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CFC and Halon replacements in the environment

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Abstract

Substitute fluorocarbons may have direct environmental impact, for example as greenhouse gases, or indirect impacts through the products of their decomposition in the environment. The mechanisms of that atmospheric decomposition are reviewed here and shown to be well established now. The end products are halogen acids and trifluoroacetic acid, all of which pre-exist in the environment in quantities greater than are expected to arise from fluorocarbon use and emissions. Furthermore, the growth in use of fluorocarbon replacements has been shown to be far less than the fall in CFC and Halon production. Hydrochlorofluorocarbons (HCFCs) have replaced less than one third of CFCs and are, themselves, ozone depleting substances that will be phased out under the Montreal Protocol. The growth in hydrofluorocarbons (HFCs) amounts to about 10% of the fall in CFCs. It is likely that the impact of new fluorocarbons on climate change will be a very small fraction of the total impact, which comes mainly from the accumulation of carbon dioxide in the atmosphere. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Chlorofluorocarbons (CFCs) were among the first commodity chemicals to have been designed, from the outset, to possess physical properties matching particular end uses. Prior to the 1930s, refrigerants in common use were ammonia, chloromethane, carbon tetrachloride, isobutane and propane [1]. As a consequence of concerns about the toxicity and flammability of these compounds, particularly in the home environment, Midgley and his colleagues at General Motors mounted a deliberate campaign to identify suitable replacement materials. The requirements for volatility, stability, low toxicity and non-flammability led the research to concentrate on compounds based on the early members of Groups IV–VII of the periodic table (H, C, N, O, F, S, Cl and Br) [2]. From this work CFCs emerged as clear favourites to meet all the criteria and remained the refrigerants of choice from the 1930s until the 1990s. As an unfortunate side effect, CFCs met the safety criteria so well that a culture grew up that tolerated leaks and disposal to the atmosphere.

Production and emissions of CFCs 11 and 12 (trichlorofluoromethane, CCl_3F , and dichlorodifluoromethane,

CCl_2F_2), the original compounds in the group, remained comparatively low through to the 1950s, then increased rapidly with the spread of refrigeration in the developed world and as new uses, such as in aerosol spray cans, became commonplace. The growth in CFC emissions is shown in Fig. 1a. By the early 1970s, CFCs 11 and 12 had become ubiquitous trace constituents of the troposphere [3].

At the same time as releases of CFCs 11 and 12 were growing [4,5], so did production, use and consequent release of other volatile fluorocarbons. Thus CFC-113 (1,1,2-trichlorotrifluoroethane, $\text{CCl}_2\text{FCClF}_2$), CFC-114 (1,2-dichlorotetrafluoroethane, $\text{CClF}_2\text{CClF}_2$), CFC-115 (chloropentafluoroethane, CF_3CClF_2) [6], Halon-1211 (bromochlorodifluoromethane, CBrClF_2), Halon-1301 (bromotrifluoromethane, CBrF_3) [7], carbon tetrachloride (CCl_4) and methyl chloroform (1,1,1-trichloroethane, CCl_3CH_3) [8,9] all showed vigorous growth in the period up to the late 1980s.

Based on Lovelock's work, which showed that a substantial portion of the CFCs produced up to 1972 had accumulated in the atmosphere [10], Molina and Rowland propounded their hypothesis of stratospheric ozone depletion by these chemicals [11]. Their original reaction scheme is incorporated into Fig. 2 which also shows additional reaction sequences identified more recently. It is now known that bromine, which in the stratosphere is present as bromine

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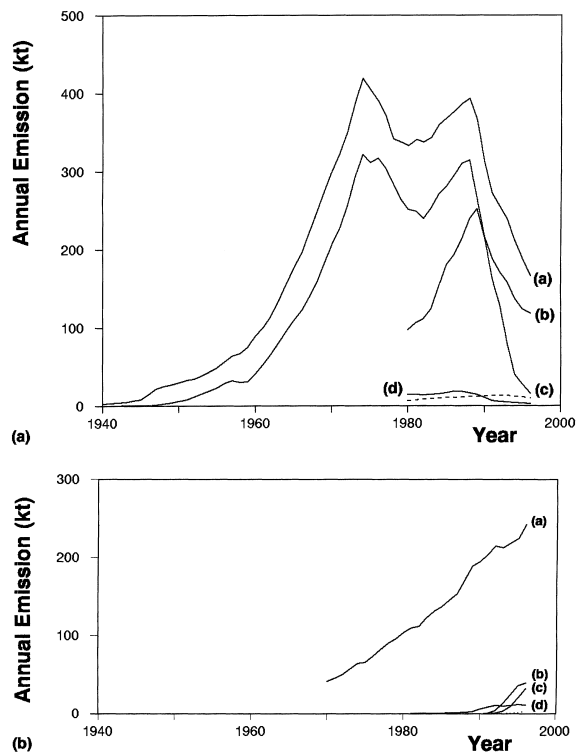


Fig. 1. Annual emissions of fluorocarbons. (1a) Chlorofluorocarbons: (a) CFC-12, (b) CFC-11, (c) CFC-113, (d) solid line CFC-114, dashed line CFC-115. (1b) Fluorocarbon alternatives: (a) HCFC-22, (b) HCFC-141b, (c) HFC-134a, (d) solid line HCFC-142b, dashed line HCFC-124.

oxide radical ($\text{BrO}\cdot$), can combine with $\text{ClO}\cdot$ to release halogen radicals that enhance ozone depletion significantly [12]. The fluorine released from CFC decomposition forms hydrogen fluoride but, by virtue of its bond strength, this is inert in the stratosphere and acts as a permanent sink so that fluorine does not deplete ozone [13].

