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FLUOROCARBONS AND SF_6

Global emission inventory and options for control

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SUMMARY

This study surveys current knowledge on global emissions of several halocarbons and presents scenarios for future emissions (up to 2100). The compounds studied here are not regulated under the Montreal Protocol. These include HFCs, PFCs, FICs and SF_6 and are mainly used as substitutes for CFCs, halons, CH_3CCl_3 and HCFCs, which will be phased out when the Montreal Protocol to protect the ozone layer is implemented.

It has been estimated in this study to what extent HFCs, PFCs, FICs and SF_6 replace the demand for CFCs, halons and CH_3CCl_3 as would have been the case without the Montreal Protocol. The most realistic substitution rates are estimated for aerosols (9-11%), cleaning (<5%), open-foam blowing (1-2%), closed-foam blowing (40-45%), stationary refrigeration (>50%), mobile airconditioning (<75%), fixed fire extinguishing (45-50%) and other (30%). In addition, it is assumed that 75% of the historical HCFC-22 market will be replaced by HFCs after an HCFC phase-out.

Actual emissions differ from the annual use. For a number of applications emissions occur almost immediately. However, when compounds are used as cooling or blowing agents, emissions may be delayed by many years.

Future emissions are presented for six scenarios (Fig. 1). In the **reference scenario** assumes implementation of the Copenhagen amendments to the Montreal Protocol, and no further regulations for HFCs, PFCs, FICs and SF_6. The **closed applications only scenario** assumes use of HFCs, PFCs, FICs and SF_6 to be restricted to stationary cooling and closed-foam blowing, and in the **low-GWP scenario** it is assumed that only compounds are used with a GWP less than 250. These three scenarios are presented for a situation without emission control (no control), and assuming maximum effort to reduce emissions through good housekeeping, recycling and destruction of halocarbon wastes (+ MAX).

In the reference scenario global use of HFCs increases to about 1440 kt y^{-1} in 2040. This is in good agreement with an estimate of the industrial Alliance of Responsible Atmospheric Policy, that estimated the use of HFCs by 2035 to be 1100 - 1400 kt y^{-1}. When CFCs and HCFCs are phased out, the most important halocarbon applications in the reference scenario are stationary cooling (60%), closed foam (19%) and cleaning (8%). The most widely used halocarbon is HFC-134a (40% of global use). Second most important are HFC-125, HFC-143a, and HFC-152a (7 - 9% each).

Maximum emission control by good housekeeping, recycling and destruction of halocarbon wastes (scenario reference + MAX) reduces emissions by 40 - 45% relative to the reference scenario. Part, but not all, of the assumed emission control may be realized without additional regulations.

When expressed in CO_2-equivalents, emissions of HFCs, PFCs, FICs and SF_6 amount to 14% of the 1990 global CO_2 emissions in the reference scenario, and could be reduced to 8% by maximum emission control (reference + MAX). Some better housekeeping, recycling and destruction of halocarbon wastes may be realized without additional regulations. Therefore, the 2040 fluorocarbon emissions could, without specific fluorocarbon policy, equal 8 - 14% of the 1990 CO_2 emissions as are probably at the higher end of this range. These results are within the range of 7 - 17% as published earlier by RIVM.

The average GWP of the halocarbon mix emitted increases by about 25% between 2005 and 2040 in the reference scenario. This is mainly the result of the HCFC phase-out: the mix of HFCs used have on average higher GWPs than the HCFCs they replace.

Restricting use to stationary cooling and closed-foam blowing, which are applications with the lowest annual loss rates, decreases halocarbon emissions by about 40 - 50% relative to the reference scenario (closed applications only scenario).

In the low-GWP scenario only compounds with global warming potentials lower than 250 are

used, including pure and blended fluorocarbons. In this scenario the CO_2-equivalent emissions are 90% lower than in the reference scenario. A GWP of 250 is about 10% of the average GWP of the mix of halocarbons emitted in the reference scenario. Non-halocarbons are, or will become, available for all major applications in the near future. Some of these are toxic, flammable or less energy efficient. However, in many cases this can be overcome by redesigning equipment or by a change in processing and servicing. The costs involved depend on the price of the compounds used, the costs of retrofitting or redesigning equipment and the costs of servicing. For users of halocarbons, the costs of a phase-out can be kept low if the timing is such that early replacement of equipment is not necessary.

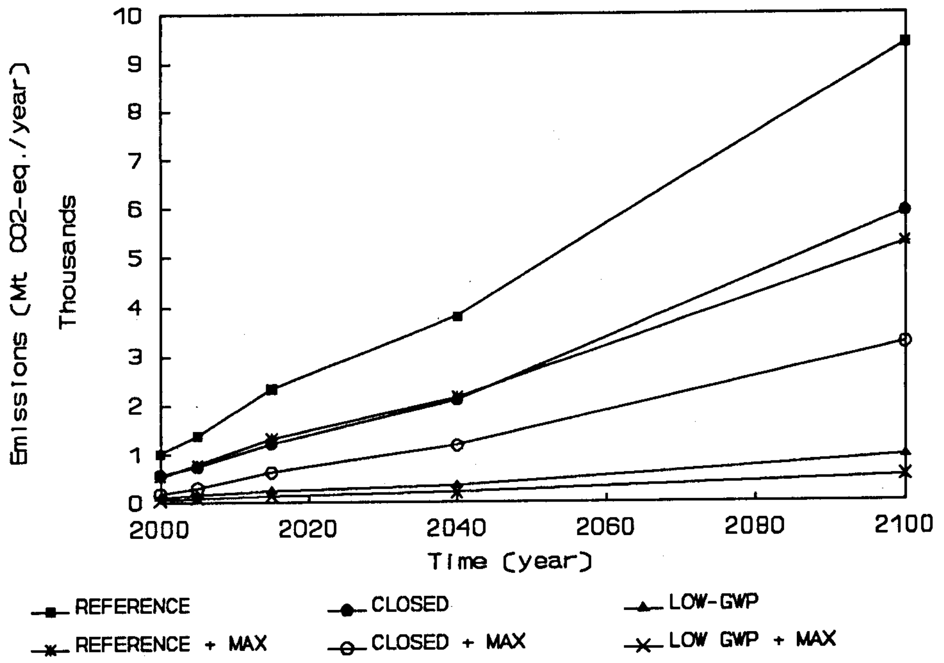

Fig. 1. Emissions of HCFCs, HFCs, PFCs, FICs and SF_6) in the reference scenario, closed applications only scenario and low GWP compounds only scenario, all three with (+ MAX) and without maximum emission control. Emissions are in Mton CO_2-equivalents per year.

SAMENVATTING

Dit rapport geeft een overzicht van de huidige kennis over wereldwijde emissies van een aantal halogeenkoolwaterstoffen en presenteert scenario's voor emissies gedurende de volgende eeuw. De studie concentreert zich op stoffen, waarvan het het gebruik niet is geregeld in het Montreal Protocol: HFKs, PFKs, FIKs en SF_6. Deze zijn alle belangrijke vervangers van CFK's, halonen, CH_3CCl_3 en HCFK's, waarvan het gebruik zal worden gestaakt wanneer het Montreal Protocol ter bescherming van de ozonlaag wordt geimplementeerd.

Het het gebruik van HFK's, PFK's, FIK's en SF_6 is geschat als percentage van de vraag naar CFK's, halonen en CH_3CCl_3 zoals deze zou zijn geweest zonder Montreal Protocol, voor gebruik als drijfgas (9-11%), oplosmiddel (<5%), blaasmiddel voor open schuimen (1-2%), blaasmiddel voor gesloten schuimen (40-45%), koelmiddel in stationare koeling (>50%), koelmiddel in auto-airconditioning (<75%), niet-draagbare brandblussers (45-50%) and overige (30%). Verondersteld is dat 75% van de historische HCFC-22 markt vervangen zal worden door HFK's na een produktiestop van HCFK's.

De actuele emissie van halogeenkoolwaterstoffen is niet gelijk aan het jaarlijkse gebruik. Bij een aantal toepassingen vindt direkt emissie plaats. Wanneer de stoffen echter gebruikt worden als koelmiddel of als blaasmiddel ligt het tijdstip van emissie jaren na het tijdstip van gebruik.

In deze studie worden toekomstige, wereldwijde emissies gepresenteerd voor zes scenario's (Fig. 1). In het referentiescenario (**reference scenario**) is aangenomen dat de aanscherping van het Montreal Protocol, zoals overengekomen in Kopenhagen, wordt geimplementeerd en dat er geen additioneel beleid wordt geformuleerd voor HFK's, PFK's, FIK's en SF_6. Het scenario **closed applications only** verondersteld dat gebruik van halogeenkoolwaterstoffen is beperkt tot stationaire koeling en het blazen van gesloten schuimen. In het **low-GWP scenario** is aangenomen dat slechts stoffen worden gebruikt met een Global Warming Potential lager dan 250. Deze drie scenario's worden gepresenteerd voor een situatie zonder verdere emissiereductie en aannemende dat maximaal wordt ingezet op *good housekeeping*, hergebruik en vernietiging van afgedankte halogeenkoolwaterstoffen (+ MAX).

In het referentiescenario bedraagt het wereldwijde gebruik van HFK's in 2040 1440 kt per jaar. Deze resultaten komen goed overeen met een schatting van de industriële *Alliance of Responsible Atmospheric Policy*, die het gebruik van HFK's in 2035 1100 - 1400 kt per jaar schatte voor een situatie zonder specifiek beleid. De belangrijkste toepassingen voor halogeenkoolwaterstoffen in het referentiescenario zijn stationaire koeling (60%), het blazen van gesloten schuimen (19%) en als oplosmiddel (8%). De meest gebruikte halogeenkoolwaterstof is HFK-134a (40% van de wereldconsumptie). Andere belangrijke halogeenkoolwaterstoffen zijn HFK-125, HFK-143a en HFK-152a (7 - 9% elk).

Maximale emissiereductie door *good housekeeping*, hergebruik en vernietiging van afgedankte stoffen (MAX) reduceert de emissies met 40 - 45% in het referentiescenario. Een deel van deze reductie zou kunnen worden gerealiseerd zonder additioneel beleid.

Uitgedrukt in CO_2-equivalenten bedragen de emissies van HFK's, PFK's, FIK's en SF_6 in het referentiescenario in 2040 14% van de mondiale CO_2 emissie in 1990. *Good housekeeping*, hergebruik en vernietiging van afgedankte stoffen zou dit percentage kunnnen reduceren tot 8%. Een deel van deze reductie zou gerealiseerd kunnen worden zonder additioneel beleid. Dus zonder specifieke maatregelen kan de emissie van deze stoffen in 2040 8 - 14% van de CO_2 emissie in 1990 bedragen en ligt waarschijnlijk aan de bovengrens van deze range. Dit valt in range van een eerdere schatting van het RIVM (7 - 17%).

De gemiddelde Global Warming Potential (GWP) van de mix van geëmitteerde halogeenkoolwaterstoffen stijgt met ongeveer 25% tussen 2005 en 2040 in de scenario's. Dit wordt vooral veroorzaakt door een produktiestop van HCFK's: de HFK mix die daarna gebruikt wordt heeft gemiddeld een hogere GWP dan de HCFK's die worden vervangen.

In het scenario waarin het gebruik van halogeenkoolwaterstoffen wordt beperkt tot stationaire koeling en het blazen van gesloten schuimen (toepassingen met de laagste lekverliezen) is de emissie van halgeenkoolwaterstoffen ongeveer 40 - 50% lager dan in het referentiescenario.

In het low-GWP scenario worden slechts stoffen met een GWP lager dan 250 gebruikt. Dit kunnen mengsels zijn die halogeenkoolwaterstoffen bevatten. In dit scenario zijn de CO_2-equivalente emissies 90% lager dan in het referentiescenario. Een GWP van 250 is ongeveer 10% van de gemiddelde GWP van de mix die geëmitteerd wordt in het referentiescenario. Voor alle belangrijke toepassingen zijn of komen niet-halogeenkoolwaterstoffen in de nabije toekomst. Soms zijn deze toxisch, brandbaar of minder energie-efficient. In veel gevallen kunnen deze nadelen echter worden tenietgedaan door aanpassing van de apparaten, de processen of de manier waarop met de stoffen wordt omgegaan. De kosten worden bepaald door de prijs van de gebruikte stoffen, de kosten van het modificeren dan wel opnieuw ontwerpen van apparatuur en de kosten die gemoeid zijn met de benodigde service. De kosten van een totale produktiestop van stoffen kunnen voor gebruikers laag gehouden worden, wannneer een vervroegde vervanging van apparatuur niet nodig is.

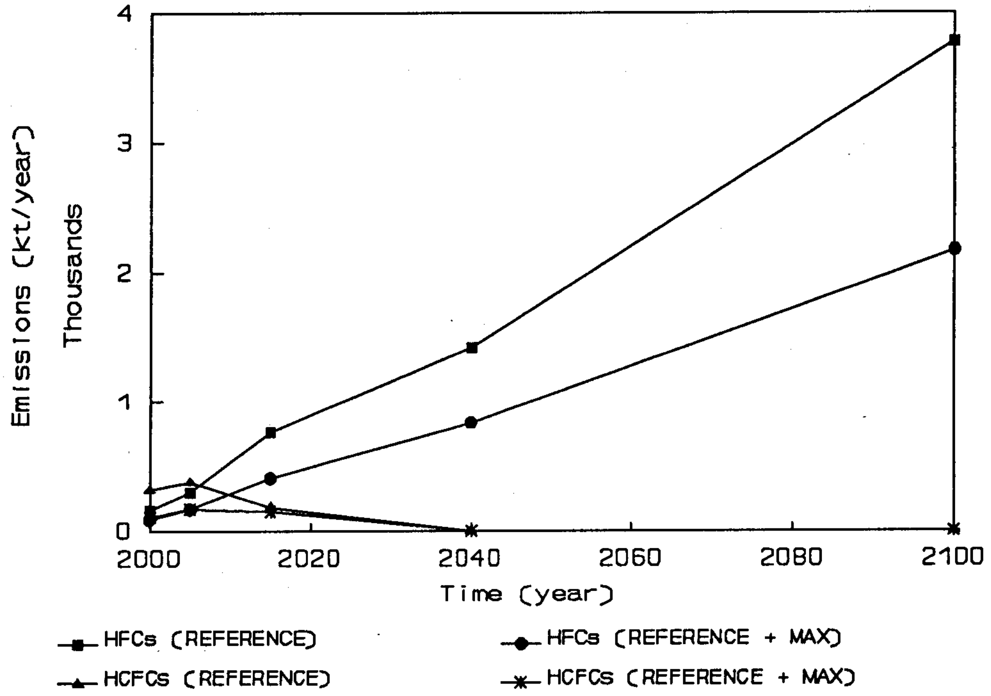

Fig. 1. Emissies van HCFK's, HFK's, PFK's, FIK's en SF_6 in het referentescenario (reference) en de scenario's closed applications only low-GWP compounds only. Deze drie scenario's zijn gepresenteerd voor een situatie met (+ MAX) en zonder maximale emissiereductie door *good housekeeping*, hergebruik en vernietiging van afgedankte stoffen. Emissies zijn in Mton CO_2-equivalenten per jaar.

1 INTRODUCTION

A 1994 RIVM report concluded that by the year 2035, HFC emissions could equal 7 - 17% of the 1990 global emissions of CO_2 (Kroeze, 1994). This estimate was largely based on readily available information. Due to recent developments an update was deemed desirable. The results of such an update constitute this report.

The Montreal Protocol is an international agreement for protection of the ozone layer (UNEP, 1987). The first version of 1987 has been reinforced twice (UNEP, 1991, 1992). When the 1992 amendments are implemented, use of chlorofluorocarbons (CFCs), 1,1,1 trichloroethane (CH_3CCl_3) and chlorobromocarbons (halons) will be stopped before the year 1996 (Table 1-1). Hydrochlorofluorocarbons (HCFCs), which are used as substitutes for CFCs and halons, are to be phased out by 2030. In Europe CFCs and halons are no longer allowed, while HCFCs are to be phased out by 2015. In Europe there are restrictions for HCFCs in several applications.

One of the countries that formulated additional regulations is the USA. The US government started the Significant New Alternatives Program (SNAP), which regulates substitution of CFCs and halons (EPA, 1994a). Whether compounds are accepted as substitutes for CFCs and halons as compounds in certain applications depends on their "overall risk to human health and the environment". As a result, several HCFCs are not allowed in applications where alternatives seem available. Several perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) are subject to limits for use (EPA, 1994a). Outside the USA there are in general no regulations for fluorocarbons such as HFCs and PFCs.

This report surveys current knowledge on global use and emissions of several groups of halocarbons. The purpose of the study is to investigate the impact of regulations for HFCs, PFCs, FICs (fluoroiodocarbons) and SF_6 (sulfurhexafluoride) on global warming. Therefore, the compounds considered in this study are first described, including some general characteristics and production processes (Chapter 2). Next, an overview is given of the applications, and it is estimated to what extent halocarbons and SF_6 will be used to replace compounds regulated in the Montreal Protocol (Chapter 3). Chapter 4 investigates options to reduce emissions for each application and Chapter 5 describes how actual emissions can be calculated. Finally, Chapter 6 summarizes all information of the previous chapters in scenarios for future emissions of halocarbons. These scenarios investigate the emissions for a situation without further limits, and the impact of several levels of control.

Table 1-1. Overview of existing regulations (UNEP 1987, 1991, 1992)

	Compounds	Timing
Montreal 1987	CFCs	50% reduction in production relative to 1986, beginning in mid-1998
	Halons	Freeze at 1986 levels in 1992
London 1990	CFCs	Phase-out by 1-1-2000
	Halons	Phase-out by 1-1-2000
	CCl_4	Phase-out by 1-1-2000
	CH_3CCl_3	Phase-out by 1-1-2005
Copenhagen 1992	CFCs	Phase-out by 1-1-1996
	Halons	Phase-out by 1-1-1994
	CCl_4	Phase-out by 1-1-1996
	CH_3CCl_3	Phase-out by 1-1-1996
	HCFCs	Freeze in 1996, phase-out by 1-1-2030
	HBFCs	Phase-out by 1-1-1996
	Methyl bromide	Freeze in 1995 at 1991 level
Additional European regulation	CFCs	Phase-out by 1-1-1995
	Halons	Phase-out by 1-1-1994
	CCl_4	Phase-out by 1-1-1995
	CH_3CCl_3	Phase-out by 1-1-1996
	HCFCs	Phase-out by 1-1-2015[2]
	Methyl bromide	25% reduction in 1998
U.S. SNAP	HCFC-22,-124,-141b,-142b, HFC-23, -125, -227ea PFCs	In some applications unnacceptable, or subject to use conditions

[1] With a 10-year delay for developing countries; [2] HCFCs are only allowed for use as solvent, cooling agent, blowing agent for insulation and integral foam, laboaratory applications and feedstock; in 1996 and 1998 the number of applications will be decreased

2 THE COMPOUNDS CONSIDERED IN THIS STUDY

2.1 INTRODUCTION

This chapter shortly surveys the compounds considered in the present study. The study focuses on several halocarbons not regulated by the Montreal Protocol (HFCs, PFCs, FICs) and SF_6. The use of these compounds cannot be studied without taking into account the compounds they replace. Therefore, CFCs, halons, CH_3CCl_3 and HCFCs are also considered. First, some general characteristics of these groups of compounds will be described (2.2) followed by the production processes (2.3).

