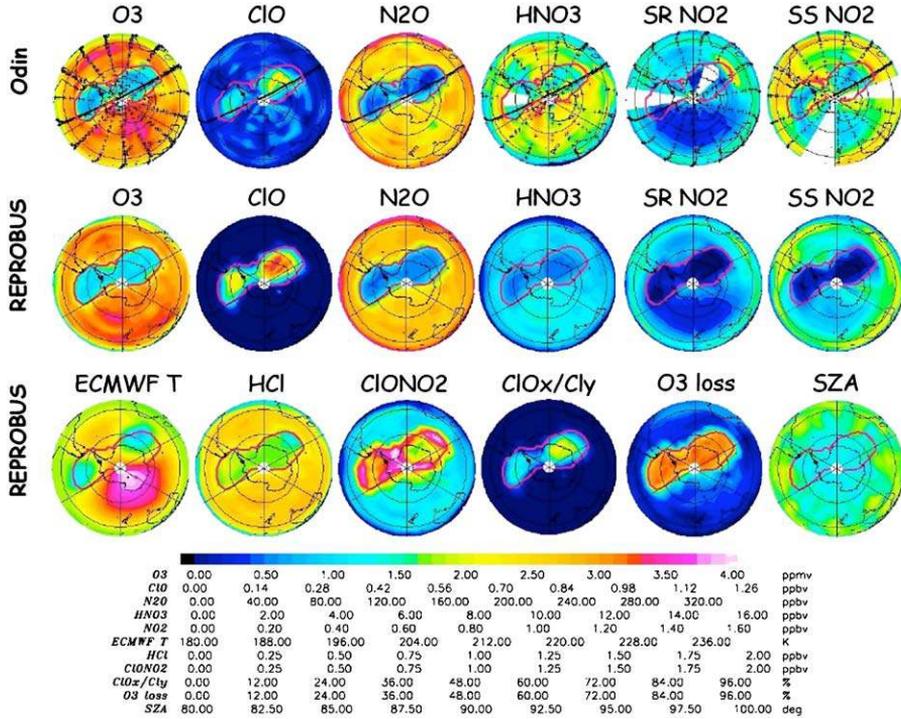
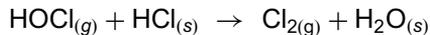
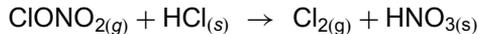
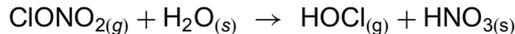
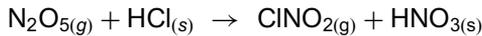
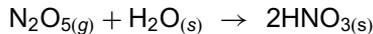


Fig. 11. Polar stereographic projection of the Antarctic polar vortex split in September 2002, as traced by different stratospheric constituents at 20 km as measured by the Odin satellite (top row), and as calculated by a 3D chemical-transport model (middle and bottom rows). Taken from Ricaud *et al.* [16].

On the surface of PSCs, heterogeneous reactions alter the partitioning of inorganic chlorine, since reservoir species HCl and ClONO₂ convert into Cl₂, HOCl, and ClNO₂:



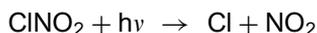
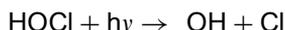
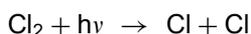
where the subscript (g) means gas phase and (s) means solid phase. Gas-phase N₂O₅ is essentially produced during the night



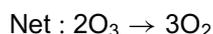
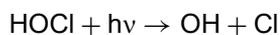
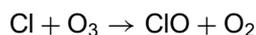
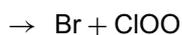
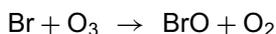
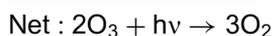
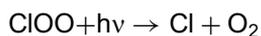
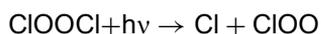
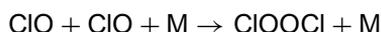
and destroyed during daytime



The gas-phase species produced by heterogeneous reactions photolyze readily at the edge of the polar vortex in winter or later in early spring:



yielding the catalytic ozone-destroying cycles involving both chlorine and bromine families:



Because they do not require the presence of oxygen atoms O, these catalytic cycles can operate at low altitudes where the concentration of ozone is largest.