For some years after the basic hypothesis was published no ozone depletion was observed and the first real evidence came from Farman and his colleagues at the British Antarctic Survey who, in 1985, linked severe seasonal ozone

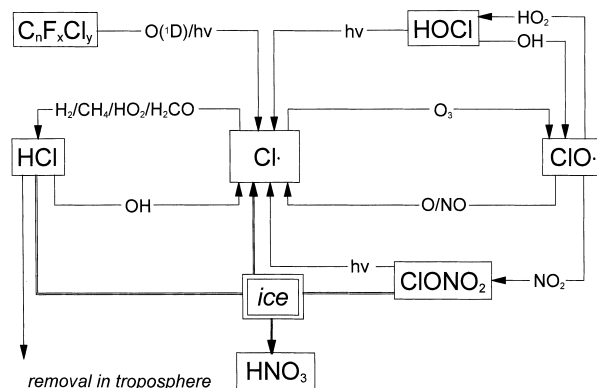


Fig. 2. Schematic of odd chlorine chemistry in the stratosphere. The double lines indicate additional reactions that occur on ice or sulphuric acid surfaces to regenerate active chlorine from relatively inert sinks.

depletion in the Antarctic to the growth in chlorine from CFCs in the stratosphere [14]. Fig. 2 also shows the mechanism for polar ozone depletion due to the influence of chemically reactive surfaces in the stratosphere, such as polar stratospheric clouds (PSCs). These clouds of water ice and nitric acid hydrates profoundly influence stratospheric chlorine concentration by reforming it from stable 'sinks' such as HCl and chlorine nitrate (ClONO_2) [15]. Farman's results and the work that followed (reported in the World Meteorological Organization's Assessments of 1985 and 1988 [16,17]) were instrumental in promoting agreement that specific measures were needed, and the Montreal Protocol on Substances that Deplete the Ozone Layer was signed by 24 countries in September 1987. Subsequently, it has been modified in scope as a result of additional scientific assessments [18–21] and ratified by 165 countries.

The Protocol now covers all CFCs and most Halons (1211, 1301 and 2402, 1,2-dibromotetrafluoroethane), together with carbon tetrachloride and methyl chloroform. Consumption of these compounds is prohibited in the developed world, although their use in existing equipment, and limited manufacture for essential uses and for use by the developing world, is still permitted. The protocol has also been extended to some of the alternative materials — hydrochlorofluorocarbons (HCFCs), which are also ozone depleting substances [22]. Production of HCFCs is frozen in the developed world, with progressive phase-out scheduled for the first decades of next century.

2. Substitution of CFCs and Halons

2.1. Technical requirements

Table 1 lists the CFCs and potential fluorocarbon alternatives, together with one of their most important physical properties: volatility, characterised here by the boiling point at atmospheric pressure. In addition to having volatility appropriate to the application, there are a number of thermochemical properties that should be optimised. For example, a good gas for blowing plastic insulating foam would also have low thermal conductivity, generally associated with relatively high molecular weight. Refrigerant gases and solvents should be miscible with oils but should not be such good solvents that they dissolve parts of the equipment. Common to all applications, the material should be non-toxic, non-flammable and have an acceptably short environmental lifetime so that it does not cause problems by accumulating in a particular environmental compartment. There is some interaction between the latter set of requirements and optimal thermochemical properties and the choice of material tends to be a compromise.

In the light of what is now known about environmental effects, the pool of source elements identified by Midgley in 1937 has shrunk [2]. Bromine is ruled out on environ-

mental grounds because of the high ozone depletion potential that it can confer; chlorine is less problematic in this respect but can give rise to high ozone depletion, if the compound has sufficient atmospheric lifetime; sulphur compounds are generally likely to be too toxic, leaving elements C, H, O, N and F. Significantly, this still includes ammonia (NH₃), a well-used refrigerant (where safety can be maintained), and water vapour. However, in the 1980s when alternatives to CFCs were first sought, the group of compounds that appeared to offer the best compromise were the compounds formed from C, H, F and Cl: hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). Subsequently, hydrofluoroethers (HFEs e.g. CHF₂OCHF₂ and CH₃OCF₂CHF₂) have attracted some attention as refrigerants but are still at an early stage of evaluation [23,24].

2.2. Extent of substitution

Due to their wide range of physical properties, the scope for substitution even between CFCs is limited. Viable alternative compounds must match the properties needed to provide the specific effect desired. This is not a requirement for alternative technologies that, in general, will require completely new systems. Given that users will likely use the phase-out of CFCs as an opportunity for radical change, it is expected that significantly more than half of the demand will be taken up by chemicals other than fluorocarbons or by other technologies. This was predicted by market research in the early 1990s, which suggested 25% substitution by HCFCs and 15% by HFCs [33]. These values were subsequently confirmed to a remarkable degree in 1998 by analyses of global values derived from the annual survey of sales carried out by the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), which showed HCFCs and HFCs to have satisfied, respectively, 33% and 11% of world-wide demand [34]. In the European Union in recent years substitution of CFCs by HCFCs was 26% and the HFC share was only 6% [35]. In both cases the values are representative of the real demand for new fluorocarbons; replacements are needed there and then when CFCs cease to be available, and so substitution must be contemporary with phase-out of CFCs. Because most uses are now in capital equipment it is unlikely that operators will make second changes to their systems, so any rise in the extent of substitution should be modest.