2.2 GENERAL CHARACTERISTICS OF HALOCARBONS AND SUBSTITUTES

Types of halocarbons

Halocarbons include several groups of chlorinated, fluorinated, brominated and/or iodated carbon compounds. Halocarbons to be phased out according to the Montreal Protocol include the widely used chlorofluorocarbons (CFCs), chlorobromocarbons (halons), and chlorocarbons such as 1,1,1-trichloroethane (CH_3CCl_3) and tetrachlorocarbon (CCl_4). They will be partly replaced by other halocarbons, such as hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), hydrobromofluorocarbons (HBFCs), perfluorocarbons (PFCs), and fluoroiodocarbons (FICs). Sulfur hexafluoride (SF_6), which is also included in this study, is not a halocarbon. The halocarbons mentioned so far, along with SF_6, are synthetic compounds. Natural halocarbons include CH_3Cl, CH_3Br, and CH_2I, which are mostly produced in oceans; their atmospheric lifetimes are in general less than two years (Ramanathan et al., 1987).

Atmospheric lifetimes

The atmospheric lifetime is an important characteristic of halocarbons. Compounds with longer atmospheric lifetimes have in general higher Global Warming Potentials and, if they contain chlorine or bromide, higher Ozone Depleting Potentials, but lower toxicity, flammability, and have less impact on tropospheric chemistry. Halocarbon lifetimes vary between less than a day and 50000 years (Appendix 2-1). CFCs and halons are broken down in the stratosphere by photolysis or oxidation and have therefore longer lifetimes (45 - 2700 years) than HCFCs and HFCs (1 - 250 years) which are predominantly oxidized in the troposphere. PFCs and SF_6 are photolyzed in the mesosphere, as a result of which their lifetimes can be extremely long (3000 - 50000 year). FICs, on the other hand are photolyzed in the troposphere quickly, CF_3I even within a day (Solomon et al., 1994).

Ozone Depleting Potentials (ODPs)

Chlorine, bromide and iodine containing halocarbons have a potential to cause ozone depletion. The fully halogenated CFCs and halons are chemically inert in the troposphere. The only known sink of CFCs and halons is decomposition in the stratosphere. About three years after release, CFCs are well mixed throughout troposphere and stratosphere. In the stratosphere CFCs and halons are slowly broken down by ultraviolet radiation. Thus all chlorine in CFCs and halons is eventually released in the stratosphere, causing ozone depletion.

The partly halogenated HCFCs are partly broken down in the lower atmosphere by oxidation, after which the chlorine is deposited on the earth's surface, mainly as HCl. This tropospheric sink prevents part of the chlorine from being released in the ozone layer. Thus their long-term effect on the ozone layer is much smaller than that of CFCs and halons. Nevertheless, the impact of HCFCs on stratospheric ozone may be considerable, especially during the first decade or so after release.

FICs contain iodine, which is very effective for stratospheric ozone destruction, if it ever reaches the stratosphere. However, because of their short atmospheric lifetimes, FICs have probably low ODPs. For one of the FICs, CF_3I, the ODP was calculated at less than 0.008, and more likely below 0.0001 (Solomon et al., 1994).

HFCs do not contain ozone-destroying chlorine. It has been suggested that an intact CF_3 group can catalyze ozone reduction. However, the reactions involved have very low rate-coefficients. Even a relatively long-lived compound like HFC-23 has an ODP of less than 0.001. It is assumed here that this also holds for the long lived PFCs (Table 2-1). Summarizing, the ODPs of HFCs are low (Ravishankara et al., 1994) and generally considered 0.

Direct Global Warming Potentials (GWPs)

Most halocarbons are relatively powerful greenhouse gases. Halocarbon molecules have, in general, a greater ability to absorb infrared radiation than most other greenhouse gas molecules. In addition, their atmospheric lifetimes are long. As a result, the long-term radiative effect of 1 kg of CFCs emitted exceeds that of 1 kg CO_2 by a factor of 4000 - 11700. These numbers refer to the direct Global Warming Potentials (GWPs), i.e. the extra amount of longwave radiation absorbed by these molecules over a 100-year period.

Halocarbons differ largely in their direct Global Warming Potentials (Fig. 2-1.). CFCs and halons have direct GWPs of 4000 - 11700. Direct GWPs of HCFCs are in general one order of magnitude smaller, and those of FICs probably two or three orders of magnitude smaller. HFCs show a wide range of GWPs (150 - 10000). Several HFCs have higher direct GWPs than the CFCs they replace. Taking indirect radiative effects into account, which are negative for CFCs and positive for HFCs, the number of HFCs having GWPs exceeding CFC-GWPs would increase. SF_6 has an extremely high GWP of 24900.

Indirect effects on global warming and ozone depletion

Global warming and stratospheric ozone depletion are not independent environmental problems. Several linkages between the two processes exist.

First, stratospheric ozone depletion may have a cooling effect on the troposphere. Thus halocarbons affect the radiative budget directly by absorption of longwave radiation, but may indirectly cause atmospheric cooling as a result of ozone depletion. There are two mechanisms involved. First, ozone depletion may result in decreased longwave irradiation into the troposphere (Ramaswamy et al., 1992). Second, due to ozone depletion ultraviolet radiation in the troposphere increases, as a result of which formation of tropospheric OH radicals increase (Thompson 1991; Toumi et al., 1994). This has a cooling effect because (i) it may increase the albedo as a result of increased cloud formation and (ii) it may shorten the lifetime of, for instance, CH_4 and thus its direct warming effect (Isaksen, 1994). Both indirect effects may locally and temporarily offset part of the direct radiative forcing by CFCs, halons, CCl_4 and CH_3CCl_3. However, this cooling cannot be simply regarded as a fully compensating effect (IPCC, 1994). Even if at the earth's surface the net radiative effect were zero, the vertical energy transport in the atmosphere would be considerably disturbed (Gribbin, 1992). For HCFCs the indirect cooling effect is probably one order of magnitude smaller than the direct radiative forcing. It is zero for HFCs, PFCs, FICs and SF_6.

Some halocarbons may indirectly warm the troposphere. Halocarbons with relatively short lifetimes such as HCFCs, HFCs, FICs and CH_3CCl_3 are mainly broken down in the troposphere.

The reactions involved may lead to decreased OH levels, which in turn may lead to inceased warming by, for instance, methane. Including indirect radiative effects could, for these gases, lead to an increased GWP. Alternatively, enhancement of the greenhouse effect may cool the stratosphere, making halocarbons possibly more effective ozone destroyers (Austin et al., 1992).

Which of these, or other indirect effects is dominant on a global scale, is at present unclear and to what extent they may affect world temperatures can at present not be quantified. Therefore, in Figure 2-1 only direct GWPs and ODPs are presented.

Flammability

CFCs and halons are not flammable, but several of the substitutes are (some HCFCs and HFCs and most other hydrocarbon substitutes). The non-flammability and non-toxicity of CFCs resulted historically in low leakage control. Flammable compounds can therefore not be used as drop-in substitutes in a number of applications. A few technical modifications in equipment may, however, make flammable compounds suitable substitutes. This was clearly shown in household refrigerators, in which propane and butane are being increasingly used as cooling agents, while a few years ago flammability of these compounds was regarded as a major problem (see 3.2.4.1). The household refrigerator may not be an exception; currently the possibility of hydrocarbon cooling agents in mobile airconditioning, a relatively "leaky" application, are under consideration (GECR, 1994) and tested (Van Gerwen and Jansen, 1994). Thus reducing leakage will not only reduce emissions, but also make flammable compounds more suitable substitutes. Another solution to flammability problems may be blending flammable with non-flammable compounds.

Toxicity, environmental degradation products

The fully halogenated CFCs, halons and PFCs are not toxic, which is one of the reasons for their widespread use. The partly halogenated have, in general, low toxicity (Table 2-1). HCFC-22 has a Threshold Limit Value of 1000 ppm (a value to which nearly all US workers may be exposed repeatedly, day after day, during an 8-hour day, 40-hour week without adverse effect); this is the highest value allowed for any organic compound in the USA. Dupont further established Acceptable Exposure Limits (AEL) of 1000 ppm for HCFC-142b and HFC-152a (Dupont, 1988). However, it is recognized that breathing high concentrations (exceeding 1000 ppm) of HCFC-22, -142b or HFC-152a may produce cardiac irregularities, unconsciousness or even death; this could affect the central nervous system and produce a narcotic or anaesthetic effect (Dupont, 1988).

HCFC-123 is relatively toxic. The AEL for HCFC-123 was initially set at 10 ppm, but was recently raised to 30 ppm (Dupont, 1993) based on 2-year inhalation studies.

The toxicity of fluoroiodocarbons (FICs) has undergone limited testing. Iodide-containing halocarbons were until recently regarded too reactive, and therefore potentially toxic, to be serious substitutes for CFCs and halons. However, it has been recently recognized that the C-I bonds in FICs of the structure $C_nF_{n-2}I$ may be relatively strong (IKON, 1994). As a result, their acute toxicity may be lower than of other FICs. Toxicity, longer term effects and the toxicity of degradation products need to be further investigated.

CFCs are not broken down in the lower atmosphere, but HCFCs and HFCs are and decomposition products such as hydrogen fluoride (HF), hydrogen chloride (HCl) or trifluoro acid (TFA) may be toxic or irritating (Dupont, 1988; Rusch, 1994).

SF_6 is in itself non-toxic. However, its degradation products are toxic. At high temperatures (hundreds of degrees Celsius) of electrical discharges several oxides of fluoride, metal fluorides and thionylfluoride may be produced, which are toxic at ppm level (Annema, 1989).

Commercial availability / costs

The following HCFCs, HFCs and PFCs are presently commercially available: HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b, HCFC-225ca/cb, HFC-134a, HCF-125, HFC-152a, HFC-143a, HFC-23, HFC-32, HFC-227ea, CF_4, C_2F_6, and a number of other PFCs (perfluoropropane, perfluorobutane, perfluoropentane, perfluorohexane, perfluoroheptane, perfluorooctane, perfluoro-N-methylmorpholine, perfluoro-N-ethylmorpholine and perfluoro-N-ispropyl morpholine). Production of FICs in pilot plants has been announced in 1993 and CF_3I is presently produced in pilot plants.

To evaluate the costs of switching from one compound to another, one should consider (i) the price of the compounds used, (ii) the costs of equipment modification, (iii) the costs during use, including energy use and servicing.

(i) Prices of halocarbons depend on the quantities produced or available. Non-restricted halocarbons are in general cheaper when they are produced in larger quantities. This has been shown clearly for CF_3I, for which prices dropped within a year from about $1300 to less than $300 per kilo, and is expected to further decrease to 10 - 40 US $/kg by 1995 (Nimitz, 1994a,b,c). Prices of HFCs such as HFC-134a, -125 and -227ea are in the order of 15 - 30 $/kg (Nimitz, 1994d). HFCs are in general 3-5 times as expensive as CFCs before the Montreal Protocol. In the USA a tax on CFCs and halons of about 12 US $/kg has been introduced, making CFCs in fact more expensive than HFCs. As the use of CFCs is more and more restricted, prices go up. Thus at present there is not much difference in price between halocarbons. Hydrocarbons such as propane and butane are in general cheaper (about 2$/kg) and when these are used as a refrigerant less is needed (Maclaine-cross, 1994).

(ii) Retrofitting equipment for use of new chemicals may be expensive. If drop-in substitutes are not available, and the equipment would otherwise not have been replaced, the extra costs may be significant. This is one of the reasons why blends which could be used as drop-in substitutes are so popular. On the other hand, when equipment is replaced for other reasons, the extra costs involved can be negligibly low.

(iii) Costs of servicing are relatively high for compounds that are restricted under the Montreal Protocol. Trained personnel may be needed for leakage testing, refilling and other servicing. After use the restricted compounds need to be recycled or destroyed. For cooling and insulation the performance of the compounds used may affect the costs of energy use. Increased costs may particularly occur when new compounds are used as drop-in substitutes. When new equipment is designed for the newly used chemicals, energy efficiency can be improved for almost all applications.

Summarizing, additional costs of switching from one compound to another can be kept low. The largest costs may involve equipment modification. These can be kept low if (i) a drop-in substitute is available or (ii) a new chemical is introduced when replacing equipment for other reasons. Servicing costs can be considerable for halocarbons, but are lower for non-halocarbons. Energy efficiency can be increased when new equipment is designed for the new chemicals. Thus the net costs of replacement depend on several factors. In mobile airconditioning a switch to propane/butane was calculated to be cheaper than a switch to HFC-134a (Maclaine-cross, 1994). This because the price of hydrocarbons is lower, less is needed and no expensive servicing is required. These benefits outweigh the extra costs as a result of inflammation risk.

Suitability as substitute

Substitutes for CFCs and halons can be of different types. Users prefer "drop-in" substitutes, which can be used instead of CFCs or halons without modification of the equipment. Substitutes that require modest retrofitting of equipment may also be considered drop-in substitutes. Drop-in substitutes have similar properties to the compounds they replace. Since this is hardly ever the case, different compounds are often mixed in blends in order to achieve desirable performance. Blends can have advantages for the users because (i) they can be used as drop-in substitutes, and (ii) flammable and toxic compounds can be mixed so that a non-flammable, non-toxic refrigerant is created. Their disadvantages are that (i) recycling is considered difficult and (ii) the composition of non-azeotropes may change over time, with the result that the performance changes and flammable or toxic compounds can be released in more concentrated form.

A number of substitutes for CFCs and halons require major modifications, so that they can only be applied in new equipment. The most drastic changes occur when an alternative product or alternative process is chosen.

Total Equivalent Warming Impact (TEWI)

In some studies it is argued that not only the GWP of the compounds used is important, but also the indirect CO_2 emissions due to energy used in the appliance. Fos instance, in case CFC substitutes result in a less energy efficient refrigerator, the extra CO_2 emissions could be taken into account when evaluating the climatic impact of the substitution. The global warming effects of direct emissions of greenhouse gases and the CO_2 emissions due to energy use are combined in the Total Equivalent Warming Impact (TEWI). TEWI aims at evaluating the total warming impact over the lifetime of the equipment, and is in particular applied to cooling systems and insulation foam (Fisher et al., 1994b).

The TEWI approach could give insight in the "best" alternatives for CFCs and halons with respect to global warming. However, the results of TEWI studies appear to depend largely on assumptions and boundary conditions. This is clearly illustrated for the household refrigerator (PRI, 1994). Hydrocarbon refrigerators were found to have lower TEWI values than HFC or CFC refrigerators, if the aging of the foam was taken into account. Without these aging effects, the conclusions could be opposite (PRI, 1994).

Another problem in estimating TEWI values is that it is difficult to estimate the exact CO_2 emissions due to energy, especially for future years. When using renewables sources of energy, there are no CO_2 emissions. Also fossil fuels differ largely in emissions per GJ.

In addition, assumptions on the degree of equipment modification or availablility of new technologies influence the results considerably. For instance, when introducing thicker insulation panels in refrigerators, a less energy efficient blowing agent would not result in a less energy efficient refrigerator. If, on the other hand, a present-day refrigerator is taken as a reference, a loss in insulation capacity could lead to higher TEWI values. Assumptions on the extent to which energy efficiency can be improved is a factor of importance. Conservative studies most probably lead to other conclusions than studies that are optimistic about future developments.

Finally, the GWPs used to evaluate the total warming impact largely influence the results (PRI, 1994). For instance, different time horizons over which GWPs are calculated can be used. As described earlier, indirect radiative effects are usually not taken into account. Inclusion of, for instance, cooling of the lower atmosphere by ozone depletion, would increase TEWI values of HFC systems relative to those containing HCFCs, CFCs and halons.

From the above may be concluded that it is important to consider the effects of compounds on the energy efficiency of equipment. The TEWI approach may be useful in comparing different compounds in the same application, and in investigating how the total greenhouse gas emissions from a particular system can be reduced by equipment modification. On the other hand, it should be realized that calculated TEWI values depend largely on assumptions. It can therefore be questioned to what extent TEWI analyses should guide in chosing low-GWP alternatives for CFCs, HCFCs and halons.

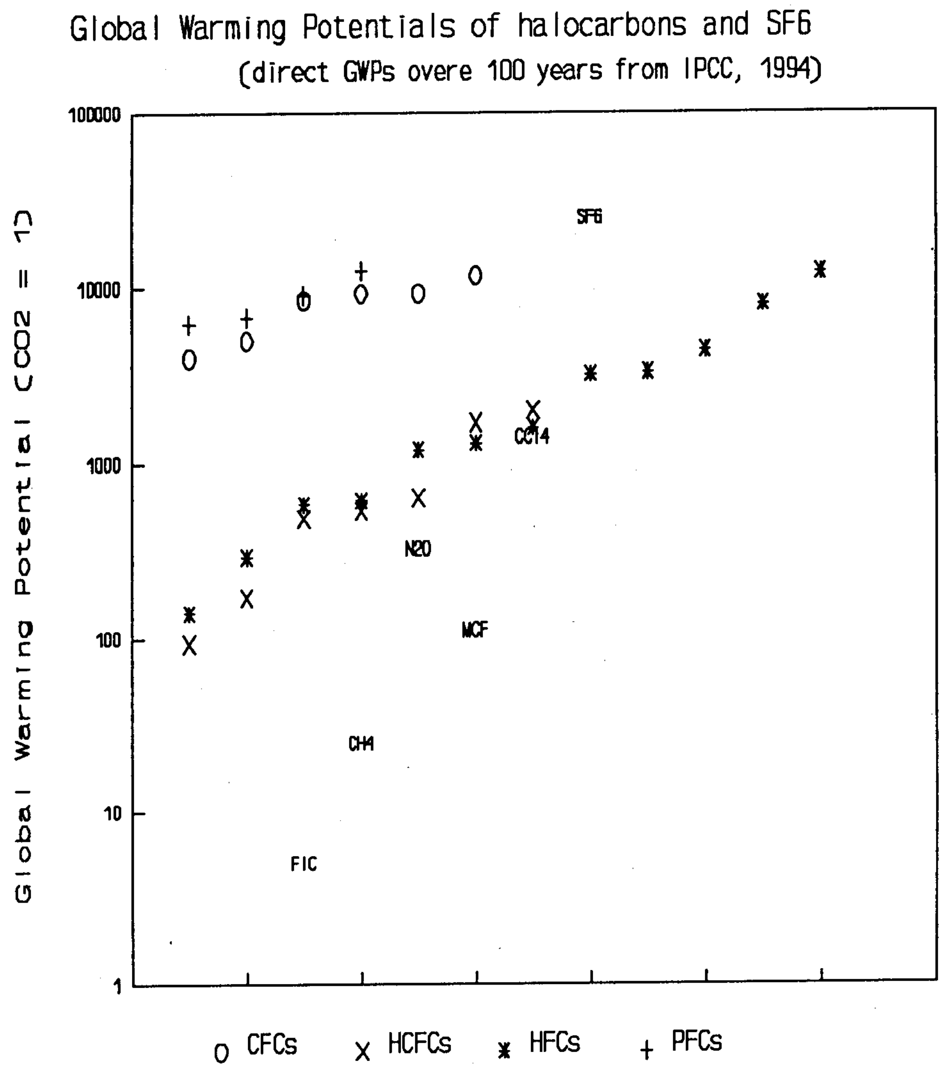

Fig. 2-1. Direct Global Warming Potentials of several halocarbons and SF_6 over 100 years (IPCC, 1994). CFCs, CCl_4 and CH_3CCl_3 may have an indirect GWP, partly offsetting the direct GWP. The indirect effects of HCFCs, HFCs, PFCs and SF_6 are negligible, zero or may enhance the direct GWP. Note logarithmic scale.