4. RADIATIVE IMPACTS

Global warming potentials (GWPs) are used to estimate the integrated climate forcing of various greenhouse gases compared with a reference gas, usually chosen to be carbon dioxide (CO₂). They provide a simple way of gauging how

decisions affecting greenhouse gas emissions (e.g., in the Kyoto Protocol) may influence our future climate in a relative sense. Furthermore they allow the effects of these potential actions to be roughly assessed in terms of a “carbon dioxide equivalent” emission. Radiative effects of CFC alternatives are also assessed with the use of GWPs.

Furthermore the accurate calculation of the radiative forcing of the CFCs and related species relies on good quality data on the absorption cross sections at thermal infrared. For some gases, a spread exceeding 25% of the mean cross sections was found and there was little agreement of the sign, or indeed even the existence, of any temperature dependence. The radiative forcing owing to CFCs and their related species also depends on the knowledge of the spectroscopy of overlapping species such as water vapor, carbon dioxide, and ozone. Remaining spectroscopic uncertainties from the HITRAN database [17] are estimated to cause errors of no more than 5% in the radiative forcing. Hence, errors from this source are likely to be smaller than current uncertainties in the absorption cross sections of the halocarbons.

The GWP of a particular compound is defined as the ratio of the time-integrated radiative forcing from the instantaneous emission of 1 kg of some gas relative to that of 1 kg of a reference gas. Mathematically, the GWP is given by

$$\text{GWP}_x(TH) = \frac{\int_0^{TH} a_x[x(t)]dt}{\int_0^{TH} a_r[r(t)]dt}$$

where a_x is the radiative forcing of a unit mass of species x added to the current atmospheric composition, $x(t)$ the atmospheric decay function of the pulse of species x , a_r , and $r(t)$ the corresponding quantities for the reference gas, and TH the time horizon over which the calculation is performed.

The global and annual mean radiative forcing induced by halocarbons is indeed positive at about 0.5 W m^{-2} and of a high degree of scientific understanding (Fig. 12). They participate to the $2.43 (\pm 10\%) \text{ W m}^{-2}$ positive radiative forcing induced by other greenhouse gases (namely CO_2 , CH_4 , and N_2O) within a small uncertainty range.

In addition to the direct GWP of the species listed in Table 2, chlorinated and brominated halocarbons can lead to a significant indirect forcing through their destruction of stratospheric O_3 . Indeed, since O_3 is a greenhouse gas, halocarbons destroying stratospheric O_3 induce a negative indirect forcing that counteracts some or perhaps all (in certain cases) of their direct forcing. Furthermore, decreases in stratospheric O_3 act to increase the ultraviolet field of the troposphere and hence can increase OH and deplete those gases destroyed by reaction with the OH radical (particularly CH_4); this provides an additional negative forcing that is very difficult to quantify.

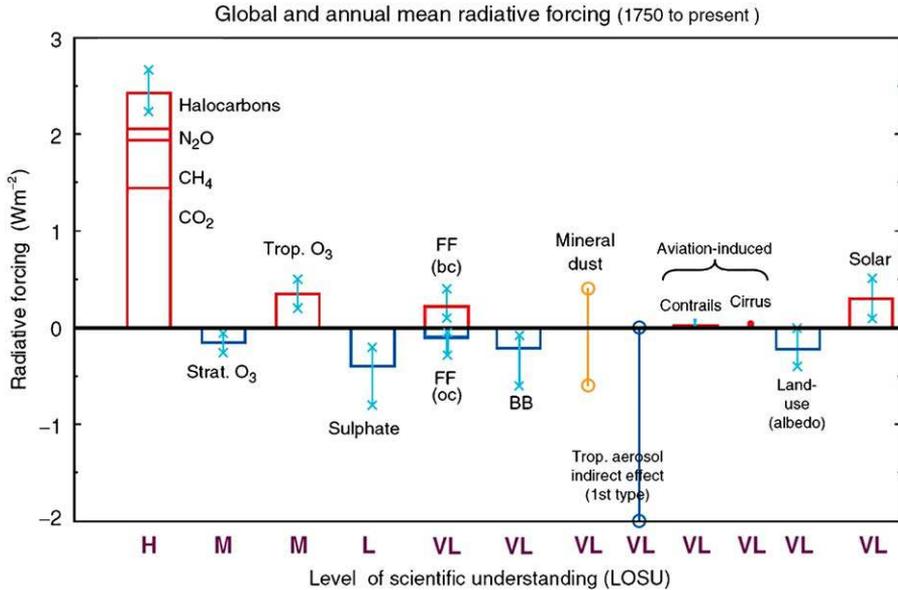


Fig. 12. Global and annual mean radiative forcings (W m^{-2}) according to different climate parameters from pre-industrial (1750) to present (2000) and their associated level of scientific understanding (H, high; M, medium; L, low; VL, very low). Taken from IPCC [18].