2.3. Nature of the fluorocarbon substitutes

The fluorocarbon alternatives to CFCs currently in global use are HCFC-22 (CHF₂Cl, chlorodifluoromethane), HCFC-141b (CH₃CFCl₂, 1,1-dichloro-1-fluoroethane), HCFC-142b (CH₃CF₂Cl, 1-chloro-1,1-difluoroethane) and HFC-134a (CF₃CH₂F, 1,1,1,2-tetrafluoroethane), with minor amounts of HCFC-123 (CF₃CHCl₂, 1,1-dichloro-2,2,2-trifluoroethane), HFC-32 (CH₂F₂, difluoromethane),

HFC-125 (CF₃CHF₂, pentafluoroethane) and HFC-143a (CH₃CF₃, 1,1,1-trifluoroethane) [36–38]. Substitutes for the principal uses of CFCs and Halons are summarised in Table 1, which includes some compounds that have not yet been adopted broadly by society. While there are many technologies and, indeed, fluorocarbons which have been claimed to provide the effects shown, only those which are technically viable now, and hence may be expected to be commercially available in the near future, are considered. In the longer term it is expected that the needs identified in Table 1 will be met by a variety of techniques and technologies. Fluorocarbon-based technologies are expected to play an important, but not necessarily predominant, role.

It is clear that there is no single replacement for each CFC and that other materials and technologies play a variety of roles in substitution, which acts against wholesale adoption of fluorocarbons (HCFCs, HFCs and PFCs) as tonne-for-tonne replacements.

In the past, considerable quantities of CFCs were used as propellants in aerosol sprays but the bulk of this demand is now met by hydrocarbons and other technologies. However, because of possible adverse clinical effects, hydrocarbons are not used in metered dose inhalers (MDIs) and the current propellants (CFCs 11 and 12) are being superseded by HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane, CF₃CHFCF₃) and HFC-134a.

After aerosols, refrigeration was the next most important use for CFCs and is the most important for their replacements. In the longer term, towards the middle of next century, it is probable that refrigeration will be provided by a wider range of technologies than at present. However, unless there is a breakthrough in some of the emerging technologies, the vapour compression cycle is likely to remain dominant and, depending on location and the degree to which the fluids are contained, will operate using HFCs, ammonia, carbon dioxide or hydrocarbon refrigerants [39]. For domestic refrigerators, which are sealed units containing only a few hundred grams of refrigerant, the preferred replacements for CFC-12 are HFC-134a and hydrocarbons. In mobile air-conditioning, HFC-134a is used almost exclusively [31].

CFC-113 was used extensively to clean electronic components during the assembly process. The relatively small parts of this market that required high precision have adopted HCFC-141b, although there are some water-based systems, and considerable success has been attributed to changes in engineering that entirely remove the need to clean components [40].

Almost one third of CFC-11 production was used to blow plastic insulating foam; the current replacements are HCFC-141b in polyurethane and HCFC-142b in expanded polystyrene [31]. In the longer term, the diminished market where there remains a real need for efficient blown-foam insulation is likely to be met partly by HFC-134a and partly by other HFCs; judging on volatility alone, HFC-245ca (1,1,2,2,3-pentafluoropropane, CHF₂CF₂CH₂F) would seem suitable [31,32].

Table 1
Properties and uses of ozone depleting substances and fluorocarbon replacements