Table 2-1. Costs, Ozone Depleting Potentials (ODP), direct Global Warming Potentials (GWP), toxicity and flammability of halocarbons, SF_6 and some non-halocarbons substitutes

	Costs US $/kg	ODP	Direct GWP	Toxicity	Flammability
Regulated compounds					
CFCs, halons	increasing[1]	0.4-1	>1000	none	none
HCFCs		<0.1	>90	low-medium	none
Not regulated halocarbons					
HFCs	15 - 30[2]	<0.001	>140	low-medium	some
PFCs	25 - 100	<0.001	>6300	none	none
SF_6		0	24900	none	none
FICs	50 - 100[2]	<0.008	5	medium[4]	none
Chlorinated hydrocarbons		0	<1?	medium	some
Non halocarbons					
Hydrocarbons: e.g. propane, butane pentane	<3[3]	0	<1?	low	all
Alcohol, ketone, ester: e.g. isoproanol, exetone, methylethylketone	<3[3]	0	<1?	medium	all
Terpene		0	<1?	high	all
Ammonia	<3	0	<1?	high	none
O_2, N_2, zeolite, water		0	0	none	none

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[1] <10 US $/kg before the Montreal Protocol (excluding taxes), nowadays often more expensive than HFCs; [2] e.g. Treadwell, 1994; Nimitz, 1994d; [3] Maclaine-cross, 1994; [4] to be tested

2.3 PRODUCTION OF HALOCARBONS AND SF_6

2.3.1 CFCs, halons and HCFCs

Chlorinated or fluorinated compounds are produced by fluorination or chlorination reactions in which the hydrogen atoms on a hydrocarbon molecule are replaced with either chlorine or fluoride (Appendix 2-1).

Usually CCl_4 is used as feedstock for CFCs. CCl_4 is produced as by-product during the manufacture of chloromethanes (e.g. dichloromethane, chloroform and methyl chloride). More than 95% of CCl_4 produced is used as feedstock for CFCs (UNEP, 1994a). During fluorination of CCl_4, highly specified catalysts determine which of the halocarbons is predominantly formed. There is always formation of by-products, to be separated from the required product. For instance (UNEP, 1994a):

$$CCl_4 + HF \text{ -> } CCl_3F + CCl_2F_2 + HCl + \text{trace impurities of } CClF_3 + \text{unreacted } CCl_4$$

Methyl chloroform, CFC-113, and chloroform can be used as a feedstock for HCFCs and HFCs. Production of controlled substances for feedstock use will not be affected by the Montreal Protocol. HCFC-22 is in turn used as feedstock for fluoropolymers and halons. HCFC-22 can be produced from chloroform ($CHCl_3$) and HF with antimony(v)chloride ($SbCl_5$) as catalyst (Ros, 1994). The impurities can be removed by condensation and aqueous cleaning:

$$CHCl_3 + 2\ HF \text{ -> } CF_2HCl + 2\ HCl + \text{trace amounts impurities}$$

Major CFC producing countries were in the USA, Japan, South Africa, Australia and countries in Europe, but all are to phase out their production by the end of 1994 or 1995, except when the compounds are produced for export. In China, India, Latin America and Asia CFC production capacity is still increasing. Nowadays, most of the former CFC-producing countries produce HCFCs: USA, Japan, Canada, Italy, The Netherlands, France, Spain, UK, Australia, Greece, Germany, Argentina, Brazil, Venezuela, China, India, South Korea, Taiwan (Table 2-3). During the production processes, feedstocks, by-products and end-products may be emitter (Table 2-2). During CFC and HCFC production 0.1 - 1% is lost during the process, and another 0.1 - 1.5% as "handling losses". Total emissions may be about 0.5% of CFC and HCFC production (UNEP, 1994a).

2.3.2 HFCs

HFCs are produced through essentially the same processes as HCFCs, with CFC-113 as major feedstock. HFC-134a has been produced in UK, Japan and USA since 1991 (Enquete comission, 1994) and in Germany since 1993. HFCs are now being produced in Europe (Italy, France, Germany, UK), Japan, USA, Brazil and China (Table 2-3). HFC-23 is a by-product of HCFC-22 production. It has been estimated that HFC-23 emissions amount to 4% of the HCFC-22 production (EPA, 1994b).

2.3.3 PFCs

Perfluocarbons (PFCs) are produced as byproduct of primary aluminum production (Van Amstel et al., 1994), and as commercial product.

One of the steps in aluminum production is the Hall-Heroult electrolytic reduction process, during which aluminumoxide is diluted in cryolite (about 50% fluoride). Disruption of this process known as the anode effect results in production of PFCs. Estimates indicate that for each metric ton of aluminum produced in the USA 0.3 - 0.9 kg of CF_4 and 0.03 - 0.09 kg of C_2F_6 are emitted (EPA, 1994b). Emission rates may depend on the specific process conditions. Aluminum production may cause 80% of the present PFC emissions (Aluminium Delfzijl, 1992).

Commercial production of PFCs is done through several processes. One of these involves electrochemical fluorination of hydrocarbons:

$$C_nH_{2n+2} + (2n + 2)\, HF \rightarrow C_nF_{2n+2} + (2n + 2)\, H_2$$

Electrochemical fluorination is an energy intensive process. PFCs are produced in Belgium, USA, Italy, UK, Russia and China (Table 2-3).

2.3.4 Sulfur hexafluoride (SF_6)

Sulfur hexafluoride is produced in three steps. First sulfur vapour reacts with elementary fluoride to a mixture mainly containing SF_6. In the second step the by-products are washed with alkaline solutions or decomposed by heating (400 °C). Finally, the pure SF_6 (usually 99.9%) is dried. Major producers are in Italy, Germany, USA and Japan (Annema, 1989).

Table 2-2. Feedstock, by-product and end-product emissions during production of halocarbons and SF_6

Feedstock	Product	Product emissions (% of production)	Other emissions
Hydrocarbons	CCl_4	0.1%	0.006% as trace impurities in chlorinated products
Hydrocarbon	CH_3CCl_3	0.1%	
CCl_4	CFCs	0.5 (0.2-2.5)%	0.1% of CCl_4 used
CFC-113	HCFCs	0.5%	0.1% of CFC-113 used + 0.25% as trace impurity + 4% of HCFC-22 produced as HFC-23
CH_3CCl_3	HCFC-141b/-142b	0.5%	0.1% of CH_3CCl_3 used + 0.25% as trace impurity
CFC-113, HCFC-142b, -22	fluoropolymers		0.1% of CFC/HCFC used
CFC-113	HFCs	0.5%	<0.1% of CFC-113 used + 0.25% as trace impurity
Trichloroethylene	HFCs	0.5%	<0.1% of TCE used + <0.1% as HCFC-133a
Aluminumoxide	aluminum		0.3 - 0.9 kg of CF_4 and 0.03 - 0.09 kg of C_2F_6 per ton of Al
Hydrocarbons	PFCs	0.5%	
S, F	SF_6	0.5%	

Source: UNEP, 1994a; EPA, 1994b; other data estimated

Table 2-3. Major producers of halocarbons and SF_6 (prior to 1995; list may not be complete)

Company	Compound produced	Country
AlliedSignal	CFCs	Europe, N America
	HCFC-22, -123, -124, -141b, -142b, HFC-134a	USA
	HFC-32, HFC-125, HFC-143a	USA (pilot/semi-commercial)
Ausimont	CFCs	Europe
	HCFC-22, -123, PFCs	Italy
	HCFC-141b, -142b	USA
	HFC-134a	Europe (Italy)
	HFC-125	Italy (pilot/semi-commercial)
Elf-Atochem	CFCs	Europe
	HCFC-22	France, Spain, USA
	HCFC-141b, -142b	France, USA
	HFC-134a	Europe (France), USA
	HFC-32, HFC-125	France (pilot/semi-commercial)
	HFC-143a	USA (pilot/semi-commercial)
ICI	CFCs, Halon 1211	Europe
	HCFC-22	UK
ICI Klea	HFC-134a	Europe (UK), Japan, USA
	HFC-32	UK (pilot/semi-commercial)
Hoechst	HCFC-22	Germany
	HFC-134a	Europe (Germany), Brazil (pilot)
Solvay	HCFC-22	Germany
	HCFC-141b, -142b	France, Germany
Rhône-Poulenc	CFC-11, -12	Europe
SCING	CFCs	Europe
	HCFC-22	Greece
DuPont	CFCs, Halon 1301	N America
	CFC redistillation	Argentina
	CFCs, HCFC-22	Brazil
	CFCs, HCFC-22	Mexico
	HCFC-22	Canada, USA, The Netherlands, Japan
	HCFC-123	Canada
	HCFC-124, HFC-134a, HFC-152a	USA
	HFC-32, HFC-125, HFC-143a	USA (pilot/semi-commercial)
	PFCs	
Du Pont-Mitsui	CFCs, HFC-134a	Japan (Du Pont-Mitsui)
Great Lakes	Halons, HFC-227ea	USA
LaRoche	CFCs	N America
	HCFC-141b, -142b	USA
Asahi Glass	CFCs, HCFC-22, HFC-134a	Japan
Central Glass	CFCs, HCFC-22	Japan
Daikin	CFCs, HCFC-141b, -142b, HFC-134a	Japan
	HCFC-22	Japan, USA
	HFC-32, HFC-125	Japan (pilot/semi-commercial)
Showa Denko	CFCs, HCFC-22, HFC-134a	Japan
AECI	CFCs, HCFC-22	S Africa

Table 2-3. Major producers of halocarbons and SF_6 (prior to 1995; list may not be complete)

PCI	CFCs	Australia
>40 plants	CFCs, HCFC-22 HFC-152a PFCs	China China (pilot)
>2 plants	CFCs, HCFC-22	India
	PFCs	Russia
Frio (Chicago Bridge/J B Pezza)	CFCs	Argentina
Quimbascicos (Allied/Cydsa)	CFCs, HCFC-22	Mexico
Produven (Ato/Pequiven)	CFCs, HCFC-22	Venezuela
Ulsan	CFCs, HCFC-22	South Korea
Formosa Plastics	CFCs, HCFC-22	Taiwan
	HCFC-22	Argentina
3M	PFCs, (HFCs)	Belgium, USA
Ikon	FICs	USA (pilot)
Kali-Chemie	SF_6	Germany
Air Products & Allied Chemicals Co.	SF_6	USA
Sumitp	SF_6	Japan
Montecatini Edison	SF_6	Italy
BNFL	PFCs	UK

Source: Mainly from OORG, 1994; Annema, 1989

3. USE OF HFCs, PFCs AND SF_6 - general description

3.1 INTRODUCTION

The purpose of this chapter is to describe use of HFCs, PFCs, FICs and SF_6. HFCs and PFCs will be increasingly used to replace banned halocarbons. Therefore this chapter also describes use of CFCs, halons, CH_3CCl_3 and HCFCs. The most important applications for CFCs, halons and CH_3CCl_3 were as aerosol (3.2.1), in cleaning (3.2.2), as blowing agent (3.2.3), as cooling agent (3.2.4) and in fire extinguishing (3.2.5). For each of these applications is described (i) which of the halocarbons was used before the Montreal Protocol was signed, (ii) which of the halocarbons can be used to replace the halocarbons to be banned, and (iii) what non-halocarbon alternatives are available. Not all of the CFCs, halons and CH_3CCl_3 used before the Montreal Protocol will be replaced by halocarbons such as HCFCs and HFCs. A considerable part of the demand will be met by non-halocarbons and recycling. Chapter 3.3.1 estimates to what extent HCFCs, HFCs and PFCs will replace CFCs and halons for a situation without recycling. Chapter 6 the effects of recycling on use, emission and production are investigated. HCFCs, HFCs and PFCs are not only used to replace CFCs and halons. Some of them were already used before the Montreal Protocol and have their own, historical market. These "other uses" are described in 3.3.2. In this report, the annual "use" is defined as the actual amount of a compound used in a year, regardless whether this compound was recycled or not. Thus "production" of new compounds may be less than the annual use, if compounds are recycled.

3.2 USE OF REGULATED COMPOUNDS AND ALTERNATIVES

This chapter surveys the different applicationsof the compounds considered. Worldwide, the most important applications appeared in 1990: aerosol propellant (19%), open foam (8%), closed foam (14%), solvent (13%), refrigeration excluding mobile airconditioning (25%), mobile airconditioning (10%), fire extinguishing (2%) and other applications (9%) (Kroeze and Reijnders, 1992). But in the future this may change.

3.2.1 AEROSOLS

3.2.1.1 AEROSOL PROPELLANTS

Use before the Montreal Protocol

Use of CFCs as aerosol propellant has been restricted in the USA since 1978. In the rest of the world no such restrictions existed before the Montreal Protocol. Up until recently at least half of the aerosols used in Europe were CFC-11 and CFC-12. The most important aerosol applications include medical (e.g. metered dose inhalors, antiseptic sprays), industrial and technical applications (e.g. high quality moulded plastics and elastomers, electronics and electrical cleaners, lubricants and aircraft maintenance products), and household and personal care products (e.g. hairsprays, deodorants and anti-perspirants (Cohen and Pickaver, 1992). In addition, minor amounts of CFC-114 were used in medical applications (EPA, 1994a).

Halocarbon alternatives: regulated compounds

Because CFCs have been banned in the USA for some time, a wide variety of alternatives is available (Table 3-1). So far, HCFCs and HFCs have been used only to a limited extent as aerosol propellant, because CFCs and hydrocarbons are in general cheaper. Some of them can be mixed in blends with hydrocarbon propellants.

- *HCFC-22* is non-flammable and used in some blends to reduce the flammability of the aerosol propellant;
- *HCFC-142b* is flammable and therefore mainly used in blends.

Halocarbon alternatives: non-regulated compounds

Several HFCs can be used as aerosol propellant (EPA, 1994a). The most important may be HFC-134a and HFC-152a (DuPont, 1994). HFC-227ea has been mentioned as an alternative to CFC-12 and may also be used in metered dose inhalors. Aerosol propellants were mentioned as a potential market for the recently developed FICs, for which performance and toxicity tests are have not yet been performed (Nimitz, 1994c).

Non-halocarbon alternatives

About 90% of the aerosol market is expected to be taken over by non-halocarbon substitutes such as non-spray application, alternative spray dispension, compressed non-flammable gases as propellants, or other non-halocarbon propellants (Tables 3-9 and 3-11; mainly based on an estimate by the industry (Fay, 1995). They can, however, replace almost all CFCs. For every major application in the aerosols sector, a non-halocarbon alternative is available. An exception is the metered dose inhalors for asthmatic patients, although dry powder inhalors, nebulizers, mechanical pump sprays and non-inhalant methods can, at least partly, replace CFCs (Cohen and Pickaver, 1992). In addition, there may be industries where non-flammable, non-conductive aerosol propellants other than halocarbons are difficult to find. However, these are exceptions and probably do not comprise more than 5% of the market.

- *Alternative process.*
  - Non-spray application methods, such as roll-ons and sticks can be used instead of sprays. Deodorants and hair products are available nowadays in non-spray forms like gels or creams (Cohen and Pickaver, 1992).
  - Alternative spray dispension. Mechanical vaporizors, requiring no aerosol propellants, are available.
  - Powder inhalors and nebulizers. In medical applications dry-powder inhalors and nebulizers may avoid CFC use. Dry-powder inhalors contain the drug in powder form, which cannot be used by children under four years, nor by patients whose inspiratory flow is below a certain level. Nebulizers provide an air-propelled delivery system for inhalant drugs; the disadvantage of nebulizers is the relatively long inhalation time. Both dry-powder inhalors and nebulizers are relatively costly (Cohen and Pickaver, 1992).
- *Compressed non-flammable gases.* Compressed gases can be used instead of halocarbon aerosol propellants. For instance, carbon dioxide (CO_2), nitrogen (N_2) and air can be used (Cohen and Pickaver, 1992).
- *Other non-halocarbon propellants.* A number of non-halocarbon propellants is currently available: dimethyl ether (DME, CH_3OCH_3), methyl chloroform (CH_3CCl_3), propane, butane and isobutane. In the USA 85% aerosols used now are hydrocarbons.

3.2.1.2 AEROSOL SOLVENTS

Use before the Montreal Protocol

In aerosols most CFCs are used as propellants, but they can also be used as solvent when the product itself requires dissolving (Cohen and Pickaver, 1992). CFC-11, CFC-113 and 1,1,1 trichloroethane (or methyl chloroform, MCF) are the most widely used aerosol solvents.

Halocarbon alternatives: regulated compounds

- *HCFC-141b* or blends of HCFC-141b are already used as alternative solvents (EPA, 1994a) and could be used as substitutes.

Halocarbon alternatives: non-regulated compounds

- *HFCs.* HFC-4310mee is a recently developed compound that could be used as aerosol solvent. In the future other HFCs may be introduced which could be used as solvents.
- *PFCs.* One of the PFCs (C_6F_{14}) is mentioned as a solvent (EPA, 1994a).
- *Chlorinated solvents.* that could be used instead of CFCs or MCF include trichloroethylene, perchloroethylene and methylene chloride (EPA, 1994a). Monochlorotoluene could also be used.

Non-halocarbon alternatives

Non-halocarbon alternatives include:

- *Alternative processes*. There are many alternatives to the use of aerosol solvents. These are described in 3.2.2.
- *Water-based formulations*. Water-based formulations reduce the need for a halocarbon solvent.
- *Hydrocarbons*. Several hydrocarbons (petroleum) could be used.
- *Oxygenated organic solvents* that could be used instead of halocarbons include esters, ethers, alcohols and ketones (EPA, 1994a). Monochlorotoluene and benzotrifluorides could also be used.
- *Other* solvents that could replace halocarbons include terpenes and benzotrifluorides.

Table 3-1. Aerosols: possible alternatives to CFCs and 1,1,1 trichloroethane (MCF)

Aerosol propellants	CFC-11	CFC-12	CFC-114
Regulated halocarbon substitutes			
HCFC-22	x		
HCFC-142b	x		
Non-regulated halocarbon substitutes			
HFC-125	x		
HFC-134a	x		
HFC-143a			
HFC-152a	x		
HFC-227ea		x	
FICs	x	x	
Non halocarbon substitutes			
Alternative process			
- non-spray dispending	x		
- mechanical spray dispending/pump	x		
- dry-powder inhalors			x
- nebulizers			x
Compressed gas propellants	x		
Hydrocarbon propellants	x		
Dimethyl ether	x		

Aerosol solvent	CFC-11	CFC-113	MCF
Regulated halocarbon substitutes			
HCFC-141b	x	x	x
Non-regulated halocarbon substitutes			
HFC-4310mee	x	x	x
PFC (C_6F_{14})	x	x	x
Chlorinated solvents	x	x	x
Monochlorotoluene	x	x	x
Non halocarbon substitutes			
Alternative process	x	x	x
Water-based formulations	x	x	x
C6-C20 petroleum hydrocarbons	x	x	x
Oxygenated organic solvents	x	x	x
Terpenes	x	x	x
Benzotrifluorides	x	x	x

3.2.2 CLEANING

Use before the Montreal Protocol

Used mainly for solvent cleaning were CFC-113 and 1,1,1 trichloroethane (sometimes referred to as methylchloroform, MCF). Up until 1990 this was one of the fastest growing CFC markets. A commonly applied technique is vapour degreasing, in which CFC-113 can be used pure or in blends with methanol and trans-1,2-dichloroethylene/methanol.