5. MEASUREMENTS

The monitoring effort on the temporal evolutions of CFCs, HCFCs, HCFs, and PFCs is conducted via two programs: (1) the Atmospheric Lifetime Experiment (ALE), Global Atmospheric Gases Experiment (GAGE), and Advanced Global Atmospheric Gases Experiment, namely ALE/GAGE/AGAGE program and (2) the former NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) which has recently merged into the Earth System Research Laboratory (ESRL) as part of its Global Monitoring Division (GMD).

In the ALE/GAGE/AGAGE global network program [19], continuous high-frequency gas chromatographic measurements of two biogenic/anthropogenic gases (CH_4 and N_2O) and six anthropogenic gases (chlorofluorocarbons CFCl_3 , CF_2Cl_2 , and $\text{CF}_2\text{ClCFCl}_2$; methyl chloroform, CH_3CCl_3 ; chloroform, CHCl_3 ; and carbon tetrachloride, CCl_4) are carried out at five globally distributed sites. Additional important species such as hydrogen (H_2), carbon monoxide (CO), methyl chloride (CH_3Cl), methyl bromide (CH_3Br), HFC-134a, HCFC-141b, HCFC-142b, HCFC-22, and Halons-1211 and -1301 have been added at select sites in recent years. The program, which began in 1978, is divided into three parts associated

Table 2. Global warming potential of long-lived fluorinated species in the atmosphere. Taken from WMO [12]

Common name	Chemical formula	Global warming potential		
		20 years	100 years	500 years
Carbon dioxide	CO ₂	1	1	1
<i>Chlorofluorocarbons</i>				
CFC-11	CCl ₃ F	6330	4680	1630
CFC-12	CCl ₂ F ₂	10,340	10,720	5230
CFC-13	CClF ₃	10,160	14,190	16,520
CFC-113	CCl ₂ FCClF ₂	6150	6030	2700
CFC-114	CClF ₂ CClF ₂	7560	9880	8780
CFC-115	CClF ₂ CF ₃	4990	7250	10,040
<i>Hydrochlorofluorocarbons</i>				
HCFC-22	CHClF ₂	4850	1780	552
HCFC-142b	CH ₃ CClF ₂	5170	2270	709
<i>Hydrofluorocarbons</i>				
HFC-23	CHF ₃	9500	12,240	10,350
HFC-125	CHF ₂ CF ₃	5970	3450	1110
HFC-143a	CH ₃ CF ₃	5540	4400	1600
HFC-227ea	CF ₃ CHFCF ₃	5760	3660	1200
HFC-236fa	CF ₃ CH ₂ CF ₃	7620	9650	7700
<i>Bromocarbons</i>				
Halon-1211	CBrClF ₂	4460	1860	578
Halon-1301	CBrF ₃	7970	7030	2780
<i>Fully fluorinated species</i>				
Sulfur hexafluoride	SF ₆	15,290	22,450	32,780
Trifluoromethylsulfurpenta	SF ₅ CF ₃	12,370	17,500	21,500
FC-14	CF ₄	3920	5820	9000
FC-116	C ₂ F ₆	8110	12,010	18,280
FC-218	C ₃ F ₈	5940	8690	12,520
FC-31-10	C ₄ F ₁₀	5950	8710	12,550
FC-318	c-C ₄ F ₈	6870	10090	14,740
FC-41-12	C ₅ F ₁₂	6120	9010	13,330
FC-51-14	C ₆ F ₁₄	6230	9140	13,350
<i>Halogenated alcohols and ethers</i>				
HFE-125	CHF ₂ OCF ₃	12,970	14,670	8530
HFE-134	CHF ₂ OCHF ₂	11,470	6220	1970
H-Galden 1040x				
CHF ₂ OCF ₂ OC ₂ F ₄ OCHF ₂		1840	572	
	5940			
HFE-236ca12	CHF ₂ OCF ₂ OCHF ₂	7560	2780	864
HFE-338pcc13				
CHF ₂ OCF ₂ CF ₂ OCHF ₂		1480	459	
	4770			
<i>Gases whose lifetimes are determined by indirect means</i>				
Nitrogen trifluoride	NF ₃	7780	10,970	13,240
Perfluorocyclopropane	c-C ₃ F ₆	> 11,950	> 17,070	> 21,920
HFE-227ea	CF ₃ CHFOCF ₃	4270	1520	471