Compound	Chemical formula	Boiling point at 1 atm (°C) ^a	Principal use	Atmospheric life time years	ODP relative to CFC-11 ^b	GWP relative to CO ₂ at 100 years ^{c,d}	Principal current substitute
<i>Compounds already phased out under the Montreal Protocol in developed countries</i>							
CFC-11	CCl ₃ F	23.8	Foam blowing agent	50	1	4000	HCFC-141b
CFC-12	CCl ₂ F ₂	-29.8	Refrigerant	102	1	8500	HFC-134a
CFC-113	CCl ₂ FCClF ₂	47.6	Solvent	85	0.8	5000	Other technology
CFC-114	CClF ₂ CClF ₂	3.6	Propellant	300	1	9300	Hydrocarbon
CFC-115	CClF ₂ CF ₃	-38.7	Refrigerant	1700	0.6	9300	HFC-134a
Halon-1211	CBrClF ₂	-4	Fire extinguishant	20	3	No data	Dry powder
Halon-1301	CBrF ₃	-57.8	Fire extinguishant	65	10	5600	HFC-227ea
Carbon tetrachloride	CCl ₄	76.8	Raw material	42	1.1	1400	-
Methyl chloroform	CH ₃ CCl ₃	74.1	Solvent	5.4	0.1	110	Other technology
<i>Compounds scheduled for future phase out under the Montreal Protocol</i>							
HCFC-22	CHClF ₂	-40.8	Refrigerant	13.3	0.055	1700	HFC blends
HCFC-123	CHCl ₂ CF ₃	27.1	Refrigerant	1.4	0.022	93	HFC blends
HCFC-124	CHClFCF ₃	-12	Refrigerant	5.9	0.022	480	HFC 134a
HCFC-141b	CH ₃ CCl ₂ F	32	Foam blowing agent	9.4	0.11	630	-
HCFC-142b	CH ₃ CClF ₂	-9.2	Foam blowing agent	19.5	0.065	2000	-
HCFC-225ca ^g	CHCl ₂ CF ₂ CF ₃	51.1	Solvent	2.5	0.025	170	Other technology
HCFC-225cb ^g	CHFClCF ₂ CF ₂ Cl	56.1	Solvent	6.6	0.033	530	Other technology
<i>Potential alternatives; emissions controlled under the Kyoto Protocol</i>							
HFC-23	CHF ₃	-82.1	By-product	264	0	11,700	-
HFC-32	CH ₂ F ₂	-51.7	Refrigerant	5.6	0	650	
HFC-125	CHF ₂ CF ₃	-48.5	Refrigerant	32.6	0	2800	
HFC-134a	CH ₂ FCF ₃	-26.5	Refrigerant	14.6	0	1300	
HFC-143a	CH ₃ CF ₃	-47.6	Refrigerant	48.3	0	3800	
HFC-152a	CH ₃ CHF ₂	-24.7	Propellant	1.5	0	140	
HFC-227ea ^f	CF ₃ CHFCF ₃	-16.5	Propellant	36.5	0	2900	
HFC-236fa ^e	CF ₃ CH ₂ CF ₃	-0.7	Foam blowing agent	209	0	6300	
HFC-245ca ^h	CHF ₂ CF ₂ CFH ₂	25.4	Foam blowing agent	6.6	0	560	
HFC-43-10mee	CF ₃ CHFCHFCF ₂ CF ₃	45	Solvent	17.1	0	1300	
PFC-218 ^e	CF ₃ CF ₂ CF ₃	-36	Refrigerant	2600	0	7000	

^a From [25], unless otherwise stated.

^b From [26].

^c From [27].

^d From [28].

^e Boiling point from [29].

^f Boiling point from [30].

^g Boiling point from [31].

^h Boiling point from [32].

The quantities of Halons in existing equipment are much larger multiples of the annual demand than is the case for CFCs, consequently the principal source of Halons for new installations and servicing is equipment at the end of its service life [7]. It is estimated that the Halon bank is being depleted at the rate of 11% per year, in the case of Halon-1211, and 4% per year for Halon-1301 so that there is sufficient to last well into the next century [41]. It is expected that neither HFC-227ea nor HFC-23 will reach the same level of deployment as Halons 1211 and 1301, partly due to the abundance of recycled material and partly due to their lower effectiveness in extinguishing fires.

The recent history of emissions of replacement fluorocarbons is shown in Fig. 1b and, in comparison with the CFC case shown in Fig. 1a, it is clear that contemporary sub-

stitution is small but growing rapidly. Judgements about the environmental impacts of these compounds in the long term therefore requires a view on their future production and emissions. Table 2 shows a potential scenario for emissions of HCFCs, HFCs and perfluorocarbons (PFCs) over the coming century [42,43]. For HCFCs, this follows the phase-down schedule imposed by the Montreal Protocol [44]. For the substitute compounds, this was constructed by analysing the records of CFC production and sales maintained by industry and developing a mathematical trend expression for each end use that could be fitted to the new substitutes and extrapolated for 100 years [45,46]. In some cases the potential replacement compounds have not yet been commercialised, so the demand might be met by the materials identified in Table 2 or by chemicals with similar

Table 2
Emission scenario for Halocarbons (in kt)

Year	HCFC-22 (refrigeration)	HCFC-141b (foam blowing)	HCFC-142b (foam blowing)	HFC-134a (in cluding HFC-32) (refrigeration & foam blowing)	HFC-245ca ^a (foam blowing)	HFC-125 ^a (refrigeration)	HFC-143a ^a (refrigeration)	PFC-218 ^a (refrigeration)	HFC-227ea ^a (MDIs ^b & fire extinguishers)	HFC-23 (HCFC-22 byproduct)	PFC-14 (CF ₄) (aluminium byproduct)
2000	274	78	39	94	0	5	5	1	20	10	15
2010	158	70	21	208	69	16	16	6	20	7	18
2020	99	47	13	429	145	33	33	13	20	2	20
2030	31	18	4	570	193	44	44	18	20	1	23
2040	2	7	1	625	212	48	48	19	20	1	27
2050	6	1	0	654	222	50	50	20	20	1	31
2060	0	0	0	657	222	51	51	20	20	1	31
2070	0	0	0	663	224	51	51	20	20	1	31
2080	0	0	0	671	227	52	52	21	20	1	31
2090	0	0	0	678	230	52	52	21	20	1	31
2100	0	0	0	686	232	53	53	21	20	1	31

^a Indicates that the material is a model compound; the actual material used may be different.

^b Metered dose inhalers.

properties. The actual nature of the compounds is, however, of secondary importance; at a molecular level their environmental properties are quite similar and it is the extent to which the compounds can accumulate in the environment that differentiates environmental impacts.