CFC-113 and MCF were mainly used for (i) cleaning metals, involving mainly removal of cutting oils and residual metal filings by MCF, (ii) cleaning electronics, involving removal, mainly by CFC-113, of flux residues left after mounting parts on printed circuits boards and (iii) precision cleaning, using mostly CFC-113 in industrial cleaning operations, preparation of pacemakers, manufacture access storage devices (DASDs) for computers, etc. (EPA, 1994a; Table 3-2). Other cleaning applications include dry-cleaning of textiles or in hand or maintenance cleaning. CFC-11 is used incidentally as a cleaning solvent.

Halocarbon alternatives: regulated compounds

There are several HCFCs that can be used as alternative cleaning agents. HCFC-123, HCFC-141b and HCFC-225ca/cb will expectedly replace some CFC-113. These HCFCs can also be used in blends with methanol.

- *HCFC-141b*. HCFC-141b can be used pure or in blends as substitute for CFC-113 and MCF in vapour degreasing equipement, in particular for electronics or precision cleaning (EPA, 1994a; Lermond et al., 1989). For metal cleaning 100% HCFC cleaning agents may be the most suitable. In the US HCFC-141b was not allowed as solvent after 1995 because of its high ODP and because other alternatives exist (EPA, 1994a).
- *HCFC-123* has been mentioned as a cleaning agent, but it is so aggresive that the surface to be cleaned may be damaged (EPA, 1994a). It is therefore doubtful whether this HCFC will be used to a great extent.
- *HCFC-225ca/cb*. HCFC-225 may also replace part of the cleaning agents, especially for manufacture and maintenance of precision parts and equipment.

Halocarbon alternatives: non-regulated compounds

Non-regulated halocarbons with solvent properties include HFC-4310mee, PFCs, chlorinated solvents and dibromomethane (EPA, 1994a).

- *HFCs*. HFC-4310mee will become commercially available in the near future and can be used as cleaning agent. HFC-4310mee could also be used instead of PFCs (Dupont, 1994). There will probably be other HFCs suitable for cleaning purposes. Although so far none other than HFC-4310mee has been mentioned, it is likely that new HFCs may replace PFCs and HFC-4310mee in the future.
- *PFCs*. Several PFCs are used or investigated for use as cleaning agents: C_5F_{12}, C_6F_{12}, C_6F_{14}, C_7F_{16}, C_8F_{18}, $C_5F_{11}NO$, $C_6F_{13}NO$, $C_7F_{15}NO$, and C_8F_{16} (EPA, 1994a). PFCs are already used as drying agents, but also have solvent properties and can therefore replace CFC-113. PFCs could be used after aqueous cleaning in a rinsing/drying step. PFCs are in general more expensive than other substitutes. In the US use of PFCs is allowed only in applications where other substitutes cannot provide the required performance or safety requirements.
- *Chlorinated solvents*. Other halocarbons that could be used for cleaning include chloroform, trichloroethylene (TCE), methylene chloride and perchloroethylene, while monochlorotoluene and benxotrifluorides are being investigated. These are all toxic compounds. Trichloroethylene

(TCE), methylene chloride, and perchloroethylene used to be first choice cleaners in industries, but were replaced by MCF for toxicity reasons. A phase-out of MCF may result in renewed interest. Adaptation in equipment may reduce emissions and improve the acceptability of toxic compounds to be used (EPA, 1994a).

- *Dibromomethane.* Dibromomethane (CH_2Br_2) is a non-regulated compound with an ODP of 0.17 (EPA, 1994a); it can be used as solvent.
- *FICs.* Cleaning was mentioned as a potential market for the recently developed FICs (Nimitz, 1994c). However, their performance and toxicity need to be tested.

Non-halocarbon alternatives

It is expected that more than 95% of CFCs and CH_3CCl_3 (MCF) used as solvent will be replaced by non-halocarbons (Tables 3-9 and 3-11). The remaining small market are niche use of HCFCs, HFCs and PFCs for medical implants, sensitive aerospace components and drying high quality optics (Fay, 1995). Thus non-halocarbons have the technical potential to replace virtually all CFCs and MCF. Use of cleaning agents can be reduced considerably, in some applications by up to 80% of the pre-Montreal Protocol use, by good housekeeping, recycling and equipment modification. In addition, process modification may make a cleaning step unnecessary. If a cleaning agent is needed, several non-halocarbon cleaning agents are available for aqueous, semi-aqueous and non-aqueous cleaning.

- *No-clean alternatives.* Process changes may make a cleaning step unnecessary. Fluxes or oils could be used that leave none, or only water-soluble residues to be removed. This is increasingly applied in metal preparation and electronics.
- *Aqueous cleaning.* Water can be used as primary solvent in many cleaning operations. In metal cleaning it is increasingly applied, but aqueous cleaning can be more widespread (EPA, 1994a). Usually detergents, surfactants or other additives are used in combination with water. The cleaning process includes a washing, rinsing and drying phase. The water is usually heated.
- *Semi-aqueous cleaning.* Semi-aqueous cleaners can be used in most applications where CFC-113 and MCF were used (EPA, 1994a). In semi-aqueous cleaning terpenes, C6-C20 petroleum hydrocarbons, or oxygenated organic solvents such as alcohols are emulsified in water, or applied in a concentrated form and rinsed with water. These mixtures could be used as drop-in substitutes. In general, they show good performance and are now available (Dishart and Wolff, 1990).
- *Organic solvents.* The following non-aqueous cleaning agents can be used to replace CFC-113 and MCF: alcohols, ethers (including propylene glycol ethers), esters, ketones, terpenes and synthetic or natural C6-C20 petroleum hydrocarbons. Most of these are organic compounds with short atmospheric lifetimes, contributing to formation of tropospheric (smog) ozone. Several of them are toxic, for instance, xylene and toluene (EPA, 1994a).
- *VMSs.* Volatile methyl siloxanes (VMSs) are being investigated for replacement of CFC-113 and MCF in metals, electronics and precision cleaning. They seem promising substitutes for use in defense and the aerospace industry. VMSs are easily recovered and recycled, because they have a high purity (EPA, 1994a).
- *Ultrasonic cleaning.* Sound waves could be used in combination with a heated water-based cleaner, for instance, as an alternative to a solvent vapour degreaser using CFC-113. Ultrasonic cleaning of stainless steel was found to be equally efficient as the CFC system, but cheaper. The payback period in an evaluation project was 1.6 years (Kranz et al., 1994).
- *Other.* Supercritical fluid cleaning, plasma cleaning and UV-ozone cleaning are high technology methods (EPA, 1994a). Ozone water could be an alternative to CFCs used in dry cleaning.

Table 3-2. Cleaning: possible alternatives to CFCs and 1,1,1, trichloroethane (or methylchloroform, MCF); mainly from EPA (1994a)

Cleaning	Metal cleaning (CFC-113/MCF)	Electronics cleaning (CFC-113/MCF)	Precision cleaning (CFC-113/MCF)
Regulated halocarbon substitutes			
HCFC-123			x
HCFC-141b	x	x	x
HCFC-225ca/cb			x
Non-regulated halocarbon substitutes			
HFC-4310mee		x	x
PFCs		x	x
chlorinated solvents	x	x	x
dibromomethane	x	x	x
FICs	x	x	x
Non halocarbon substitutes			
no-clean alternatives	x	x	x
aqueous cleaning	x	x	x
semi-aqueous cleaning	x	x	x
organic solvents	x	x	x
VMSs	x	x	x
other	x	x	x

3.2.3 FOAM BLOWING

3.2.3.1 CUSHIONING AND PACKAGING (open foams)

Use before the Montreal Protocol

Foams for cushioning (polystyrene, polyolefin) and packaging (polyurethane or PUR, polyolefin) have an open structure from which the blowing agents leak quickly. Before the Montreal Protocol CFC-11 was mainly used for flexible polyurethane and polyurethane skin. In addition, minor amounts of of CFC-12 (polyolefin, polystyrene extruded sheet) and CFC-114 (polyolefin) were also used. Most substitutes for blowing agents that are flammable or toxic require process modifications in order to ensure safety of workers and consumers.

Halocarbon alternatives: regulated compounds

Halocarbons are not expected to be major substitutes for CFCs in cushioning and packaging. Expectedly less than 5% of the CFCs previously used will be replaced by fluorocarbons (Fay, 1995). The following HCFCs were expected to be mainly used for cushioning (Table 3-3).

- *HCFC-123 and HCFC-141b* or blends containing these HCFCs can be used as substitutes for CFC-11 in blowing polyurethane integral skin. HCFC-22 and CFC-142b could also be a substitute for CFC-11, although they have lower boiling points than CFC-11, which makes investments in technical and process modifications necessary.
- *HCFC-22 and HCFC-142b* or blends containing these HCFCs could be used to replace CFC-12 in blowing polyolefin foams.

Halocarbon alternatives: non-regulated compounds

So far, no HFCs have been used for foam blowing. However, there are some possibilities.

- *HCFC-152a and HFC-134a.* HFCs may be applicable as blowing agents instead of CFC-11, but their use requires significant changes in the foam formulation or processes. HCFC-152a and HFC-134a could be considered short- or intermediate-term substitutes for CFC-12 in extruded polystyrene (EPA, 1994a). The flammability and toxicity of HFC-152a may, however, require investments to ensure that workers and consumers are not exposed to high concentrations.
- *HFC-143a and HFC-125* are also considered as future alternatives (EPA, 1994a; Dupont, 1994).
- *Methylene chloride.* This is a commercially available substitute for CFC-11 in flexible polyurethane. It is cheap, but toxic (EPA, 1994a).
- *FICs* are being tested as foam blowing agents (Nimitz, 1994b). For foam blowing CF_3I and $CF_3CF_2CF_2I$ seem most promising. They could be used pure or in blends with flammable agents such as acetone, isobutane, dimethyl ether, pentane or 1,1-difluoroethane. Their performance and toxicity need to be investigated.

Non-halocarbon alternatives

Non-halocarbon alternatives, in particular hydrocarbons and water/CO_2, will expectedly take over at least 98% of the market (Tables 3-9 and 3-11; mainly based on Fay, 1995).

- *Alternative materials.* For packaging a variety of non-foam alternatives is available, such as paper, cardboard and expanded polystyrene. In addition, fiberfill, natural latex foams or polyester batting may be alternatives to flexible polyurethane foam (EPA, 1994a).
- *Alternative processes.* Flexible polyurethane could be blown with so-called "AB technology", in

which formic acid is used in combination with water. Alternatively, flexible polyurethane could be blown in the Enviro-Cure process in development and the electroset process (in development) may be used for foam blowing (EPA, 1994a).

- *Saturated light hydrocarbons C3-C6.* Light hydrocarbons are already used in foam blowing, and can be applied for most foams, with the exception of flexible polyurethane (EPA, 1994a). Cyclopentane has physical properties that resemble CFC-11 in many ways, and is therefore a leading alternative blowing-agent candidate (EPA, 1994a). Hydrocarbons are flammable.
- *Carbon dioxide (CO_2).* CO_2 or blends thereof can be used in all foams in cushioning and packaging.
- *Aceton.* Acetone is a commercially available substitute for CFC-11 in flexible polyurethane and can be used instead of methylene chloride (EPA, 1994a).
- *2-Chloropropane.* This compound could replace CFC-11 in polyurethane integral skin.

3.2.3.2 INSULATION (closed foams)

Use before the Montreal Protocol

Insulation foams include polyurethane (PUR), polystyrene, phenolic insulation boards and polyolifin, and were prior to the Montreal Protocol blown with CFCs. Of these CFC-11, used for polyurethane foam and phenolic insulation board, was the most important. In addition CFC-12 was used for polystyrene foam and polyolefin, CFC-113 for phenolic insulation boards, and CFC-114 for polyolefin.

Halocarbon alternatives: regulated compounds

It is expected that a major part of the CFCs used as blowing agents for insulation foams will be replaced by HCFCs and HFCs (Table 3-3). Major substitutes will be HCFC-123 and HCFC-141b.

- *HCFC-123 and HCFC-141b* or blends thereof can replace CFC-11 in all polyurethane foams (EPA, 1994a).
- *HCFC-22 and HCFC-142b* or blends thereof can also replace CFC-11 in most polyurethane foams. Because of differences in boiling points process modifications may be needed. These HCFCs can also replace CFC-12 in polystyrene, extruded boardstock and billet (EPA, 1994a), and CFC-11 and CFC-113 in phenolic insulation board.

Halocarbon alternatives: non-regulated compounds

Some HFCs may be applicable as blowing agents in the near future.

- *HFC-152a and HFC-134a.* These HFCs could replace CFC-11 in polyurethane foams, CFC-12 in polystyrene, extruded boardstock and billet (EPA, 1994a). These may be the most widely used HFCs in foam blowing during the coming decades (DuPont, 1994).
- *HFC-143a* can replace CFC-11 and CFC-113 in phenolic insulation board.
- *HFC-356 and HFC-245ca.* These presently not yet commercially available HFCs, may become important blowing agents in the future (DuPont, 1994).
- *2-Chloropropane.* This compound could be used instead of CFC-11 in polyurethane and CFC-11 and CFC-113 in phenolic insulation board.
- *FICs* may replace CFCs and HCFCs insulation foam (Nimitz, 1994b). CF_3I and $CF_3CF_2CF_2I$ seem most promising and could be used pure or in blends with flammable agents such as acetone, isobutane, dimethyl ether, pentane or 1,1-difluoroethane. It was calculated that FICs have better insulation properties than CFCs and HCFCs. This has to be verified in tests. Also their toxicity needs to be investigated (Nimitz, 1994b).

Non-halocarbon alternatives

About half of the CFCs used for insulation foam blowing may be replaced by non-halocarbon alternatives (Tables 3-9 and 3-11; mainly based on Fay, 1995). Their technical potential is, however, much higher. Vacuum panels and aerogels are attractive alternatives, with extremely high insulation properties (Geuzendam and Gilijamse, 1994). Once these become available, which in some applications may be this year, the technical potential of non-halocarbons to take over the market may be 90-100%. But also presently the potential of non-halocarbons is high.

- *Alternative materials.* The following products could be used for insulation instead of foams (EPA, 1994a):

Currently used foam:	Alternative material:
polyurethane	expanded polystyrene, fiberboard, fiberglass
polyisociarunate	expanded polystyrene, fiberboard, fiberglass
rigid laminated boardstock	expanded polystyrene, fiberboard, fiberglass
rigid polyurethane	fiberglass, vacuum panels
appliance foams	fiberglass, vacuum panels
rigid slabstock	fiberglass, expanded polystyrene
rigid pray	fiberglass, expanded polystyrene
commercial refrigeration foams	fiberglass, expanded polystyrene
sandwich panels	fiberglass, expanded polystyrene
phenolic foam	fiberglass, expanded polystyrene
polystyrene	expanded polystyrene, fiberboard
extruded boardstock and billet	expanded polystyrene, fiberboard
polyolefin	paper, cardboard, expanded polystyrene

- *Alternative processes.* Electroset process in development (EPA, 1994a)
- *Saturated light hydrocarbons C3-C6.* These could replace CFCs in all types of foam that are used for insulation (EPA, 1994a).
- *Carbon dioxide (CO_2).* CO_2 also could replace CFCs in all types of foam that are used for insulation (EPA, 1994a).

Table 3-3. Blowing agents: possible alternatives to CFCs

Cushioning, packaging	CFC-11 flexible PUR	CFC-11 PUR integral skin	CFC-12 polystyrene	CFC-11/12/114 polyolefin
Regulated halocarbon substitutes				
HCFC-22		x		x
HCFC-123		x		
HCFC-141b		x		x
HCFC-142b				x
Non-regulated halocarbon substitutes				
HFC-134a	x	x	x	x
HFC-152a	x	x	x	x
HFC-143a				x
Methylene chloride	x	x		x
2-Chloropropane	x	x		
FICs	x	x	x	
Non halocarbon substitutes				
Alternative product	x	x	x	x
Alternative process	x			
Hydrocarbons C3-C6		x	x	x
CO_2	x	x	x	x
Aceton	x			

Insulation	CFC-11 PUR	CFC-12 polystyrene	CFC-11/-113 phenolic board	CFC-11/-12/-114 polyolefin
Regulated halocarbon substitutes				
HCFC-22	x	x	x	x
HCFC-123	x			
HCFC-124		x		
HCFC-141b	x		x	x
HCFC-142b	x	x	x	x
Non-regulated halocarbon substitutes				
HFC-134a	x	x		x
HFC-152a	x	x		x
HFC-143a		x	x	x
HFC-356	x			
HFC-245ca, -236fa	x			
2-chloropropane	x		x	
FICs	x	x		
Non halocarbon substitutes				
alternative product	x	x	x	x
alternative process				
hydrocarbons C3-C6	x	x	x	x
CO_2	x	x	x	x

3.2.4 REFRIGERATION AND AIRCONDITIONING

CFCs were originally developed as safe cooling agents. In 1960 about 60% of the CFCs were used in refrigeration worldwide. This number dropped to less than 30% in the late 1980s. In 1987 more than 250 kton of CFCs were used worldwide as cooling agents of which about 40% in mobile airconditioning, about 10% in stationary airconditioning and about 50% in other refrigeration. Less than 3% is used in household refrigerators (AFEAS, 1993). It is expected that in the future most halocarbons will be used as cooling agents (DuPont, 1994; McCulloch, 1994a,b).

As in many other applications, refrigeration systems were not developed to be closed systems. There was no need to avoid leakage of cooling agents at any cost: CFCs were cheap, non-toxic and non-flammable. Leakage control could reduce demand for cooling agents substantially. Substitutes are not seldomly toxic or flammable, which makes leakage control more urgent. Demand for cooling agents is growing at a rate of 3 - 4% per year in industrial countries and 6 - 8% in developing countries.

In this study three types of refrigeration systems are distinguished: (i) refrigeration (excluding airconditioning), (ii) stationary airconditioning and (iii) mobile airconditioning. There are many alternatives to CFC refrigerants available, ranging from other halocarbons to alternative cooling techniques. The German Federal Authority of the Environment formulated a hierarchy of refrigerants based on their environmental impact, in which non-halocarbon refrigerants are to be preferred over halocarbon refrigerants. For non-halocarbons the hierarchy is as follows:

1. Natural substances
2. Hydrocarbons
3. Alcohol, ketone, ester
4. Terpene, ammonia

3.2.4.1 REFRIGERATION (excluding airconditioning)

Use before the Montreal Protocol

CFC-12 used to be the most widely used cooling agent. In addition, CFC-11 and a blend of CFC-12 and CFC-115 (R-502) are used. Most of the cooling agents are used in storage and retail.

- Cold storage warehouses used to store meat, produce, dairy products and other perishable goods. Ammonia is also widely used as refrigerant in storage.
- Retail food refrigeration, chilling or freezing food for commercial sale (including store reach-in counters and restaurant walk-in refrigerators).

Other refrigerator applications include (from EPA, 1994a):

- Industrial process refrigeration. In industries a wide variety of refrigerators operating at different temperatures are being used.
- Ice-skating rinks for recreational use.
- Uranium isotope separation processing, which needs a cooling step.
- Refrigerated transport, including refrigerated shipholds, truck/lorry trailers, railway freight cars and other shipping containers.
- Vending machines, from which chilled or frozen goods are sold.
- Water coolers, providing chilled water for drinking.
- Commercial ice machines, which are used to make ice for consumption.
- Household refrigerators with or without freezing compartment.
- Household freezers, used for freezing only.

The cooling technique most applied is a mechanical system using a vapor compression cycle, in which an electrically driven pump is used for compression and expansion of a gas, as a result of which heat is transferred during condensation and evaporation. There are alternative techniques available which have been used for decades (see below).