with three changes in instrumentation: the ALE, which used Hewlett Packard HP5840 gas chromatographs; the GAGE, which used HP5880 gas chromatographs; and the present Advanced GAGE (AGAGE). AGAGE uses two types of instruments: a gas chromatograph with multiple detectors (GC–MD), and a gas chromatograph with mass spectrometric analysis (GC–MS). The current station

locations are Cape Grim, Tasmania (41°S, 145°E); Cape Matatula, American Samoa (14°S, 171°E); Ragged Point, Barbados (13°N, 59°W); Mace Head, Ireland (53°N, 10°W); and Trinidad Head, California (41°N, 124°W). Stations also previously existed at Cape Meares, Oregon (45°N, 124°W); and Adrigole, Ireland (52°N, 10°W). The current Mace Head station replaced the Adrigole station and the station at Trinidad Head replaced the Cape Meares station.

NOAA measurements of climatically important gases began on an expanded scale in the mid-1970s [20] for carbon dioxide (CO₂), nitrous oxide (N₂O), chlorofluorocarbons (CFCs), and ozone (O₃). Over the years, a number of other gases have been added, including methane (CH₄), carbon monoxide (CO), hydrogen (H₂), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), methyl halides, and sulfur hexafluoride (SF₆). Numerous types of platforms are used, including ground-based stations, towers, ocean vessels, aircraft, and balloons. Electropolished, stainless-steel flasks are collected weekly in pairs, and analyzed for N₂O, CFC-11, and -12 on an electron-capture gas chromatograph (GC-ECD). Flask samples for HCFCs, HFCs, and other atmospheric halogens are analyzed by gas chromatography with detection by mass spectrometry (GC-MS). Flasks are filled at nine sites, five of which are considered remote locations (Fig. 13): Barrow, Alaska (71.32°N, 156.60°W); Trinidad Head, California (41.05°N, 124.15°W); Mauna Loa, Hawaii (19.53°N, 155.57°W); Samoa (14.23°S, 170.56°W); South Pole (89.99°S, 102.00°W). Measurements of nitrous oxide (N₂O), the chlorofluorocarbons: CFC-12 (CCl₂F₂), CFC-11 (CCl₃F), and CFC-113 (CCl₂F-CClF₂) and the chlorinated solvents: methyl chloroform (CH₃CCl₃) and carbon tetrachloride (CCl₄) are being made once an hour by using gas chromatographs. These instruments also have the capability of measuring sulfur hexafluoride (SF₆), Halon-1211 (CBrClF₂), HCFC-22 (CHClF₂), HCFC-142b (CClF₂-CH₃), carbonyl sulfide (OCS), methyl chloride (CH₃Cl), and methyl bromide (CH₃Br).

In parallel to these two ground-based measurement networks, we must mention some activities within the international Network for the Detection of Stratospheric Change (NDSC), now changed into the Network for the Detection of Atmospheric Composition Change (NDACC). Indeed, combining different sorts of ground-based remote-sensing instruments (essentially within the IR domain using Fourier Transform IR spectrometers), some integrated columns of halogen compounds can be identified over long-term periods. For instance, at the Jungfraujoch (46.5°N) and the Mauna Loa (19.53°N) stations, more than a decade of CFCs measurements are available.

Balloon- and air-borne measurements of halogen compounds are also performed during dedicated campaigns: in situ instruments HALOZ, ASTRID, DESCARTES, DIRAC, BONBON, ACATS, SPIRALE, MANTRA, SAKURA, etc., and the remote sensing spectrometers LPMA, MIPAS-B, FIRS-2, MkIV, etc. Another vector for studying the temporal evolution of halogen compounds comes from



Fig. 13. Two NOAA sites where measurements of CFCs are performed: (above) Barrow, Alaska, USA and (below) Mauna Loa Observatory, Hawaii, USA.