3. Environmental considerations

The properties of the compounds that are technically important, particularly volatility and hydrophobicity, mean that the atmosphere is the likely compartment for accumulation of emissions [47]. Broadly categorised, the substitute fluorocarbons are either compounds that can accumulate significantly and for which the properties of the chemicals themselves are important or compounds that are sufficiently reactive that substantial atmospheric concentrations build up only with large emission rates. For the latter, not only are molecular properties important but so is the mode of decomposition in the environment and reaction products.

3.1. Accumulation in the atmosphere: effects on climate change

Fluorocarbons are particularly good absorbers of infrared radiation, particularly in the 1000–1400 cm^{-1} spectral range, where the atmosphere is relatively transparent [48]; thus any fluorocarbon accumulation in the atmosphere will increase opacity in a critical region of the spectrum and will tend to augment radiative forcing of climate. In short, CFCs, HCFCs, HFCs and PFCs are ‘greenhouse gases’.

Fig. 3 shows the radiative forcing impact of these fluorocarbons over the next 100 years in relation to the predicted forcing from all greenhouse gases. The scenario used is newly developed for the intergovernmental panel on climate change (IPCC) and predicts a future in which there is comparatively little change to mankind’s habits. (This is in contrast to the storylines for other scenarios that would require very high growth rates to be sustained in the less developed regions of the world or rapid adoption of a high level of environmental and social consciousness [49].) Under the scenario for Fig. 3, emissions of fluorocarbons are approximately 22 times those shown in Table 2 (which were calculated from historic trends). The IPCC scenario is used here because it contains predictions for all greenhouse gases. Contributions to radiative forcing are calculated using the model described by Wigley’s group [50].

Carbon dioxide dominates radiative forcing now and in the future by virtue of very large emission rates, compounded by a long environmental lifetime which means that 40% of its emissions partition into the atmosphere, almost permanently. Fluorocarbons are emitted in much smaller quantities so, despite their high intrinsic efficiencies, their total effect on radiative forcing is comparatively small. Nevertheless in some countries fluorocarbons may

become an important part of the national emission inventory.

The relative potency of each substance for climate change effects is parameterised in the global warming potentials (GWPs) shown in Table 1. The numbers indicate the calculated effects on radiative forcing arising from a small emission of each compound relative to the same amount of carbon dioxide; owing to the very long lifetime of CO_2 , the calculations are truncated at 100 years. Atmospheric ozone is a powerful greenhouse gas, with a particularly strong influence in the lower stratosphere, so that ozone depletion by CFCs and HCFCs might be considered to reduce their GWPs [51]. However, while reductions offsetting GWP values because of ozone depletion are recognised as probably being real, they are not normally included [28].

In view of the relatively narrow range of molecular forcing constants — the lowest is ten times less than the highest [28] — the principal influence on GWPs is the extent to which each compound is retained in the atmosphere, dependent upon its atmospheric lifetime (also shown in Table 1). Atmospheric lifetimes vary several thousand-fold, from 1,1-difluoroethane (HFC-152a) at 1.5 years, to tetrafluoromethane (PFC-14) at 50,000 years. Perfluorocarbons are particularly stable in the atmosphere: they are not oxidised in the troposphere, nor are they photolysed in the stratosphere and the principal, but relatively ineffective, removal mechanism has been identified to be their pyrolysis in the air flowing through combustion processes [52].

The most abundant PFC in the current atmosphere is tetrafluoromethane, with a mixing ratio of 75 ppt (parts per trillion, 1 in 10^{12}). Approximately half of this is natural, released from fluoride minerals on a geological timescale [53,54]. Most of the remainder is a consequence of control problems during the electrolytic primary production of aluminium in Hall–Héroult cells: during the so-called ‘anode events’, the cryolite (Na_3AlF_6) flux is electrolytically reduced instead of the main electrolyte (alumina), causing tetrafluoromethane and, to a much less extent, hexafluoroethane and trifluoromethane to be produced at the carbon anodes [55]. Despite the efforts of the aluminium industry to improve cell design and control, which have resulted in a marked improvement in the last 50 years, such emissions are likely to continue and tetrafluoromethane may remain the predominant atmospheric PFC in the 21st century [56].

The atmospheric concentrations of manufactured PFCs are over 1000 times less than those of tetrafluoromethane at present [57]. Currently, PFCs have applications as adjuncts in plastic foam blowing, as specialised solvents and as minor components of refrigerant blends [58]. However, their cost and somewhat specialised utility (for example, they are generally poor solvents for oils and greases) means that they are unlikely to be used as generally as CFCs or even HFCs. A few hundred tonnes per year of various PFCs are used at present in the microelectronics industry in the plasma etching of integrated circuits [59]. The character-