There are many alternatives to refrigerants, but not all alternatives can be used for all end-uses. Thus if in Table 3-4 is shown that HCFC-22 can be used in industrial process refrigeration, it does not mean that HCFC-22 can replace CFCs in all industrial processes. Since CFCs are non-toxic, non-flammable and cheap, leakage never was a serious problem. Flammable or toxic refrigerants may not be suitable substitutes in all present equipment, but with few technical modifications this may change.

The CFCs used until recently have specific cooling properties. With the exception of household refrigerators, cooling systems show considerable leakage, so that regular refilling is needed. Since less than 3% of the cooling agents are used in household refrigerators, a phase-out of CFC refrigerants makes a drop-in substitute desirable for existing equipment that cannot be retrofitted. As shown in Table 3-4, there are many alternative cooling agents available. However, most of these have slightly different cooling properties, which does not always make them suitable as drop-in substitute. Therefore, several blends containing HCFCs, HFCs or hydrocarbons have been composed that are mixed so that they are suitable drop-in substitutes.

Halocarbon alternatives: regulated compounds

In refrigeration HCFC-22 and HCFC-124 can be used instead of CFCs. In order to resemble the properties of CFC cooling agents, in a number of appliances blends containing these HCFCs are preferred. The blend names in Table 3-4 are adopted from EPA (1994a).

- *HCFC-22.* HCFC-22 can be used to replace CFC-11, CFC-12 and R-502 most cooling systems. In water coolers and ice machines use of HCFC-22 requires hardware adjustment. For many users HCFC-22 is a first-choice CFC substitute.
- *Blends R-401A and R401B.* These blends contain HCFC-22, HCFC-124 and HFC-152a and are

non-flammable and near azeotrope. They can be used to replace CFCs in many cooling systems.

- *Blends R-402A and R402B.* These blends contain HCFC-22, HFC-125 and propane, and are non-flammable and near azeotropes. They can be used in industrial process refrigeration, cold storage warehouses, refrigerated transport, retail food refrigeration and ice machines.

Halocarbon alternatives: non-regulated compounds

Non-regulated halocarbon alternatives to refrigerants include HFCs, blends of HFCs, PFCs and chlorine.

- *HFCs.* The most important HFCs will probably be HFC-134a, -143a, -125, -152a, and -23 (DuPont, 1994). In most refrigeration systems HFC-134a can replace CFCs. Ice machines need to be adjusted before HFC-134a can be used. HFC-152a has cooling properties that resemble those of CFC-12 and is therefore suitable for many systems now using CFC-12. However, it is a flammable component. From an energy point of view HFC-152a is probably the best of the HFC refrigerants (Devotta et al., 1993). HFC-227ea may replace some CFC-12 in industrial process refrigeration, cold storage warehouses and retail food refrigeration.
- *Blends R-404A and R404B.* These blends contain HFC-125 and HFC-134a, and are non-flammable and azeotropes. R-402A can be used in industrial process refrigeration, cold storage warehouses, refrigerated transport, retail food refrigeration and ice machines.
- *Blend R-507.* This blend contains HFC-125, HFC-134a and HFC-143a, and is non-flammable and near azeotrope. R-507 can be used in industrial process refrigeration, cold storage warehouses, refrigerated transport, retail food refrigeration and ice machines.
- *PFCs.* PFCs can replace CFC-114 in uranium isotope separation processing. This process requires a refrigerant with specific requirements, which the PFCs listed below in Table 3-4 fullfil. According to the US EPA (1994a) there are no other suitable alternatives to this application.
- *Chlorine.* Chlorine is a highly reactive chemical that could be used as cooling agent. In refrigeration in industries where chlorine is processed, chlorine could be used as refrigerant.
- *FICs.* First test results have demonstrated that blends containing FICs could be used as drop-in substitutes for CFC-12 in a household refrigerator. Based on theoretical considerations, blends have been mentioned as potential substitutes for CFCs: Ikon-12C (HFC-152a and CF_3I) for CFC-12 and Ikon-22a (HFC-152a, HFC-134a, and CF_3I) for HCFC-22 (Nimitz, 1994a). The blends contain 30 - 50% (volume) FIC. Both performance and toxicity need to be tested.

Non-halocarbon alternatives

It is expected that, on the global level, most of the cooling agents will remain halocarbons. Nevertheless, the market may decrease by about 25% between 1986 and 2000, because it is expected that due to equipment modification the charges in refrigerators will decrease (Fay, 1995; see Tables 3-9 and 3-11). Non-halocarbons will, for instance, be used in European household refrigerators (hydrocarbons). The technical potential of non-halocarbon refrigerants is much higher. If hydrocarbons were widely accepted as cooling agents, probably 90-100% of the cooling agents could be replaced by non-halocarbons. The need for cooling agents could be reduced by alternative cooling techniques, improved leakage control, or by better housekeeping and recycling. Leakage control not only reduces the amount of cooling agent needed, it also facilitates the introduction of cooling agents that are flammable or toxic. In addition there are a wide variety of non-halocarbon cooling agents available: NH_3, hydrocarbons (propane, butane, isobutane), CO_2, water and air. Some were commonly used before CFCs were available.

- *Alternative cooling techniques.* Cooling techniques that would reduce the need for halocarbon cooling agents include the following alternatives to vapour compression:
  - Evaporative cooling uses water evaporation as a means of cooling. In direct cooling, water is

directly evaporated into the air stream. In indirect cooling, primary air is cooled sensibly with a heat exchanger generating vapour, which is carried away by secondairy air (UNEP IE, 1994). Currently, evaporative cooling is most widely used in airconditioning and cooling towers which remove waste heat (Cohen and Pickaver, 1992). It could be applied more widespread in cold storage warehouses and industrial applications, for instance (EPA, 1994a; UNEP IE, 1994).

- Desiccant cooling uses a desiccant, for instance lithium bromide, to make evaporative cooling possible in high humidity areas (Cohen and Pickaver, 1992).
- The Stirling Cycle, in which heat transfer is accomplished through compression and expansion of a gas without changing its physical state; there is no evaporation and condensation. Helium is the usual refrigerant, but hydrogen could also be used. The Stirling Cycle is extremely efficient and could use waste heat as a source of energy. It has been applied in refrigerated transport and cryogenics. It could be applied in most other applications because it has a wide range of temperatures (Cohen and Pickaver, 1992; EPA, 1994a). Helium-based Stirling cycle systems could enter the market in the short term (Cohen and Pickaver, 1992; EPA, 1994a). However, UNEP IE (1994) doubts whether Stirling Cycle cooling will be commercially available in applications such as household refrigerators before the year 2000.
- Gas expansion can be used for cooling when a pre-cooled liquid (e.g. CO_2 or N_2) is sprayed into a refrigerated area. Cooling results from evaporation of the liquid. Direct gas expansion is currently used in refrigerated transport and the food industry (UNEP IE, 1994).
- Absorption refrigeration uses a pair of refrigerants. It differs from vapour compression in that high pressures are obtained by heating instead of compressing, so that no electricity is used. In absorption refrigeration usually two compounds are used (e.g. ammonia/water or lithium bromide/water), of which one is the refrigerant and the other the absorber. Absorption systems are currently used for food preservation, industrial processes, cold storage, in mobile homes, hotel rooms, minibars and hospitals (UNEP IE, 1994). Absorption systems can use waste heat as a source of energy.
- Adsorption refrigeration, in which cooling is achieved when a refrigerant attaches to a solid medium. Hygroscopic materials which attracts water, for instance, can be used. The water (refrigerant) can be desorbed from the solid (e.g. natural zeolite) by heating under high pressure (UNEP IE, 1994). Adsorption systems can use waste heat. They could be used as mobile coolers and domestic refrigerants (Cohen and Pickaver, 1992). UNEP IE (1994) does not expect commercialization before the end of this century.
- Air cycle. Air can be used as refrigerant or heater because the air temperature drops while expanding and rises while compressing. The air cycle could be used in transport trucks and railway refrigeration (UNEP IE, 1994).
- Thermoelectric and magnetic cooling. When an electric current is passed through a semi-conductor, heat is produced at one junction and cooling at another (UNEP IE, 1994). Heat can also be removed from objects in a magnetic field using superconductors (UNEP IE, 1994). Thermoelectric cooling is available for car cooling, small pieces of biomedical equipment and fiber optic techniques, but it could be applied more widespread in refrigeration and freezing.
- Thermoacoustic cooling. Sound waves could cool gases such as HFCs, hydrocarbons or helium (UNEP IE, 1994). This technology needs further development.

- *Water.* Water can be used in a vapour compression cycle when it is kept below atmospheric pressure (Cohen and Pickaver, 1992). The volume of water needed is larger than the volume of halocarbons needed. Water vapour compression is already applied in district heating and mine-tunnel cooling.
- *Ammonia (NH_3).* Ammonia is an efficient refrigerant and has been long used in larger vapour compression cooling systems, although it is moderately flammable and toxic. It has been used in household refrigerators in the past (Cohen and Picakver, 1992). Nowadays ammonia is used in many food processing and industrial applications (EPA, 1994a) and it is expected that it will replace CFCs in other applications as well. A double circuit with, for instance, glycol could

reduce the risks of leakage.

- *Hydrocarbon cooling agents.* Several hydrocarbons can be used as cooling agents in a vapour compression cycle: propane (R290), propylene, butane (R600) and isobutane. They can be used in almost all cooling appliances and in several as drop-in substitutes to CFCs. Hydrocarbon refrigerants have a number of advantages over halocarbons: (i) low costs, (ii) zero ozone-depleting potential and low global warming potential, (iii) in general, the charge is reduced by 50% when switching from halocarbons to hydrocarbons, (iv) hydrocarbons are in general more energy efficient and (v) the decomposition products of hydrocarbons are less toxic than of halocarbons.

  Household refrigerators using propane and butane are now commercially available. Propane/butane (R290/R600) blends can be used as drop-in substitutes for CFC-12. Household refrigerators may be up to 6% more energy efficient when instead of CFC-12 a blend containing 70% propane and 30% butane is used, with the only adaptation of the refrigerator being an additional capillary tube length of about 150 cm (Liu et al., 1994). Additional changes in the hardware could raise the energy savings to 10% (Liu et al., 1994).

  One disadvantage of hydrocarbons is their flammability, but in Europe it is nowadays generally accepted that, at least in household appliances, the risks involved are acceptably low. The amount of propane or butane used in a household refrigerator is in general so small (less than 100 g), that a flammable mixture is unlikely to be created in the room as a result of leakage (Richardson, 1994). Using a flammable refrigerant (HFC-152a) instead of CFC-12 in a household refrigerator increases the risk of kitchen fire by 0.04% (Liu et al., 1994). The risks of leakage inside the refrigerator can be reduced by designing the system such that it never runs at sub-atmospheric pressure (Richardson, 1994). James and Missenden (1992) performed a fire test and concluded that in the case of fire the propane/butane in a household refrigerator would not noticeably add to the conflagration. The lubricants, however, contributed to the severity of the fire. These are flammable oils that are used in both CFC-12 and propane/butane refrigerators. Richardson (1994) argues that in the case of fire the risk is not so much ignition of the cooling agent, but explosion of the system as a result of increased pressure; this is not influenced by the type of cooling agent used. He furthermore points out that a hydrocarbon refrigerant may even be safer in case of fire, because of the toxicity of the breakdown products of halocarbons. Furthermore, the insulation panels in refrigerators are often filled up with pentane, which is not considered a problem while they may contain 5 times as much flammable hydrocarbon as the cooling agent in the unit (Strong, 1994).

  Household refrigerators are the only cooling systems that may be regarded closed systems. Larger refrigerators usually have more leakage. Nevertheless also in larger systems hydrocarbons may be used as cooling agents, for instance in industrial coolers (Cohen and Pickaver, 1992).

- *Fluoroiodocarbons (FICs).* Iodine-containing chemicals, fluoroiodides, have recently been mentioned as substitutes for CFCs. FICs could be used pure or in blends. A blend of trifluoromethyl iodine (a FIC) and HFC-152a could be used as a drop-in substitute for CFC-12.

Table 3-4. Refrigeration (excl. airconditioning): possible alternatives to CFC-12, R-502 and CFC-11) R = Retrofit, N = New equipment/Not in kinds (mainly from EPA, 1994a)

	industrial process refrig.[3,4]	ice skating rinks[3]	uranium istotope separation	cold storage warehouses[3]	refrige-rated transport[3]	retail food refrig[3]	vending machines [3]	water coolers[3]	commer-cial ice[3] machines	household refrig.[2,3]	household freezers[3]
Regulated halocarbon substitutes											
HCFC-22	R,N	R,N		R,N	R,N	R,N	R,N	N	N	R,N	R,N
HCFC-124											
R401A: HCFC-22,-124, HFC-152a	R	R		R	R	R	R	R	R	R	R
R401B: HCFC-22,-124, HFC-152a	R	R		R	R	R	R	R	R	R	R
R402A: HCFC-22, HFC-125, propane	R,N			R,N	R,N	R,N			R,N		
R402B: HCFC-22, HFC-125, propane	R,N			R,N	R,N	R,N			R,N		
Blend alpha: HCFC-22,-142b										R,N	
Non-regulated halocarbon substitutes											
HFC-125											
HFC-134a	R,N	R,N		R,N	R,N	R,N	R,N	R,N	N	R,N	R,N
HFC-143a											
HFC-152a										N	N
HFC-227ea	N			N		N					
R404A: HFC-125,-143a	R,N			R,N	R,N	R,N			R,N		
R404B: HFC-125,-143a											
R507: HFC-125,-134a,-143a	R,N			R,N	R,N	R,N			R,N		
PFCs			R[1]								
Chlorine	R,N										
Ikon 12c: HFC-152a, CF_3I				N	N					N	
Non-halocarbon substitutes											
Alternative process											
- evaporative cooling	N			N							
- desiccant cooling	N			N							
- stirling cycle	N			N	N	N	N	N	N	N	N
- direct gas expansion (N_2, CO_2)				N	N						
- absorption	N			N		N				N	N
- adsorption					N					N	
- air cycle					N						
- thermoelectric / magnetic	N										
- thermoacoustic											
Water											
NH_3	R,N	R,N		N		N			N		
Hydrocarbons	R,N	R,N		R,N	R,N	R,N	R,N	R,N	R,N	R,N	R,N

[1] C_4F_8, C_4F_{10}, C_5F_{12}, C_6F_{14}, or $C_5F_{11}NO$; [2] EPA mentions R200b, a flammable blend of confidential composition as substitute for new equipment; [3] a blend of CFC-12, HCFC-22 and HCFC-142b could also be used; [4] in industrial process cooling some CFC-11 is used

3.2.4.2 STATIONARY AIRCONDITIONING

Use before the Montreal Protocol

In stationary airconditioning CFC-11 is the most common cooling agent, but CFC-12, CFC-113, CFC-114, R-500 and R-502 are also used (Table 3-5). Stationary airconditioning includes (from EPA, 1994a):

- Commercial comfort airconditioning (CFC-11, -12, -113, -114, R-500). Mechanical commercial comfort airconditioning, or chillers (cool water which is circulated through a building).
- Residential airconditioning and heat pumps (CFC-114, R-502). In most residential airconditioning and heat pumps usually HCFC-22 is used.
- Residential dehumidifiers (CFC-12, R-500). Dehumidifiers are meant to remove water vapour from air. In comfort airconditioning, the air is usually dried while cooling. When the purpose is only to dehumidify, the air is heated after condensation.
- Industrial process airconditioning (CFC-11, -12, -113, -114, R-500). In plants sometimes temperatures of 100 °C prevail. In order to keep working temperatures low enough, powerful airconditioning systems are needed.
- Heat transfer (CFC-11, -113, 114), including cooling systems that remove heat from an area by convection. Recirculating coolers use fluid pumps and thermosiphons use natural convection.

Halocarbon alternatives: regulated compounds

- *HCFC-22*. HCFC-22 can replace CFC-11, -12, -113, -114 and R-500 in new chillers for comfort airconditioning (EPA, 1994a). It is also used in heat pumps.
- *HCFC-123*. HCFC-123 can be used as drop-in substitute for CFC-11 in chillers. In new equipment HCFC-123 can also be used instead of the other CFCs currently used in centrifugal chillers (EPA, 1994a).
- *HCFC-124*. HCFC-124 can be used instead of CFC-114 in chillers and industrial process airconditioning. In new equipment HCFC-124 can be also used instead of the other CFCs used in centrifugal chillers (EPA, 1994a).
- *HCFC-141b*. HCFC-141b can replace CFC-11 in centrifugal chillers.

Halocarbon alternatives: non-regulated compounds

- *HFC-32* can be used in heat pumps instead of HCFC-22.
- *HFC-134a*. In existing chillers CFC-12 and R-500 can be replaced by HFC-134a. In new chillers HFC-134a can replace all other CFCs as well in chillers. It could also be used in heat pumps instead of HCFC-22 (EPA, 1994a)
- *HFC-152a* can be used in heat pumps instead of HCFC-22.
- *HFC-227ea* is a possible substitute for CFCs currently used in new chillers for comfort airconditioning. It can also be used instead of CFC-12 and CFC-114 in heat pumps.
- *HFC-125/-134a/-32* could be used in heat pumps instead of HCFC-22.
- *PFCs*. PFCs can be used instead of CFCs in recirculating coolers and thermosyphons (heat transfer by convection) (EPA, 1994a). These include perfluoropropane, perfluorobutane, perfluoropentane, perfluorohexane, perfluoroheptane, perfluorooctane, perfluoro-N-methyl morpholine, perfluoro-N-ethyl morpholine and perfluoro-N-isopropyl morpholine.
- *FICs*. Based on theoretical condiderations, three blends have been mentioned as potential substitutes for CFCs: Ikon-11A (diethyl ether and $CF_3(FF_2)_2I$) for CFC-11, Ikon-12C (HFC-152a and CF_3I) for CFC-12 and Ikon-22a (HFC-152a, HFC-134a and CF_3I) for HCFC-22 (Nimitz, 1994a). The blends contain 30 - 50% (volume) FIC. Both performance and toxicity

need to be tested.

Non-halocarbon alternatives for regulated compounds

Halocarbons will also be the major substitutes for CFCs in airconditioning. Nevertheless, there are many non-halocarbons available.

- *Alternative cooling techniques.* There are several alternatives to the usual vapour compression cooling cycle. The different techniques are described in 3.2.4.1 (refrigeration). Alternative technologies for airconditioning include:
  - Evaporative cooling using water evaporation. Currently, evaporating cooling is widely used in desert climates, where it performs best because of the low humidity. However, it could be applied more widespread in residential applications (UNEP IE, 1994).
  - The Stirling Cycle can be applied in space conditioning, but is currently not commercially available (UNEP IE, 1994).
  - Adsorption refrigeration, using, for instance, zeolite and water can be used for residential-size heat pumps. UNEP IE (1994) does not expect commercialization before the end of this century.
  - Air cycle. Air can be used as refrigerant in airconditioning (UNEP IE, 1994).
  - Absorption refrigeration. Ammonia/water and water/lithium bromide absorption systems could be used instead of CFC chillers in comfort airconditioning (EPA, 1994a).
  - Desiccant cooling could replace chillers for comfort airconditioning (EPA, 1994a). In this process a desiccant (e.g. lithium bromide) allows evaporative cooling in high humidity areas (Cohen and Pickaver, 1992; Heat Transfer Holland 1994).
- *Ammonia vapour compression.* Ammonia vapour compression systems can replace all CFC-chillers currently used (EPA, 1994a).
- *Hydrocarbons.* Hydrocarbon blends can replace CFC-11, -12, -113, -114 and R-500 in chillers and CFC-12 and R-500 in residential dehumidifiers (EPA, 1994a). Propane (R290) and propene (R1270) can be used as drop-in substitutes for HCFC-22 and R-502 in heat pumps (Frehn, 1994). Frehn (1994) found that in heat pumps hydrocarbons can have better performance than the currently used halocarbons and that safety risks can be substantially reduced by adopting the appropriate technical precautions.