Table 3. Lists of long-lived halogen compounds measured by space-borne instruments

Platform	Instrument	Compounds
UARS	CLAES	CFC-12, CFC-11
UARS	HALOE	HCl, HF
Space station	CRISTA	CFC-11
Space station	ATMOS	HF, HCl, CH ₃ Cl, CF ₄ , CCl ₂ F ₂ , CCl ₃ F, CCl ₄ , COF ₂ , CHF ₂ Cl, SF ₆
ENVISAT	MIPAS	CFC-11, CFC-12
AURA	MLS	HCl
AURA	HIRDLS	CFC-11, CFC-12
SciSat	ACE	HF, HCl, CCl ₃ F ₂ , CCl ₃ F, COF ₂ , CHF ₂ Cl, SF ₆ , CF ₄ , CH ₃ Cl
ADEOS	ILAS	CFC-11, CFC-12
ADEOS II	ILAS-II	CFC-11, CFC-12

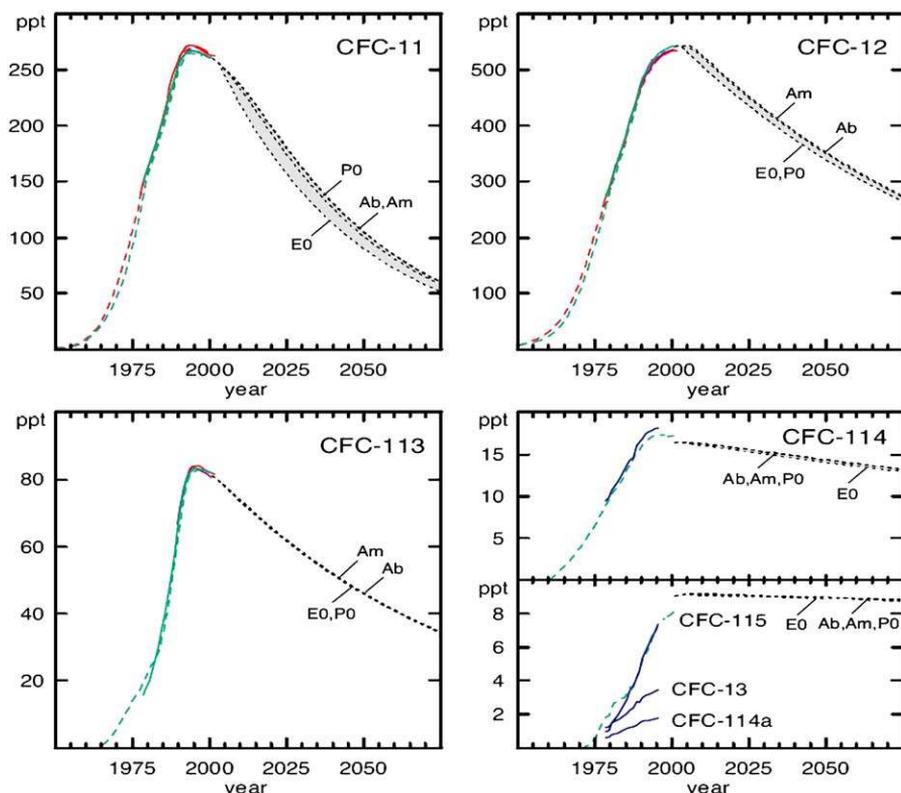


Fig. 14. Past and potential future atmospheric mixing ratios of CFCs using different scenarios. Ab, best guess; E0, zero emissions; Am, maximum allowed production; and P0, zero production. Taken from WMO [12].

space. Table 3 lists different instruments aboard space platforms dedicated to the measurements of halogen compounds, which among them are CLAES [21], HALOE [22], CRISTA [23], MIPAS [24], MLS [25], HIRDLS [26], and ILAS [27].