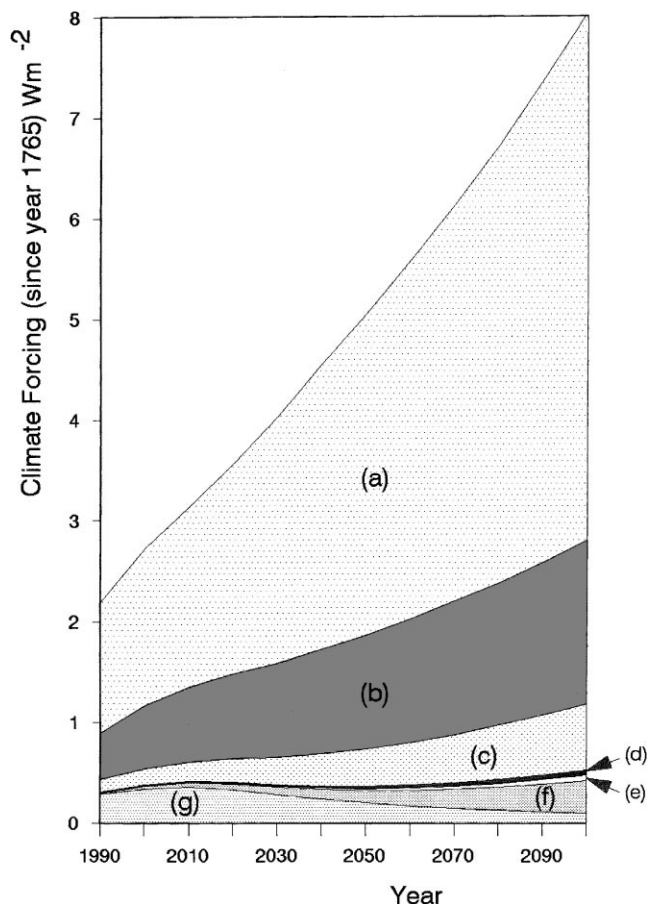


Fig. 3. Radiative forcing from future emissions of greenhouse gases. The scenario follows the 'A2' storyline from the Special report on Emissions Scenarios of IPCC [49]; (a) represents the contribution from carbon dioxide, (b) from methane, (c) from nitrous oxide, (d) from sulphur hexafluoride, (e) from perfluorocarbons, (f) from hydrofluorocarbons and (g) from ozone depleting substances.

istics of the channel etched in the semiconductor substrate critically depend on the PFC used and it is likely that, as this industry progresses towards a smaller scale of individual components, different etchants will be required. Growth in demand for PFCs in this industry is unlikely to be aligned to growth of the industry as a whole.

PFCs are likely to remain materials that are valuable for specialised applications in particular niches of markets that will be dominated by cheaper and more generally useful materials such as HFCs, which are expected to grow in use. Consequently, HFCs may accumulate to significantly large atmospheric concentrations despite having atmospheric lifetimes that are small fractions of those of the PFCs, resulting in the higher contribution to radiative forcing shown in Fig. 3. This contribution results from a predicted emission of 2.4 million tonnes of HFCs each year in the second half of the 21st century under this 'maximum' scenario from IPCC [49]. However, the maximum historic consumption of CFCs was 1 million tonnes per year and, as described in Section 2.2, HFCs have replaced only about a tenth of the CFC demand. The scenario based on analyses of

historic market trends (Table 2), with no expectation of social change, shows demand stabilising at 1 million tonnes per year. Thus scenarios are actually the least certain elements in the calculation and, treated as predictions, may be in error by a large factor. On the other hand, the properties of the substitute fluorocarbons are well known, largely as a consequence of intensive study during the early 1990s. Sound information on the mechanisms and rates of their environmental decomposition enables their behaviour in the atmosphere to be assessed with relative certainty.

3.2. Decomposition in the atmosphere

Currently the atmospheric concentrations of some hydrogenated fluorocarbon substitutes are growing significantly. Chlorodifluoromethane (HCFC-22) has been produced as a refrigerant for several decades and, despite recent slackening in production, its concentration in the atmosphere shows long term, linear growth of 5 ppt per year and the global average concentration is now 150 ppt [60]. HCFCs 141b and 142b are comparative newcomers and, consequently, show very large percentage growth on the current concentrations that each average approximately 10 ppt globally [61]. Absolute growth rates are 2 and 1.5 ppt per year, respectively [62,63]. The current concentration of over 8 ppt of 1,1,1,2-tetrafluoroethane (HFC-134a) has been reached in less than ten years and is continuing to grow at 3.5 ppt per year [62,64]. Unlike the HCFCs which are specifically targeted for phase-out under the Montreal Protocol, the controls on HFCs, uniformly with all other greenhouse gases in the Kyoto Protocol, will allow continued production and emission, so their atmospheric concentrations are likely to continue to rise. Currently the most abundant HFC, trifluoromethane (HFC-23) with an atmospheric concentration over 12 ppt, is mainly the result of overfluorination of chloroform in the process used to manufacture HCFC-22 [65].

It is now well established that substitute fluorocarbons such as these that contain hydrogen are oxidised in the troposphere in reactions analogous to hydrocarbon oxidations [66–68]. The initial oxidation product, formed by hydrogen abstraction, principally by the OH radical, is a haloalkyl radical that reacts rapidly and exclusively with molecular oxygen to yield a peroxy radical. This part of the decomposition process is identical to hydrocarbon oxidation but very much slower. It is the rate determining step, and HFCs and HCFCs have atmospheric lifetimes that are typically tens of years (although HFC-23 is so unreactive that it has a lifetime greater than 250 years). The lack of reactivity means that these compounds are well dispersed in the troposphere and so react at background concentrations of oxidants. Consequently, they are not involved in photochemical smog pollution and subsequent reduction to haloalkoxy radicals is predominantly accomplished by nitric oxide. The general reaction scheme is shown in Fig. 4. Although it is possible to form the various peripheral species (hydroperoxide, nitrate, peroxyxynitrate and nitrite)

shown in this diagram, the concentrations of the fluoro-organic radicals are so low, and the species formed so unstable, that the reactions are not important and their products will not impact on the environment significantly, even if the atmospheric burdens of the parent compounds were to grow manifold [68].