Table 3-5. Stationary airconditioning (AC): possible alternatives to CFCs; R = Retrofit, N = New equipment/Not in kinds (mainly from EPA, 1994a); U = uncertain

	Commercial comfort AC[1]	Residential AC/heat pump	Residential dehumidification[1]	Industrial process AC	Heat transfer
Regulated halocarbon substitutes					
HCFC-22	N		R,N		
HCFC-123	R,N				
HCFC-124	R,N			R,N	
HCFC-141b	R,N				
R-401A: HCFC-22,-124, HFC-152a			R		
R-401B: HCFC-22,-124, HFC-152a			R		
Non-regulated halocarbon substitutes					
HFC-32		N			
HFC-134a	R,N	N	R,N		
HFC-152a		N			
HFC-227ea	N	N			
HFC-125/-134a/-32	N	N			
PFCs					R,N
FICs	U	U	U	U	U
Non-halocarbon substitutes					
Alternative process					
- evaporative cooling	N				
- stirling cycle	N	N			
- adsorption cooling					
- air cycle					
- desiccant cooling	N				
- absorption refigeration	N				
NH_3 vapour compression	N				
Hydrocarbons	R,N	N	R,N		

[1] also a blend of HCFC-22, HCFC-142b and CFC-12 can be used.

3.2.4.3 MOBILE AIRCONDITIONING

Use before the Montreal Protocol

In buses, trains, aeroplanes and cars airconditioning systems are increasingly used for regulation of temperature and humidity within the passenger compartments. A mobile airconditiong system (MAC) usually contains less than 1 kg of cooling agent and has a cooling capacity of about 20 household refrigerators. CFC-12 is most widely used (Table 3-6). Globally speaking, MAC was one of the most important applications of CFCs, accounting for about 40% of the total use of cooling agents. Mobile airconditioning is mainly used in the US. In Europe, it still accounts for less than 5% of the use of cooling agents, but it is increasing fast. Since current mobile airconditioning systems are leaky, regular refilling is needed, which makes a preferably non-flammable drop-in substitute desirable.

Halocarbon alternatives: regulated compounds

- *R-401C (HCFC-22, HCFC-124 and HFC-152a).* In the US a blend of HCFC-22, HCFC-124 and HFC-152a is available with similar properties as CFC-12. This is a non-flammable near azeotrope drop-in substitute (EPA, 1994a).

Halocarbon alternatives: non-regulated compounds

- *HFC-134a.* HFC-134a is commercially available as a substitute for CFC-12 in retrofitted mobile airconditioning systems. It is, however, not a drop-in substitute: the equipment needs modification and another lubricant. Outside the USA this is hardly a problem, since most mobile airconditioning systems date from after the Montreal Protocol. It is expected that within a few years HFC-134a is the only halocarbon cooling agent used in MAC. The costs of changing from CFC-12 to HFC-134a may be $200 per vehicle (Maclaine-cross, 1994).
- *FICs*, in particular CF_3I and $CF_3(CF_2)_2I$, pure or in blends, have been mentioned as potential cooling agents on mobile airconditioning, based on theoretical considerations. Their performance and toxicity needs to be tested (Nimitz, 1994a).

Non-halocarbon alternatives

HFC-134a is expected to replace almost all of the CFC-12 in MAC (Fay, 1995). However, a reduction in the charge may nevertheless cause a reduction of about 25% in the volumes used (Tables 3-9 and 3-11). Nevertheless, several non-halocarbon substitutes are available or will become available in the near future. Their potential to replace CFC-12 may be in the order of 90 - 100% of CFC-12.

- *Alternative process.* Obvious options for temperature control in vehicles is improvement of ventilation, choosing a light-coloured vehicle, or window coating (Cohen and Pickaver, 1992). Other processes include (see for a description of the process 3.2.4.1 and 3.2.4.2):
  - Evaporative cooling, using water for evaporation. It could be more energy efficient than the current halocarbon MAC systems. It is already widespread in US transit buses, but it could be used more widespread (EPA, 1994a).
  - Adsorption refrigeration using zeolite and water could become a good alternative to CFC-12 using vapour compression cooling in MAC (Cohen and Pickaver, 1992; UNEP IE, 1994).
  - Stirling cycle. A full-scale Stirling motor vehicle airconditioning has been built but further development is needed to facilitate implementation (EPA, 1994a). It is a good alternative to vapour compression.

- *Propane/butane.* Propane or butane could be used as cooling agent in mobile airconditioning. Airconditiong systems using propane/butane are currently in development (GECR, 1994) and undergoing tests (Van Gerwen and Jansen, 1994). To some exent flammable refrigerants are used in vehicles in the USA (Maclaine-cross, 1994).

  If compared to CFC-12, propane/butane has a number of advantages: (i) cheap; the costs of changing from CFC-12 to propane/butane may be $50 per vehicle, as opposed to $200 for a change to HFC-134a (Maclaine-cross, 1994), (ii) only about 300 g of it is needed in an average Australian passenger car, as opposed to more than 800 g in systems formerly using CFC-12, (iii) propane/butane increases the cooling capacity by about 10% and (iv) hydrocarbons have fewer toxic combustion products than CFC-12 and HFC-134a (Maclaine-cross, 1994).

  A disadvantage of hydrocarbons is their flammability. A few preliminary studies, however, showed that the risks of a flammable cooling agent in MAC is limited (Diekmann et al., 1991; Maclaine-cross, 1994). Maclaine-cross argued that 300 g of propane/butane poses little threat to the driver or to the technicians working on the car, provided that the hydrocarbon refrigerant has been odorized with 25 mg/kg ethyl mercaptam and that drivers are instructed to wind down their windows completely to remove the odour if it appears. In the case of leakage the concentrations hardly ever reach a flammable level. There are two situations where considerable risk of ignition is present: (i) severe leakage of cooling agent while the driver is smoking; the chance that a flammable mixture is created is small, but not zero if the driver choses to ignore the smell of the gas and does not open the window, (ii) during a car accident, when the leaking cooling agent may be ignited; the accident must, however, be severe to create a situation in which ignition is possible and it is doubtful if the resulting damage from fire adds significantly to the other damage. According to Maclaine-cross (1994) replacing CFC-12 with hydrocarbons decreases the net insurance risk by about $2 per operating year, because CFC-12 needs to be recovered by licensed and trained operators.
- *Carbon dioxide.* CO_2 cooling systems could be available within five years (EPA, 1994a). When using waste CO_2 the process in this system does not add anything more to global warming than the energy needed to run the system.

Table 3-6. Cooling agents: possible alternatives to CFC-12 in mobile airconditioning; R = can be used in retrofitted equipment, N = in new equipment/not in kind; U = Uncertain

Mmobile airconditioning	CFC-12
Regulated halocarbon substitutes	
R-401C	R,N
Non-regulated halocarbon substitutes	
HFC-134a	R,N
FICs	U
Non halocarbon substitutes	
Altemartive process	
- non airco cooling	R
- evaporative cooling	N
- adsorption cooling (zeolith and water)	N
- Stirling cycle	N
Hydrocarbons	R,N
CO_2	N

3.2.5 FIRE EXTINGUISHING

Use before the Montreal Protocol

Halon 1211 and 1301 are widely used in fire extinguishing. Halon 1211 is mostly used as streaming agent in portables and halon 1301 as total flooding agent in fixed systems. In some applications halon 2402 is used (EPA, 1994a). Halons are not only used in fire fighting, but also for explosion protection.

Different types of fires exist. Fire extinguishers preferably leave no residues, do not conduct electricity and are not toxic. Halons can be used for all types of fires and can reach inaccessible areas because they are gases (EPA, 1994a). Most of the emissions of halons occur during testing, training, practice, repair and accidental release (EPA, 1994a).

Halocarbon alternatives: regulated compounds

Halocarbons will probably not be the major substitutes for halons in portables, but a number of HCFCs, HFCs and FCs have been proposed as possible alternatives in fixed systems (Table 3-7). HCFCs are in general less effective fire extinguishing agents than halons or HBFCs (hydrobromofluorocarbons), so that higher concentrations are needed for the same effect (EPA, 1994a). Some HCFCs and HBFCs are cardiotoxic, which makes them not directly suitable as total flooding agents (EPA, 1994a).

- *HCFC-22* could replace some halons (EPA, 1994a). In total flooding HCFC-22 may cause problems because of its cardiotoxicity.
- *HCFC-123*, or blends thereof, was suggested by producers as substitutes for halon 1211 as streaming agent (Dupont, 1990a,b).
- *HCFC-124*, pure or in blends, can be used both as streaming agent or for total flooding (EPA, 1994a). Its cardiotoxicity may make HCFC-124 less useful as total flooding agent.
- *HBFCs*. Brominated hydrofluorocarbons have similar properties as halons. HBFC-22B1 may be commercially available in the near future (UNEP, 1993b; EPA, 1994a), but this is also a compound to be phased out by 1-1-1996 by industrialied countries.
- *CFCs*. Some CFCs have been mentioned as alternatives to halons (EPA, 1994a).
- *Blends*. Several blends have been mentioned as alternative fire extinguishing agents, containing a variety of CFCs, HCFCs, HFCs, PFCs and others (EPA, 1994a). Their ODP, GWP and toxicity depends highly on the composition of the blend.

Halocarbon alternatives: non-regulated compounds

HFCs are also less effective fire extinguishing agents than halons or HBFCs. In addition, the decomposition products may contain more HF (toxic and irritating) than other halocarbons. On the other hand the risk of cardiotoxicity of HFCs is less than that of HCFCs and HBFCs.

- *HFCs* The most widely used HFC in fire fighting will probably be HFC-227ea (Great Lakes, 1994). This HFC is a substitute to Halon 1301 in fixed systems, but could also be used in portables. Also HFC-23 is a potential total flooding agent (EPA, 1994a), as well as HFC-125 for halon 1301 in total flooding (Dupont, 1990a,b). HFC-134a could be used both as total flooding and streaming agent (EPA, 1994a).
- *PFCs*. Some PFCs, C_4F_{10} and C_6F_{14}, may replace halon 1301 and 1211, respectively (UNEP, 1993b; EPA, 1994a). PFCs have no toxicity problems and can be used in occupied areas.
- *FICs*. Based on computer simulations and their chemical properties, CF_3I, pure or blended with HFC-125, -234a, or -227ea were mentioned as potential replacements for halon 1301 (Nimitz, 1994d). Optimal blends of CF_3I with HFCs may contain 10 - 70% of CF_3I (weight based). Their

performance and toxicity need, however, be tested.

Non-halocarbon alternatives

Non-halocarbons can probably replace not more than half the halons used in fixed fire extinguishing (Fay, 1995; Stamp, pers.comm.). In portables virtually all halons will be replaced by non-halocarbons (Stamp, pers.comm.). The technical potential of non-halocarbons to replace halons is, however, much higher and may be in the range of 95 - 100% of all halons used. The following options are currently applied and could, to some extent replace halons in fire extinguishing:

- *Improved fire prevention.* A reduction in the likelihood of fire will reduce the need for fire extinguishing.
- *Water.* Water is widely used in fire fighting, for instance, in sprinklers. It could replace part of the halon market (EPA, 1994a).
- *Carbon dioxide.* CO_2 is already used in fire extinguishing and could replace halons to some extent (EPA, 1994a).
- *Dry chemicals* are already in use and could be more widespread (EPA, 1994a).
- *Foams.* Also currently used foams could partly replace halons (EPA, 1994a). Recently a blend of etoxylated linear alcohol and sulfonated soap for use as streaming agent was developed (EPA, 1994a).

Newly developed techniques to replace halons include:

- *Inert gas mixtures.* Mixtures of nitrogen (N_2), argon (Ar) and possibly carbon dioxide (CO_2) are effective fire extinguishing agents. When used in concentrations of 35 - 50% by volume, the ambient O_2 concentration is reduced to a level that will not support flaming combustion. In some situations inert gases are not preferred because the low oxygen levels are also too low for breathing. Nevertheless, in a considerable number of applications inert gases pose no threat to people.
- *Water mist technology.* Fine water mist technology is a newly developed technique using small droplets of less than 200 µm as a spray to extinguish the fire. The mechanisms may be (i) gas-phase cooling, like a total fooding inert, (ii) oxygen depletion by steam expansion, (iii) wetting of surfaces and (iv) flame blow-off (UNEP, 1993b). It could probably be used for all types of fires (EPA, 1994a). Advantages of water mist technology are use of readily available water, which is not toxic. In addition, they use much less water than the traditional sprinklers (up to 90% less), which reduces the amount of water needed and the post-fire clean-up. Water mist manufacturers are Marioff Hi-fog (Finland), Securiplex (Canada), Ginge Kerr (U.K., Denmark, Norway), ADA Technologies (USA), FSI/Kidde Graviner (UK) and Kinne Fenwall (USA) (UNEP, 1993b).
- *Powdered aerosols.* This is a new technology for streaming and total flooding systems, in which fine powdered particulates are combined with gas (EPA, 1994a).
- SF_6 could be used for discharge testing (EPA, 1994a).

Table 3-7. Fire extinguishing: possible alternatives to halons

Fire extinguishing		Halon 1211 (portables)	Halon 1301 (fixed systems)
Regulated halocarbon substitutes (trade name, producer)[1]			
HCFC-22		x	x
HCFC-123	(FE-232, Dupont)	x	
HCFC-124		x	x
HBFC-22B1	(FM-100, Great Lakes)	x	x
Blend A[2]	(NAF S-III NAFG)	x	x
Other HCFC blends		x	x
Non-regulated halocarbon substitutes (trade name, producer)[1]			
HFC-23	(FE-13, Dupont)		x
HFC-125	(FE-25, Dupont)		x
HFC-134a		x	x
HFC-227	(FM-200, Great Lakes)	x	x
C_4F_{10}	(CEA-410, 3M)		x
C_6F_{14}	(CEA-614, 3M)	x	
FICs	(Ikon, The Ikon Corporate)		x
Non halocarbon substitutes[1]			
Fire prevention		x	x
Water		x	
CO_2		x	x
Dry chemicals		x	
Foams		x	
Inert gas mixtures:			
- $N_2/Ar/CO_2$ = 52/40/8 (IG-541, Ansul)			x
- N_2/Ar = 50/50 (IG-55, Securiplex, Ginge Kerr)			x
- other mixtures			x
Water mist technology		x	x
Powdered aerosols		x	x
SF_6		x	x

[1] UNEP, 1993b; Great Lakes, 1994; Dupont, 1990a,b; EPA, 1994a [2] 92% HCFC-22, 4.75% HCFCF-123, 4.5% HCFC-124 and 3.75% organic

3.2.6 OTHER USES

In addition to the decribed so far applications, CFCs are also used as sterilants and in tobacco expansion, while CH_3CCl_3 is also used as adhesive, for coating and in inks (Table 3-8).

Sterilants

Currently, a blend of CFC-12 with ethylene oxide (ETO) is used as sterilant. This blend usually contains 88% CFC-12. ETO is the actual sterilant, while CFC-12 acts as diluent in order to make the blend non-flammable. The mixture is used for sterilization in hospitals, medical equipment sterilization, pharmaceutical industry, spice fumigation, commercial research and development and contract sterilization (EPA, 1994a). Regulated halocarbon alternatives to CFC-12 in the ETO blend are HCFC-123, HCFC-124 and HCFC-141b, or blends containing these HCFCs. Non-regulated halocarbons that could be used instead of CFC-12 include HFC-125, HFC-134a and HFC-227ea, or blends thereof. Non-halocarbon alternatives include some currently used sterilants. The suitability of alternatives depends strongly on the material to be sterilized. Currently used sterilants that may replace some of the CFC-12 blend include steam sterilizers, gamma radiation, peracetic acid and gutaraldehyde. New sterilants in development include chlorine dioxide, gaseous ozone, vapour phase hydrogen, an ionized plasma (EPA, 1994a).

Carbon dioxide is also widespread as sterilant in ETO blends. The blend could contain 8.5 or 10% ETO, the latter being currently used but flammable. The 8.5% blend can be used in most applications where CFC-12/ETO is now used, but not as a direct drop-in; the systems needs some modification (EPA, 1994a). Pure ETO can also be used as sterilant, but it is toxic, carcinogenic, flammable and explosive. Nevertheless, it is being used (EPA, 1994a).

Tobacco expansion

In cigarette industries, tobacco is first cooled at high pressure and consecutively expanded with hot air. CFC-11 is used in the cooling step (EPA, 1994a). HFC-227ea is a possible substitute for CFC-11. At present CO_2 is already widely used in an alternative process. It cannot replace CFC-11 in existing equipment, but could in new. A third alternative is propane, the use of which may require process modification to prevent the risk of fire (EPA, 1994a).

Adhesive, coatings and inks

A widely used solvent in adhesives, coatings (such as paints) and inks is CH_3CCl_3 (MCF). Alternatives include direct substitutes for CH_3CCl_3, water-based formulation, high-solid formulations and alternative processes (EPA, 1994a). Direct substitutes for CH_3CCl_3 include petroleum hydrocarbons (e.g. hexane, heptane, toluene, xylene), oxygenated organic solvents (ketones, esters, ethers, alcohols), chlorinated solvents (perchloroethylene, methylene chloride, monochlorotoluene, chlorobenzotrifluorides) and terpenes (EPA, 1994a).

Water-based coatings and water-based inks use water as main solvent. In inks other solvents such as alcohols and alkyl acetates may be added. Currently, almost half of the adhesives are water-based (EPA, 1994a). High-solid coatings and adhesives contain less solvent than conventional coatings. They are already used in a number of applications (EPA, 1994a).

Alternative processes include (i) powder formulations, which contain the resins and pigments in powdered form, (ii) hot melts, which are pure solid thermoplastic binders to achieve rigid bonds, (iii) thermoplastic plasma spray coatings which are powdered coatings, (iv) radiation curing of adhesives using ultraviolet, infrared radiation, electron beams or gamma or X-rays, (v) some adhesives in development: moisture cured, chemically cured and reactive liquids (EPA, 1994a).

Table 3-8. Other uses: possible alternatives to CFCs and 1,1,1, trichloroethane (or methyl chloroform, MCF)

	Sterilants blend with CFC-12	Tobacco expansion CFC-11	Adhesives/coatings/inks CH_3CCl_3 (MCF)
Regulated halocarbon substitutes			
HCFC-123/ETO	x		
HCFC-124/ETO	x		
HCFC-141b/ETO	x		
HCFC-blend/ETO	x		
Non-regulated halocarbon substitutes			
HFC-125/ETO	x		
HFC-134a/ETO	x		
HFC-227ea/ETO	x		
HFC-227ea		x	
HFC-blend/ETO	x		
Chlorinated solvents			x
Non halocarbon substitutes			
Steam	x		
CO_2/ETO	x		
Pure ETO	x		
CO_2		x	
Propane		x	
Alternative technologies			x
Water-based formulations			x
High-solid formulations			x
Petroleum hydrocarbons			x
Oxygenated solvents			x
Terpenes			x

3.3 OVERVIEW OF HCFC AND HFC USE

3.3.1 USE AS SUBSTITUTES FOR CFCs, HALONS AND CH_3CCl_3

Table 3-9 summarizes the use of HFCs, HCFCs and PFCs as substitutes for CFCs, halons and CH_3CCl_3. For each application is estimated to what extent CFCs, halons and CH_3CCl_3 will be replaced by fluorocarbons. The totals per application are based on estimates subsitution rates of the industrial Alliance for Responsible Atmospheric Policy (Fay, 1995) and DuPont (1994). It was estimated that by 2000 the fluorocarbon use would equal about one-third of 1986 market (Fay, 1995; DuPont, 1994). In chapter 6 is shown that without the Montreal Protocol, the demand for halocarbons would have increased by about 45% between 1986 and 2000. Thus, by 2000, fluorocarbons may substitute about 20% of the pre-Montreal demand for CFCs, halons and CH_3CCl_3 (Table 3-9). Based on the substitution rates as estimated by Fay (1995), for each application it is estimated here to what extent HFCs, HCFCs, PFCs and FICs will be used to meet the pre-Montreal demand for halocarbons (Table 3-9).