6. TRENDS AND SCENARIOS

The timetable for the reduction in halogen source gas production and consumption, as outlined by the Copenhagen Amendment, calls for the complete phasing out of the production and consumption of CFCs 11, 12, 113, 114, and 115 by the year 1996; the phasing out of halogen production and consumption by 1994; and the phasing -out of most HCFCs by the year 2040. Projections made following the Copenhagen Amendment indicated that the peak chlorine burden would occur in late 1990s, at a value of about 4 ppbv. The total chlorine burden should decrease,

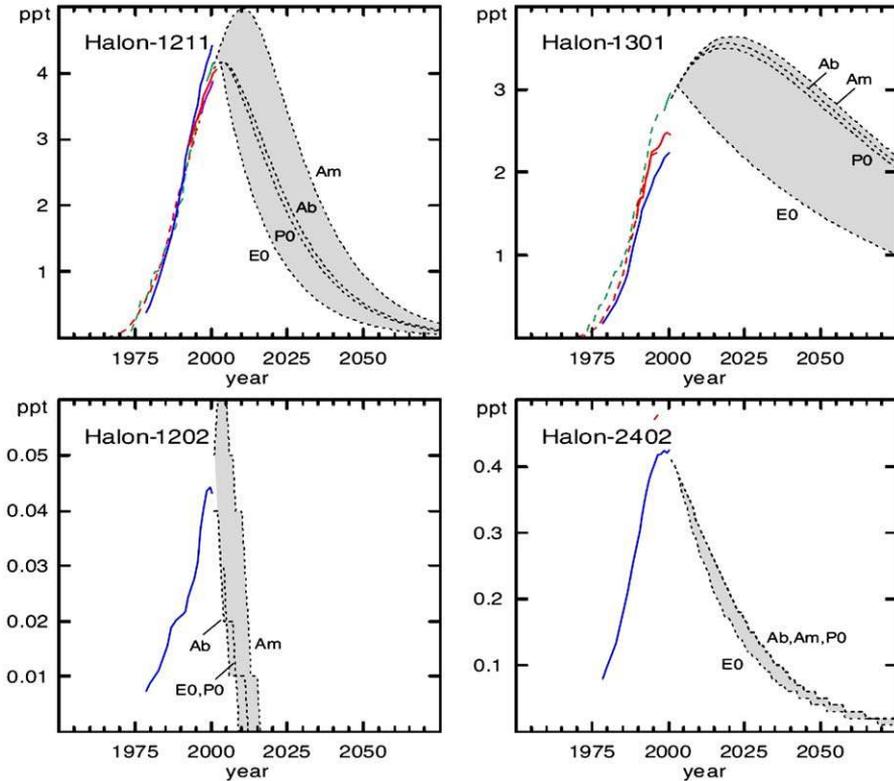


Fig. 15. Same as in Fig. 14 but for halons. Taken from WMO [12].

reaching 3 ppbv in about 2040 and 2 ppbv in about 2060. Recent measurements have indeed shown that the mean global tropospheric chlorine abundance reached a maximum in 1994 and is now decreasing at a rate of about 25 pptv per year. Trends in stratospheric chlorine loading will mirror those observed in the troposphere, after accounting for the 4–6 years time lag associated with transport of air to the stratosphere. It is important to note that the onset of the appearance of the Antarctic ozone hole coincided with chlorine levels of approximately 2 ppbv. Hence, even with current regulations on future emissions of chlorine source gases, ozone depletion in the Antarctic vortex can be anticipated to continue for at least 50 years.

Different scenarios for future ozone depleting substance (ODS) emissions are studied [18]. The Ab scenario represents the best-guess scenario following the Beijing Amendments since the future production of CFCs is supposed to be continued at the current level of capacity for “essential use” for developed countries and is allowed to continue at the current (frozen) level for developing countries. The Am scenario corresponds to the maximum production scenario in which