Reactions of the haloalkoxy radicals are interesting from the points of view of both fluorocarbon chemistry and the potential burden of stable reaction products that might be imposed on the environment. There are a number of possible decomposition pathways for haloalkoxy radicals of the type $CX_3CYZO\cdot$ or $CXYZO\cdot$, where X, Y and Z can be Cl, F or H (or any mixture of these) and Z may also be Br. If Z is Cl or Br, the most generally facile reaction is elimination of Z \cdot to yield directly a stable halocarbonyl product $CX_3C(O)Y$ or $C(O)XY$; however, if Z is H it may be abstracted by molecular oxygen, giving a hydroperoxyl radical ($HO_2\cdot$) plus $CX_3C(O)Y$ or $C(O)XY$. Scission of the C–C bond in $CX_3CYZO\cdot$ to yield $CX_3\cdot$ and $C(O)YZ$ may also be important, particularly in competition with the other possible reactions. This chemistry has been extensively examined in the laboratory and reviewed in a number of workshops and assessments, leading to the following conclusions [18–20,66,67,69,70]: $CHF_2O\cdot$ and $CH_2FO\cdot$ radicals react with molecular oxygen to give carbonyl fluorides and $HO_2\cdot$; $CX_2ClO\cdot$ and $CX_2BrO\cdot$ (in which X is any combination of H, F, Cl or Br) eliminate halogen atoms, except for $CH_2ClO\cdot$ and $CH_2BrO\cdot$ where hydrogen abstraction by O_2 dominates; $CX_3CH_2O\cdot$ radicals react mainly with molecular oxygen to give $HO_2\cdot$ and an aldehyde; $CX_3CCl_2O\cdot$ and $CX_3CFClO\cdot$ eliminate $Cl\cdot$, giving acyl halides, $CX_3C(O)Cl$ and $CX_3C(O)F$ respectively, whereas $CX_3CF_2O\cdot$ radicals undergo C–C scission only. Finally, radicals of the form $CX_3CHYO\cdot$ (in which Y is Cl or F) have two important reaction channels: scission of the C–C bond to yield $CX_3\cdot$ and $HC(O)Y$, or reaction with O_2 giving an acyl halide, $CX_3C(O)Y$. It is this reaction that is responsible for the generation of trifluoroacetic acid from CF_3CH_2F , HFC-134a, as discussed in Section 3.4.

Some of the stable carbonyl products may undergo further reaction in the atmosphere, for example the aldehydes resulting from decomposition of HCFCs 141b and 142b may photolyse [71]. However, the principal mechanism by which the stable products shown in Table 3 are removed from the atmosphere is dissolution, either in cloud/rain and surface water or in ground moisture after dry deposition. These processes operate on a timescale of a few weeks, the rate being controlled by atmospheric mixing.

3.3. Environmental burden of halogen acids

The carbonyl halides hydrolyse relatively rapidly in water so that most of the halogen in the parent HCFCs and HFCs in the atmosphere ends up as HCl and HF in the aqueous environment. From the emission scenario shown in Table 2 the maximum additional steady state flux of HCl

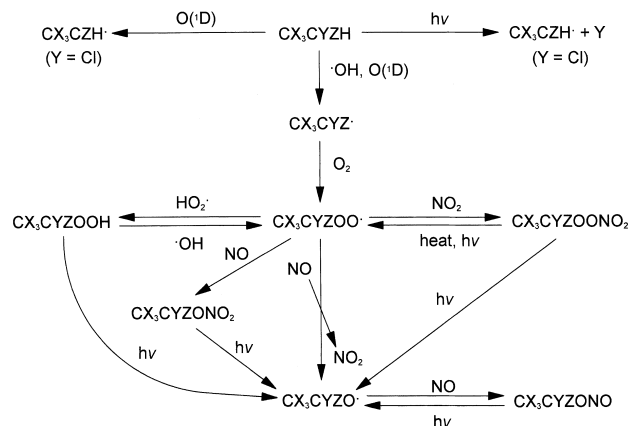
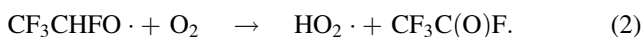


Fig. 4. Generalised reaction scheme for the atmospheric oxidation of hydrohalocarbons to haloalkoxy radicals; X may be any halogen or hydrogen but is principally F; Y and Z may be F, Cl or Br.

would be approximately 0.18 Tg yr^{-1} . This is less than 1% of the current combined natural and man-made HCl flux through the atmosphere and 0.02% of the particulate chloride flux [72]; as such the increment from HCFCs is not likely to have any environmental significance. Similarly, the additional HF flux through the atmosphere from substitute fluorocarbons could reach 0.74 Tg yr^{-1} in the second half of the 21st century. This is comparable to the current total man-made HF flux which arises mainly from burning coal, steel-making, brick-making and aluminium production [73]. Although, at about 20% of the total flux of HF through the atmosphere it is a much larger fraction than for HCl, it has not been considered to represent a significant threat to the environment, given the far wider geographical dispersion than the current flux from industrial activities [18].