Most of the aerosols used in the future will probably be non-halocarbons. By 2000, the aerosol market may amount to 15% of the 1986 market (Fay, 1995; DuPont, 1994). In other words, 9 - 11% of the pre-Montreal demand will be met by fluorocarbons in 2000. Once HCFCs are phased-out, which the most important of these will probably be HFC-134a, HFC-152a and HFC-227ea.

Also most of the solvents to be used in the future are non-halocarbons. By 2000, the fuorocarbon solvent market will expectedly be about 5% of the 1986 market (Fay, 1995; DuPont, 1994), or about 4% of the pre-Montreal demand. It is assumed here that after an HCFC phase-out, the most important fluoroarbon solvents will be HFC-4310mee and PFCs (based on DuPont, 1994). It is tentatively estimated here that these have an equal share in the substitution (Table 3-9). These substitution rates may overestimate actual use of PFCs and HFC-4310mee, since newly developed HFC liquids may in the near future become available and take over part of the market. Since it is at present not clear which HFCs this will be, this development is ignored in the present study.

It is expected that less than 5% of the CFCs previously used for open-foam blowing will, by 2000, be fluorocarbons (Fay, 1995; DuPont, 1994). HFCs to be used may be HFC-134a and HFC-152a. It is estimated here that each of these replace 0.5% of the pre-Montreal demand for open-foam blowing agents (Table 3-9).

For closed foams fluorocarbons remain imporant blowing agents. By 2000, this market may be about 60% of the 1986 market (Fay, 1995; DuPont, 1994). Thus fluorocarbons may replace 40 - 45% of the pre-Montreal demand for closed-foam blowing agents. After an HCFC phase-out, especially HFC-236fa, -245ca, and -356 may be used. It is estimated here that these replace 10% of the pre-Montreal demand each (Table 3-9). In addition, HFC-134a, HFC-143a and HFC-152a may be used.

Fluorocarbons are also expected to remain the most widely used cooling agents. By 2000, the amount of cooling agent used in stationary refrigeration may be more than 75% of the amount used in 1986 and HFC-134a may be the most important (Fay, 1995; DuPont, 1994). Thus fluorocarbons may replace about 50% of the pre-Montreal demand. It is estimated here that HFC-134a replaces 25 - 30% of the pre-Montreal demand. Other HFCs that can be used as cooling agents include HFC-23, -32, -125, -143a, -152a, and -227ea. It is tentatively estimated here that these have an equal share in the substitution (Table 3-9).

It is expected that all CFC-12 used in mobile airconditioning is to be replaced by HFC-134a (Fay, 1995; DuPont, 1994). Nevertheless, due to leakage control and recycling the total volume used may decline. It is estimated here that future use of HFC-134a equals to 75% of the pre-Montreal demand for CFC-12 (Table 3-9).

By 2000, the amount of fluorocarbons used in fire extinguishing may amount to 50 - 80% of the 1986 market (Fay, 1995; DuPont, 1994). It is therefore estimated here that 45 - 50% of the pre-Montreal demand is to be met by fluorocarbons, of which HFC-125 probably is the most important (Table 3-9).

For other uses (sterilants, tobacco expansion, adhesives, coatings and inks) it is tentatively estimated that 30% of the pre-Montreal demand is met by HFC-125, -134a and -227ea.

From Table 3-9 can be concluded that for a number of applications the expected substitution is low: aerosol propellants, aerosol solvents, cleaning agents and blowing agents for open foams will be largely of the non-halocarbon type. Thus after a phase-out of CFCs and halons, halocarbons will be mainly used as cooling agents and blowing agents for closed foams.

Table 3-9. Worldwide substitution of regulated compounds by HFCs, HCFCs, PFCs, FICs and SF_6; based on industry estimates as published by Fay (1995) and DuPont (1994) and on the previous chapters

Application	Historical use	Halocarbon substitute	Estimated replacement (% of 1986 use)	Estimated replacement (% of pre-Montreal demand to be replaced)	
			2000[1]	<2005[2]	>2015[3]
Aerosol	CFC-11,-12,-114	HCFC-22		1.5	-
		HCFC-141b		1.5	-
		HCFC-142b		1.5	-
		HFC-134a		2	3
		HFC-152a		2	3
		HFC-227ea		2	3
		total	15	11	9
Cleaning/drying	CFC-113, CH_3CCl_3	HCFC-141b		1	-
		HCFC-123		1	-
		HCFC-225ca/cb		1	-
		HFC-43-10		0.5	2[6]
		PFC		0.5	2[6]
		total	5	4	4
Open cell foams	CFC-11,-12,-114	HCFC-22		0.5	-
		HCFC-141b		0.5	-
		HFC-134a		0.5	0.5
		HFC-152a		0.5	0.5
		total	<5	2	1
Closed cell foams	CFC-11,-12,-113,-114	HCFC-22		5	-
		HCFC-141b		15	-
		HCFC-142b		15	-
		HFC-134a		0.6	2.5
		HFC-143a		1.25	5
		HFC-152a		0.6	2.5
		HFC-236fa		2.5	10
		HFC-245ca		2.5	10
		HFC-356		2.5	10
		total	60	45	40
Stationary refrigeration	CFC-11,-12,-113,-114,-115	HCFC-22		3	-
		HCFC-123		3	-
		HCFC-124		3	-
		HFC-23		2.5	3
		HFC-32		2.5	3
		HFC-134a		25	30
		HFC-125		2.5	3
		HFC-143a		2.5	3
		HFC-152a		2.5	3
		HFC-227ea		2.5	3
		PFC		2	2
		total	>75	50	50

Table 3-9. Worldwide substitution of regulated compounds by HFCs, HCFCs, PFCs, FICs and SF_6; based on industry estimates as published by Fay (1995) and DuPont (1994) and on the previous chapters

Application	Historical use	Halocarbon substitute	Estimated replacement (% of 1986 use)	Estimated replacement (% of pre-Montreal demand to be replaced)	
			2000[1]	<2005[2]	>2015[3]
Stationary refrigeration	HCFC-22	HFC-32	-	-	15
		HFC-134a	-	-	15
		HFC-152a	-	-	15
		HFC-143a	-	-	15
		HFC-125	-	-	15
		total	0	0	75
Mobile airconditioning	CFC-12	HFC-134a		75	75
		total	100	75	75
Fire extinguishing (fixed systems)[7]	Halon 1301[7]	HCFC-123		3	-
		HCFC-124		3	-
		HFC-23		3	3
		HFC-125		3	3
		HFC-134a		3	3
		HFC-227ea		25	25
		PFCs		3	3
		FICs		3	3
		SF_6		3	3
		Total	50-80	50	45
Other	CFC-11,-12	HFC-125		10	10
		HFC-134a		10	10
		HFC-227ea		10	10
		Total	<50	30	30
Total[4]	CFCs, halons, CH_3CCl_3		35	21	18
	HCFCs				75[5]

[1] fluorocarbon market in 2000 as % of the 1986 market, mainly based on Fay (1995) and DuPont (1994); [2] fluorocarbon market as % of the pre-Montreal demand (i.e. future demand as it would have been without Montreal Protocol), assuming a 45% increase in pre-Montreal use of CFCs and halons between 1986 and 2000 (see chapter 6); [3] assuming an HCFC phaseout by 2015 (see Chapter 6); [4] see Chapter 6; [5] <80% according to Fay (1995); [6] may be partly replaced by new HFC liquids in development; [7] it is assumed here that fluorocarbons only replace halons in fixed systems (Stamp, pers.comm.); replacement in portables is less than 2% of the pre-Montreal demand (some HCFC-123).

3.3.2 HISTORICAL USE OF HCFCs, PFCs AND SF_6

Several HCFCs, PFCs and SF_6 were already used before the Montreal Protocol. This chapter describes these "historical" markets.

3.3.2.1 HCFCs

HCFC-22 is used as cooling agent, and as feedstock for tetrafluoroethene (TFE) and hexafluoropropene (HFP), which in turn are feedstocks for TEFLON (polyfluorethene and co-polymers thereof) (SPIN, 1993).

3.3.2.2 PFCs

Perfluorocarbons (PFCs) have been produced commercially for 30 years. Historically, these compounds were used in specialized market segments as cooling/heating agents, and in vapour phase reflow soldering and electronic safety testing.

3.3.2.1 SF_6

In addition to substitution for halons, SF_6 is used in a number of other applications. These are listed in Table 3-10. Globally, about 80% of SF_6 is used for insulation of electrical equipment, 5 - 10% in blanketting or degassing molten reactive metals and 5 - 10% in a number of smaller applications (Ko et al., 1993). In the Netherlands about 70% of the SF_6 is used in high voltage circuit-breakers, 25% in other electrical applications and 5% in non-electric applications (Annema, 1989). Gas-filled circuitbreakers, rated 50 kV or more, usually contain hundreds to thousands kilos of SF_6 per installation. Low-voltage switchers contain 1 - 2 kg of SF_6 per installation. Not all circuit-breakers are gas-filled. In fact, most high-voltage circuitbreakers are open systems, using air for insulation. Closed systems using SF_6 are increasingly applied, because they are safer, require less space and the risk of contamination is lower. On the other hand the breakdown products of SF_6 that can be formed during discharge or at temperatures exceeding 400 °C are extremely toxic (Annema, 1989). Annema therefore recommended using SF_6 only in high-voltage circuitbreakers with strict leakage control. For switchers vacuum or air/casting resin systems are good alternatives.

Table 3-10. Applications of SF_6

Application[1]	Some alternatives[2]
Electrical	
- circuit breakers	air
- switchers	vacuum
- gas insulated transmission lines	air
- ministations	air
- wave-guides	
- accelerators	
Non-electrical	
- aluminum and magnesium casting	
- leak detection	
- gas-air tracer	
- loudspeakers	

[1] Allied Signal, 1989; Ko et al., 1993; [2] Annema, 1989

3.4 CONCLUSIONS

This chapter reviews the different applications of halocarbons, PFCs and SF_6. At present, there are a number of equally important applications, including aerosols, cleaning/drying, foam blowing and refrigeration. In the future this may change because of different substitution rates. It is expected that after a phase-out of CFCs and halons, the most important application for halocarbons will be cooling applications and closed-foam blowing.

Table 3-11 shows to what extent fluorocarbons may replace CFCs, halons and CH_3CCl_3. For aerosols it is estimated that 9 - 11% of the pre-Montreal demand (i.e. the demand for halocarbon aerosols for a situation without Montreal Protocol) is to be met by HFCs, PFCs, FICs and SF_6. These substitution rates are <5% for solvents, <2% for open-foam blowing, 40 - 45% for closed-foam blowing, more than 50% for stationary cooling, less than 75% for mobile airconditioning, 45 - 50% for fixed fire extinguishing, and 30% for other uses. Approximately 20% of the pre-Montreal demand for CFCs, halons and CH_3CCl_3 is met by these fluorocarbons, and about 75% of the pre-Montreal demand for HCFC-22.

Non-halocarbons are expected to replace 80% of the pre-Montreal demand for CFCs, halons and CH_3CCl_3. However, there are many non-halocarbon alternatives available, which have the potential to replace virtually all halocarbons presently used (Table 3-11). Several types of non-halocarbons can be distinguished: (i) drop-in substitutes that can replace CFCs and halons without major modifications to the equipment, (ii) substitutes that need major retrofitting of present equipment and (iii) alternatives that need replacement of equipment. The costs involved in the last two types of substitutes depend on the timing. When replacement or a major service of equipment is needed anyway, additional costs of switching to non-halocarbon substitutes can be kept low.

Table 3-11. Expected substitution as % of pre-Montreal demand for CFCs, halons and CH_3CCl_3 after a phase-out, and potential substution by non-halocarbons, assuming no recycling and leakage control (see also Table 3-9)

	Expected substitution[1]		Potential substitution
Application	Halocarbons	Non-halocarbons[1]	Non-halocarbons
Aerosol	9-11%	90%	>95%
Cleaning	<5%	>95%	>95%
Foam blowing			
- packaging/cushioning	<2%	>98%	>98%
- insulation	40-45%	55-60%	>90%
Refrigeration			
- stationary	>50%	<50%	>90%
- mobile airconditioning	<75%	>25%	>90%
Fire extinguishing			
- portables	<2%	>98%	>98%
- fixed systems	45-50%	50-55%	>95%
Other	30%	70%	>95%
Total	20%[2]	80%	>95%

[1] including reduced amounts needed in equipment; [2] see Chapter 6.

4. OPTIONS FOR EMISSION REDUCTION - general description and potential reduction

4.1 INTRODUCTION

This chapter investigates the options for emission control. In general, there are different ways to avoid or reduce emissions. First, emissions can be reduced by better housekeeping. For instance, spilling of cooling agent while filling a refrigerator could be reduced. Second, leakage control, can reduce releases during use of equipment in which the compounds considered are trapped. This is particularly the case in refrigeration. In addition, recovery of halocarbons for re-use or destruction when equipment is discarded could reduce emissions. And finally, emissions could be avoided by using non-halocarbon or low-GWP alternatives. In the following it is estimated for each application to what extent the above-mentioned options can reduce the use of halocarbons, and consecutively their emissions. This chapter only considers emissions of halocarbons and SF_6. In this chapter is also investigated to what extent equipment can be considered a "closed system".

4.2 EMISSIONS DURING PRODUCTION

During the production of halocarbons there are two types of emissions (see Chapter 2): (i) product itself is emitted (fugutive emissions; usually about 0.5% of the amount produced according to UNEP, 1994a), and (ii) the compounds used as feedstock may be emitted (feedstock emissions, usually 0.1% of the amount of feedstock used according to UNEP, 1994a). Most halocarbon production processes have been improved and the emission rates are therefore relatively small (UNEP, 1994a). It is doubtful whether in modern industries these emissions can be further reduced.

4.3 AEROSOLS

Emissions before and during use

Aerosol propellants are usually released shortly after production (see Chapter 5). Emissions occur (i) when filling spray cans and (ii) when the spray is used. Leakage of aerosol propellants from spray cans has not been estimated, but is expected to be low. Leakage control will therefore not have a major impact on the use of aerosol propellants. Also recycling or destruction of halocarbon wastes is considered impossible (Table 4-1).

Non-halocarbon alternatives

There is a wide variety of non-halocarbon alternatives to aerosol propellants. In Chapter 3.2.1 it is estimated that more than 95% of the CFCs used as aerosols can be replaced by non-halocarbon alternatives, including alternative processes, compressed non-flammable gases and other propellants.

Table 4-1. Halocarbon emissions after used as aerosol, potential reduction and potential replacement by non-halocarbons

	Present	Potentially falling to
Total emissions over lifetime (% of use per spray can)[1]	100	100
Annual emissions over lifetime (% of use per spray can y^{-1})[1]	100	100
Potential replacement by non-halocarbon (% of present use)		>95[2]

[1] assuming that propellants are released within one year after production; [2] Table 3-11

4.4 CLEANING

Emissions

Before the Montreal Protocol, all solvents used were eventually emitted (Table 4-2). These emissions could probably be reduced to about 20% of the pre-Montreal use by better housekeeping and, most importantly, by internal recycling (Kroeze and Reijnders, 1992).

Non-halocarbon alternatives

There are many non-halocarbon alternatives available. It is expected that these will take over more than 95% of the market (Table 4-2).

Table 4-2. Emissions due to solvent use, potential reduction and potential replacement by non-halocarbons

	Pre-Montreal situation	Potentially falling to
Total emissions over lifetime (% of use per process)	100%	20
Annual emissions over lifetime (% of use per process y^{-1})	100%	20
Potential replacement by non-halocarbons (% of present use)		>95[1]

[1] Table 3-11

4.5 FOAM BLOWING

Emissions of blowing agents may take place (i) during blowing of foams, (ii) during "use" of the faoms and (iii) when foams are discarded.

Open foam (packaging, cushioning)

In open foams there are no remains of the blowing agents used. Thus the blowing agents are released immediately during the blowing process. It is estimated that the amount of blowing agent used could be reduced by 10% by better housekeeping, and that in total about 55% of the blowing agents used may be recovered and re-used (Kroeze and Reijnders, 1992; Table 4-3).

Closed foams (insulation)

During closed-foam blowing about 10% of blowing agent is emitted immediately, while the remaining 90% is trapped in the foam and leaks away slowly (e.g. McCarthy et al., 1977). It is tentavely assumed here that the immediate emissions can be reduced to 5%. Discarded foams may still contain about 40 - 50% of the blowing agents used (Kroeze and Reijnders, 1992). It is estimated here that about 80% of this amount can be recycled or destroyed.

Non-halocarbon alternatives

In open foams probably few halocarbons will be used when CFCs are phased out. For closed foams non-halocarbons can potentially replace over 90% of the CFCs previously used (see Chapter 3).

Table 4-3. Halocarbon emissions due to foam blowing, potential reduction and potential replacement by non-halocarbons

	Packaging/cushioning		Insulation	
	Present	Potentially falling to	Present	Potentially falling to
Emissions (% of use per process)				
- during blowing	100	45	10	5
- from foam	-	-	40-50	40-50
- from discarded foam	-	-	40-50	5-10
Total over lifetime	100	45	100	50-65
Annual average over lifetime (% of use process y^{-1})	100	45	5[1]	2.5-3.5[1]
Potential replacement by non-halocarbons (% of present use)[2]		>98		>90

[1] total emission over lifetime of 20 year; [2] Table 3-11

4.6 REFRIGERATION AND AIRCONDITIONING

With respect to leakage three types of refrigeration can be distinguished: (i) domestic refrigeration, which are relatively closed systems, (ii) other stationary systems, which are leakier, and (iii) mobile airconditioning systems, which could be considered semi-open. In 1990, these three applications worldwide comprised about 3%, 47% and 50% of global annual use of CFC refrigerants, respectively (Kroeze and Reijnders, 1992).

Domestic refrigeration

During use, about 1 - 3% of the refrigerant is lost from domestic refrigeration and domestic airconditioning, and may be at the lower end of this range (Enquete Commission, 1994; McCulloch, 1994a,b). When after use all remaining refrigerant is released - which still is more or less the case - total emissions over a 15 years lifetime, amount to 100% of the charge, or 7% of the charge per year. It is estimated here that 80% of the refrigerant in a discarded refrigarator can be recycled or destroyed. Thus emissions over the lifetime of the equipment could be reduced to 30 - 60% of the charge (Table 4-4).

Other stationary refrigeration

Non-domestic cooling systems are in general larger than domestic, and release about 15 - 20% of the charge annually (McCulloch, 1994a,b). Although recycling of refrigerant is increasingly implemented, most cooling agent from discarded refrigerators is still emitted. As a result, emissions could, over a 15 year lifetime, amount to 325 - 400% of the charge. Emission control could reduce emissions during use to about 3% (McCulloch, 1994a,b). If in addition 80% of the refrigerant in discarded systems is recovered, total emissions over the lifetime of the equipment, could be reduced to about 65% of the charge (Table 4-4).