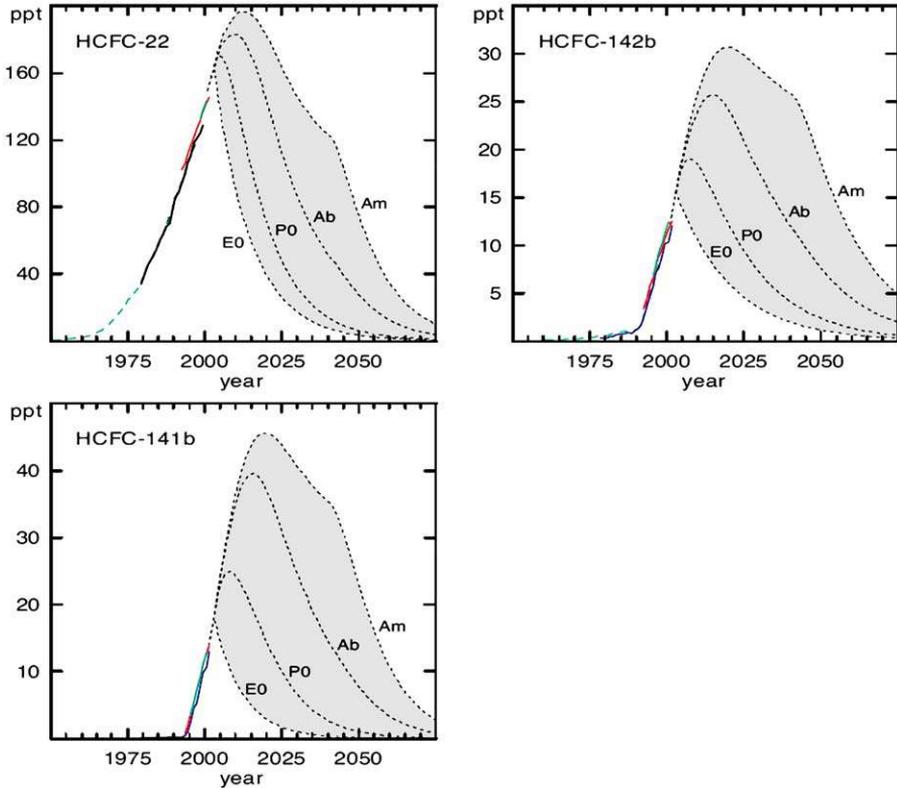


Fig. 16. Same as in Fig. 14 but for HCFCs. Taken from WMO [12].

production of CFCs, halons, and HCFCs is projected forward at the maximum allowed under the protocol. The E0 scenario corresponds to a hypothetical zero-emission scenario. Indeed, anthropogenic emissions of all ODSs (CFCs, CCl_4 , CH_3CCl_3 , halons, HCFCs, and CH_3Br) are set to zero from 2003 onward. Finally, in the P0 scenario, production of all ODSs is set to zero from 2003 onward. Figs. 14–18 and the potential future atmospheric mixing ratios using different scenarios for CFCs, halons, HCFCs, HFCs, fluorocarbons, and sulfur hexafluoride.

The updated, best-estimate scenario for future halocarbon mixing ratios suggests that the atmospheric burden of halogens will return to the 1980, pre-Antarctic-ozon-hole levels around the middle of the century, provided continued adherence is undertaken to the fully amended and adjusted Montreal Protocol. Only small improvements would arise from reduced production allowances in the future. Lack of compliance to the protocol controls would delay or prevent recovery of stratospheric ozone.

About 80% of the equivalent chlorine in today's atmosphere arises from direct anthropogenic release of ODS. Climate change could influence future