3.4. Trifluoroacetic acid

Atmospheric decomposition of *inter alia* HCFCs 123 and 124 and HFCs 134a and 227ea can lead to the production of stable trifluoroacetyl halides that would hydrolyse to trifluoroacetic acid. Most studies have focused on the reactions of HFC-134a, 1,1,1,2-tetrafluoroethane, expected to remain the most widely used of the HFCs. The tetrafluoroethoxy radical formed from HFC-134a can react either by scission of the C–C bond, generating a trifluoromethyl radical and formyl fluoride (Eq. (1)), or lose hydrogen to molecular oxygen to yield trifluoroacetyl fluoride and a hydroperoxy radical:



When the reactions were first studied, tetrafluoroethoxy radicals were generated by self reaction of $CF_3CHFO_2\cdot$ radicals [74] and, after allowing for the temperature lapse in the atmosphere (and a constant partial pressure of oxy-

Table 3
Products of atmospheric oxidation of the principal HCFCs and HFCs

Source compound		Products
HCFC-22	CHF ₂ Cl	HCl, COF ₂
HCFC-123	CF ₃ CHCl ₂	HCl, CF ₃ C(O)Cl
HCFC-124	CF ₃ CHClF	HF, HCl, CF ₃ C(O)F
HCFC-141b	CFCl ₂ CH ₃	CFCI ₂ CHO
HCFC-142b	CF ₂ ClCH ₃	CF ₂ ClCHO
HFC-23	CHF ₃	HF, COF ₂
HFC-32	CH ₂ F ₂	COF ₂
HFC-125	CF ₃ CHF ₂	HF, COF ₂
HFC-134a	CF ₃ CH ₂ F	COF ₂ , HC(O)F, F ₃ C(O)F
HFC-143a	CF ₃ CH ₃	CF ₃ CHO
HFC-152a	CHF ₂ CH ₃	COF ₂
HFC-227ea	CF ₃ CHFCF ₃	HF, COF ₂ , CF ₃ C(O)F
HFC-245ca	CH ₂ FCF ₂ CHF ₂	HF, HC(O)F, COF ₂

gen), the product yields indicated that between 30% and 40% of the tetrafluoroethoxy radical would follow the path in Eq. (2). In the real atmosphere, the formation of this radical would be accomplished by oxidation of NO to NO₂ (see Fig. 4) and, when the laboratory studies were conducted in the presence of NO, reaction (1) predominated [75]. It seems that the radicals generated with NO have sufficient vibrational excitation to open up a prompt decomposition channel [76]. Consequently, some 80–90% of the atmospheric decomposition of HFC-134a is now calculated to follow Eq. (1).

The possibility that trifluoroacetate might impact on the environment led to an intensive study of the occurrence, environmental behaviour and phytotoxicity of trifluoroacetates, resulting in a comprehensive assessment [77]. This concluded that the risk to the environment was negligible from the concentrations of trifluoroacetate that might be expected from future emissions of HFCs under the scenario in Table 2. However, during the course of this study there were some unexpected results.

In an attempt to determine whether or not trifluoroacetate could exert an undue influence on specific environments, such as vernal pools that dry out each summer and hence could concentrate involatiles, model sensitivity studies were carried out. The preliminary study [78] concluded that, at the limits of the environmental variables considered, trifluoroacetate might accumulate over decades in such ecosystems. A more complete analysis [79], however, showed that many of the environmental variables are interdependent so that their limits are mutually exclusive. Ionic species, including trifluoroacetate, do not generally accumulate in these ecosystems; as a general rule they do not become saline.

It is now clear that trifluoroacetate ion is widespread in the aqueous environment. That it is sequestered into water is not, itself, surprising given the Henry's constant [80] but the concentrations ranging from 30 to 40,000 ng l⁻¹ in rivers and lakes from around the world [81–85] indicate a degree of contamination far greater and more widespread than can be accounted to any industrial activities. The concentrations

in coastal sea-water and deep ocean water [77,86] of 75–250 ng l⁻¹ are particularly difficult to account for without long term (several hundred years) natural or anthropogenic sources. At present there is no explanation for the huge environmental burden that the measurements imply.

4. Conclusions

The Montreal Protocol, which came as a direct consequence of the accumulation of CFCs in the atmosphere due to sustained emissions, gives a very different environmental regime from that prevailing when CFCs were first commercialised. Any substitutes for CFCs should therefore be subjected to careful examination to establish that their intrinsic environmental properties are acceptable. The Kyoto Protocol, envisaged as the start of controls on greenhouse gases, goes several stages further in attempting to control emissions of a much wider range of substances and attempts to meet the requirements of this Protocol will bring into focus the interaction between use of substances like CFCs and energy efficiency.

Arguably, the environmental chemistry of the simple fluorocarbon substitutes for CFCs has been studied more intensely than any comparable industrial products. The current environmental impact of the substitute compounds themselves, in terms of their effects on ozone depletion and climate change, are very small fractions of the total impacts in these areas. In the future, while the effect on stratospheric ozone will fall, the increase in climate forcing will rise but, unless there is unprecedented growth in emissions, it should remain a small fraction of the total from all greenhouse gases. The point would seem to have been reached where it is unlikely that new compounds will be found with significantly lower intrinsic environmental impacts but which still meet the technical, cost and safety requirements for widespread societal use. Further reductions in impact are therefore dependent upon lower emissions in the future. In turn these depend on developments in engineering to maintain better containment and also on changes in society's attitude to releasing such chemicals into the environment.

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