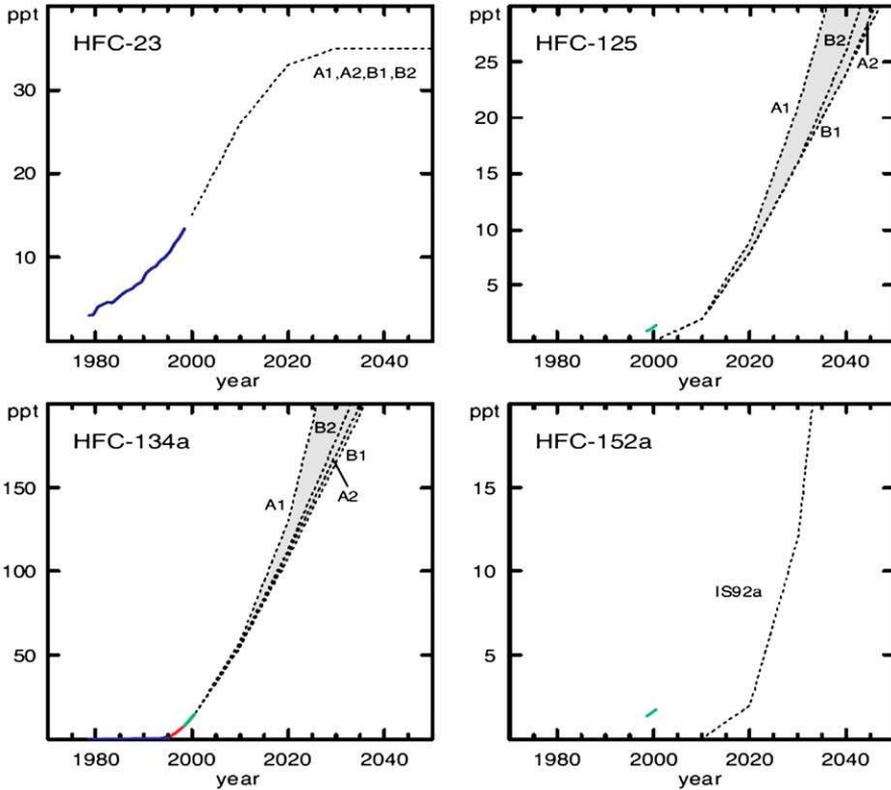


Fig. 17. Long-term trends and possible future levels of HFCs depending upon several scenarios from IPCC (2001). Taken from WMO [12].

atmospheric amounts of these gases by affecting the rates at which gases are removed from the atmosphere. For CFCs, halons, and CCl_4 , rates of atmospheric removal are governed by the flux of high-energy light in the stratosphere and the rate at which air is mixed through the stratosphere. If changes in climate were to affect rates of air transport through the stratosphere, trace gas lifetimes would be altered. The lack of predictive understanding of such changes does not allow reliable estimate of whether lifetimes would become longer or shorter in the future in an atmosphere with elevated greenhouse gas abundances. For methylchloroform, HCHCs, methyl halides, and other chemically reduced gases, climate change could influence loss rate through changes in mean global concentrations of hydroxyl radical. This oxidant plays a key role in determining the lifetime of these important ozone-depleting substances. Amounts of this short-lived, but powerful atmospheric oxidant depend directly on humidity, sunlight, temperature, and the abundance of many different trace gases likely to be affected by climate and human behavior in the future.

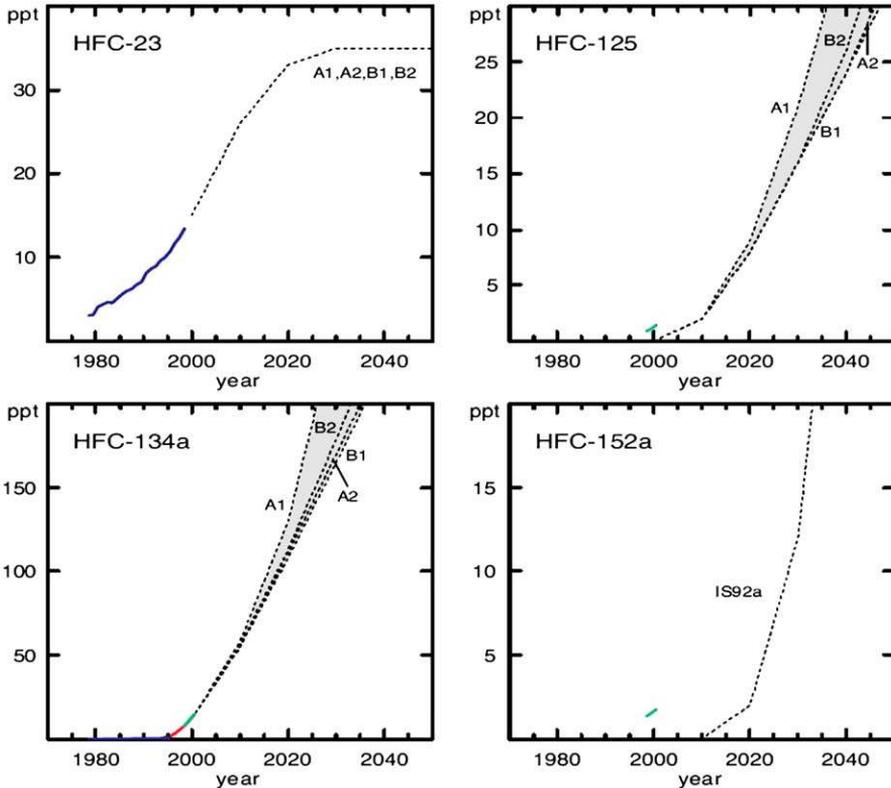


Fig. 18. Same as in Fig. 17, but for fluorocarbons and sulfur hexafluoride. Taken from WMO [12].

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