Mobile airconditioning (MAC)

Mobile airconditioning systems (MACs) are relatively leaky and sometimes considered semi-open systems. Until recently, about all of the cooling agent was released annually due to leakage and servicing. At present, these annual emissions are reduced to about one-third of the refrigerant in MACs (McCulloch, 1994a,b; Enquete Commission, 1994). The full content of a discarded MAC is generally released, although recovery systems are being implemented. It is technically possible to reduce annual leakage to 10% of the charge by good housekeeping and leakage control (Enquete Commission; 1994; McCulloch, 1994a,b). It is further estimated that 80% of the cooling agent could be recovered from discarded systems. Despite these reductions, total emissions from MAC would, over a 15 years lifetime, still amount to about 170% of the charge, or 30 - 40 times as much cooling agent as a household refrigerator. Using hydrocarbons instead of halocarbons would further reduce the total mass emitted by about 50% because in hydrocarbon systems the required charge is about half of that in halocarbon systems.

Non-halocarbon alternatives

In Chapter 3 it is shown that for all major cooling applications non-halocarbon alternatives are available. When hydrocarbons are considered viable alternatives, 90-100% of the halocarbons currently used could presumably be replaced by non-halocarbons.

Table 4-4. Emissions of cooling agents, potential reduction and potential replacement by non-halocarbons

	Present	Potentially falling to
Domestic refrigeration (no refilling)		
Annual emissions during use (% of charge y^{-1})	1	1
Emissions after use (% of charge per cooling system^{-1})	85	17
Total emissions		
- over lifetime (% of charge per cooling system)	100[1]	30 - 60[1]
- over lifetime (kg of refrigerant per cooling system)	0.25[1]	0.1 - 0.2[1]
Annual average over lifetime (% of charge y^{-1})	7[1]	2 - 4[1]
Replacement by non-halocarbons (% of use)[4]		>90
Other stationary refrigeration (regular refilling)		
Emissions during use (% of charge y^{-1})	15 - 20	3
Emissions after use (% of charge per cooling system)	100	20
Total emissions		
- over lifetime (% of charge per cooling system)	325 - 400[2]	65[2]
- over lifetime (kg of refrigerant per cooling system)	3.3 - 12.0[2]	0.6 - 2[2]
Annual average over lifetime (% of charge y^{-1})	22 - 25[2]	4[2]
Replacement by non-halocarbons (% of use)[4]		>90
Mobile airconditioning (regular refilling)		
Emissions during use (% of charge y^{-1})	30 - 35	10
Emissions after use (% of charge per cooling system)	100	20
Total emissions		
- over lifetime (% of charge per cooling system)	550 - 625[3]	170[3]
- over lifetime (kg of refrigerant per cooling system)	4.4 - 8.1[3]	1.4 - 2.2[3]
Annual average over lifetime (% of charge y^{-1})	37 - 42	11
Replacement by non-halocarbons (% of use)[4]		>90

[1] assuming a 250 g charge (= kg of refrigerant in the system) and a 15 years lifetime; [2] assuming a 1 - 3 kg charge and a 15 years lifetime; [3] assuming a 0.8 - 1.3 kg charge and a 15 years lifetime; [4] see Table 3-11.

4.7 FIRE EXTINGUISHING

Actual fires and other emissions

In 1992, annual emissions of halons were 58 and 33% of the amount of halons 1211 and 1301 produced, respectively (McCulloch, 1992). Since in a mature market the halon bank is much larger than the annual production, the annual release expressed as percentage of the bank is lower. In the replacement market the annual release as result of actual fire fighting may less than 5% of the bank (Stamp, pers.comm.).

Only 15% of annual halon 1211 emissions and 18% of halon 1301 emissions occur as a result of actual fire extinguishing. Thus 75 - 85% of the emissions result from testing, training, practice, repair and accidental releases (EPA, 1994a). It is estimated here that these can be reduced considerably, so that emissions from portable and fixed fire fighting systems can be reduced to 15 and 30% of the production, respectively (Table 4-5).

Non-halocarbon alternatives

Almost all halons previously used can be replaced by non-halocarbons (see Table 3-11).

Table 4-5. Emissions of fire extinguisher, potential reduction and potential replacement by non-halocarbons

	Present	Potentialy falling to
Total emissions over lifetime (% of production)[1]		
- Portables	60	30
- Fixed systems	35	15
Potential replacement by non-halocarbons (% of present use)[2]		>95

[1] for mature market; annual emissions due to actual fire fighting in the replacement market may currently be <5% of bank for portables and <1% of bank from fixed systems (Stamp, pers.comm.); [2] see Table 3-11

4.8 CONCLUSIONS

This chapter surveys to what extent emissions can be reduced. Table 6-4 shows that perfectly closed systems do not exist. Whenever halocarbons are used, some emissions are unavoidable. The total emission from an application depends on (i) annual leakage and (ii) the lifetime of the equipment. Applications with potentially lowest annual emissions include stationary refrigeration and closed foams. Also annual emissions from fixed fire-fighting systems are low relative to the bank. However, over their lifetimes, refrigerators and closed foams lose 30 - 65% of the charge, even if emission control is maximized. Including the equipment's lifetime would lead to the conclusion that cleaning and open-foam blowing are more closed systems, with total emissions ranging from 20 - 45% of the "charge". The potential effects of emission control are estimated here for the present applications, and probably realistic for the coming decades. However, it could be that better design of equipment would result in more emission reduction in the future than assumed here. This would, however, require major modifications in equipment

Table 4-6. Total emissions over the "lifetime" of equipment; n.q. = not quantified

	Total emission over lifetime		Annual emission over lifetime	
	Present	Potentially falling to	Present	Potentially falling to
Aerosols (% of use per spray can)	100	100	100	100
Cleaning (% of use per process)	100	20	100	20
Foam blowing (% of use per process)				
- open foam	100	45	100	45
- closed foams	100	50 - 65	5	2.5 - 3.5
Refrigeration (% of charge)				
- household appliances	100	30 - 60	7	2 - 4
- other stationary refrigeration	325 - 400	65	22 - 25	4
- mobile airconditioning	550 - 625	170	37 - 42	11
Fire extinguishing (% of production)[1]				
- portables	n.q.	n.q.	60	30
- fixed systems	n.q.	n.q.	35	15

[1] for mature market; annual emissions from replacement market due to actual fire fighting may be <5% of bank for portables and <1% of bank from fixed systems (Stamp, pers.comm.);

5 METHODS TO ESTIMATE EMISSIONS

5.1 INTRODUCTION

Emissions of halocarbons can essentially be estimated in two ways: as potential emissions and as actual emissions. Potential emissions are the emissions that could occur if all halocarbons used were emitted into the atmosphere. Potential emissions can be simply estimated as the annual production, unless the halocarbons produced are used as intermediate or feedstock. *Actual* emissions may differ from potential emissions because (i) there may be a time lag between use and emission, and (ii) emissions could be avoided by emission prevention.

- *(i) Time lag between use and emission.* A time lag may occur, when halocarbons are trapped in equipment for several years before being emitted. For instance, a considerable part of the cooling agents in a household refrigerator is not released before the refrigerator is discarded. The resulting time lag between "use" (year when refigerator was filled) and emission (year when refigerator is discarded) may be 15 years or more. Figure 5-1 shows that, indeed, in the case of a phase-out, actual emissions of cooling and blowing agents may differ considerably from potential emissions.
- *(ii) Recycling and destruction of halocarbon wastes.* The differences may be larger than shown in Fig. 5-1 when also the impact of recycling and destruction of halocarbon wastes is included. For instance, the cooling agent from discarded refrigerators could be recycled, destructed or reprocessed instead of emitted.

The extent to which actual emissions differ from potential emissions largely depends on the rate of leakage from the equipment and the extent to which halocarbons are recycled or destroyed after use. At present, there is not much recycling and destruction of halocarbons, but this may change in the future. For a priori estimates, potential emissions may be very useful. Also the Montreal Protocol asks countries to report their halocarbon use, not their actual emissions. On the other hand, estimates on actual emissions may make assessment of the environmental impact possible.

A number of methods to estimate actual emissions as published in the literature are presented in Appendix 5-1. In Chapter 5.2 the method as used in the present study will be described. The United Nations Framework Convention for Climate Change asks countries to report, if possible, actual emissions.

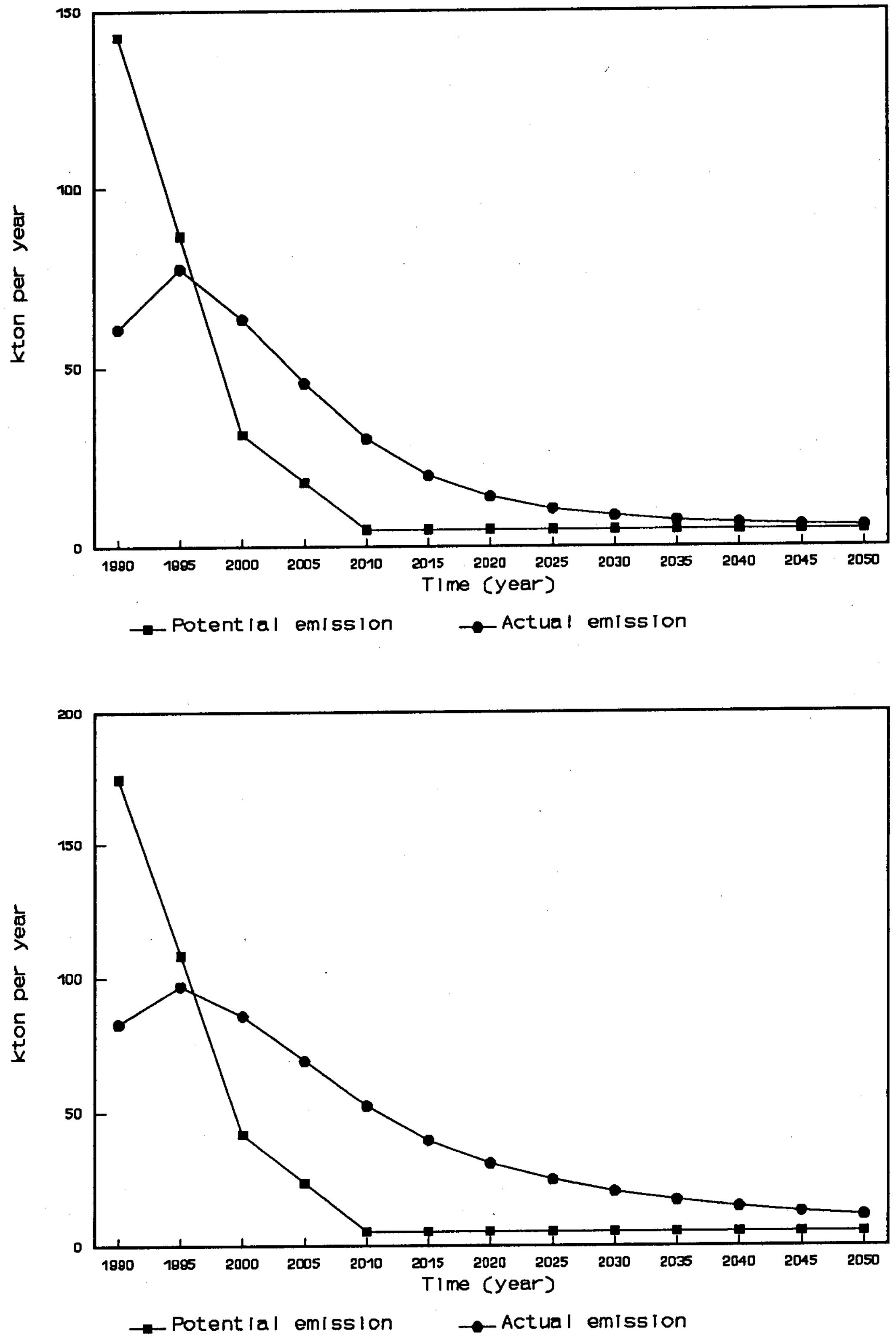

Fig. 5-1. Global use (= potential emissions) and actual emissions of CFCs in refrigerants excluding mobile airco (upper panel) and closed foams (lower panel), in the case of a phase-out around the turn of the century, with no recycling and assuming no destruction of halocarbon wastes (from Kroeze and Reijnders, 1992).

5.2 METHOD TO ESTIMATE ACTUAL EMISSIONS USED IN THIS STUDY

Table 5.1 overviews the method used in the present study for estimating global emissions. This method is the same as the method used by AFEAS (1993, 1994), except for refrigeration, which is based on McCulloch (1994a,b). The AFEAS method was chosen, because this method has been tested and used for several years, and because AFEAS monitors production and emissions of CFCs and some HCFCs annually. The AFEAS method is largely based on Gamlen et al. (1986), McCarthy et al., (1977), Fisher and Midgley (1993) and Midgley and Fisher (1993). For halons the method of McCulloch (1992) is used, and for fugitive emissions UNEP (1994a). Table 5.1 not only shows how emissions are calculated for the reference scenario (no control), but also to what extent emissions can be presumably reduced. These potential for emission reduction is described in Chapter 4 (Table 4-6). In the following the method is described for each application.

Aerosols

Aerosol propellants are usually released shortly after production. A survey in the US and in several European countries revealed that release takes place on average six months after sale. This would imply that half of the aerosols sold are released within the year of sale (Gamlen et al., 1986; Fisher et al., 1994a). Others assumed that aerosol propellants are usually emitted in the year of production (Appendix 5-1). This study adopts the AFEAS method (Table 5-1) which is the same as published by Gamlen et al., 1986). It is assumed that aerosol emissions cannot be reduced (see Chapter 4).

Foam blowing: cushioning/packaging

Emissions take place during foam blowing. Some blowing agent may be trapped in the foam and evaporate slowly. In open foams most of the blowing agent is released during the blowing process. Estimated delays between sale and release range from 2 to 6 months for most open foams (Appendix 5-1). Alternatively, it was assumed that blowing agents for all open foams are released in the year of production (Appendix 5-1). AFEAS assumed that it takes two years before the blowing agent is released (Table 5.1). The AFEAS method is adopted here. It is assumed here that emissions from open-foam blowing can be reduced by 55% (see Chapter 4).

Foam blowing: insulation

Emissions of blowing agents may take place (i) during blowing of foams, (ii) during "use" of the foams and (iii) when foams are discarded. Closed cell foams contain considerable amounts of blowing agent that leak away slowly. It has been estimated that about 10% of the blowing agent is released during blowing, and that the rest is trapped in the foam (Appendix 5-1). The trapped blowing agents are released over 20 - 25 years. AFEAS uses constant emission rates (4.5% of the initial charge) over 20 years (Table 5.1). Recycling may reduce this constant percentage to 3.5% (Chapter 4).

Cleaning

Halocarbons are usually emitted shortly after use as solvent. Fisher et al. (1994a) for instance assume that release occurs typically six months after sale (Appendix 5-1). This was also assumed by AFEAS (Table 5.1) and in the present study. In Chapter 4 is shown that internal recycling may reduce emissions considerably.

Stationary refrigeration

Table 5.1 shows that the method used in this study for refrigeration is largely based on McCulloch (1994a,b). McCulloch's method is more detailed than the AFEAS method and more suitable for the assessment of control options and therefore preferred here. Three types of cooling systems are distinguished: the household refrigerator, other stationary cooling and mobile airconditioning.

Emissions from cooling systems may take place (i) during use of the refrigerating system and (ii) once the system is discarded. During use, emissions differ per refrigerating system. A household refrigerator/freezer is usually considered a hermetically closed system from which only 1% of the charge leaks annually (McCulloch, 1994a,b). This is somewhat lower than emission rates published by others (less than 5% per year; Appendix 5-1). Household appliances account for only a few percent of the global use of cooling agents. Most other systems have higher leakage rates (Table 5.1)

The cooling agent is released from short-lived systems after about four years. Short-lived systems include most industrial and other refrigerators. According to McCulloch (1994a,b) emissions from larger systems can also be reduced substantially (Table 5.1). Other studies are less optimistic about this (Appendix 5-1).

Mobile airconditioning

Auto airconditioning systems are relatively leaky applications. Until recently, the full content of the system had been released within one year. Nowadays the leakage is reduced by making the systems more efficient (so that less cooling agent is used) and improving leakage control. At present about one-third of the cooling agent is lost annually (Table 5.1). This could be reduced to 10% (McCulloch, 1994a,b).

Fire extinguishing

Emissions from fire extinguishing, not included in the AFEAS method because halons are not monitored by AFEAS, are calculated here according to McCulloch (1992). The annual percentage of halon 1211 production emitted to the atmosphere from all sources have been decreasing since 1985 to about 35% at present (McCulloch, 1992). It is estimated here that this percentage could further decline to 15%. McCulloch's method to estimate emissions is appropriate for a mature market, when halon banks do not increase to fast. In the present replacement market most of the amount sold may be used to create a new bank, from which most emissions are from actual fire fighting, and not from testing or unwanted release. Thus estimating emissions as a percentage of production or sale could, as long as the market is not mature, overestimate actual emissions. Thus there is a case to estimate emissions as a percentage of the bank instead. However, for the time scale of the present study (up to 2100) McCulloch's method is considered appropriate here.

Other

For other applications it is tentatively assumed that all halocarbons are released within a year after production.

Emissions during halocarbon production and use as feedstock

Gamlen et al. (1986) estimated that 3.3% and 2% of CFC-11 and CFC-12, respectively, is released before it is sold. This fugitive loss is higher when the compound is more volatile. According to UNEP (1994a), emissions have been reduced substantially during the last years. The UNEP emission factors of 0.5 for product emissions and 0.1% for feedstock emissions are adopted here (see chapter 2). In this study product emissions (fugitive emissions) are taken into account, and the method used is based on UNEP (1994a). For HFCs and HCFCs feedstock emissions are not included.

Table 5.1. Method to estimate actual emissions of halocarbons as used in this study

Application	Emission in year t (no control)[2]	Potentially falling to[1] (maximum emission control)
Aerosol	$0.5*demand_t + 0.5*demand_{t-1}$	- (no reduction possible)
Open foam	$0.5*demand_t + 0.5*demand_{t-1}$	$0.23*demand_t + 0.23*demand_{t-1}$ (55% reduction by recycling and better housekeeping)
Closed foam	10% immediately + 4.5% of original charge for 20 years	5% immediately of $stock_t$ + 3.5% of the original charge over 20 years (by leakage control and recycling)
Cleaning	$0.5*demand_t + 0.5*demand_{t-1}$	$0.1*demand_t + 0.1*demand_{t-1}$ (80% reduction by recycling, better housekeeping)
Household refrigeration	1% of $stock_t$ + 85% of the original $charge_{t-15}$	1% of $stock_t$ + 20% of the original $charge_{t-15}$ (by recycling)
Other stationary refrigeration[3]	17% of $stock_t$ + 100% of the original charge used for new $equipment_{t-15}$	3% of $stock_t$ + 20% of the original $charge_{t-15}$ (by leakage control and recycling)
Mobile airconditioning[3]	33% of $stock_t$ + 100% of the original charge used for new $equipment_{t-15}$	10% of $stock_t$ + 20% of the original $charge_{t-15}$ (by leakage control and recycling)
Fire extinguishing (fixed systems)	actual fire fighting + other emissions = 35% of use_t	15% of use_t (mainly by other testing and practicing procedures)
Other	$demand_t$	- (no reduction possible)
Fugitive emissions	0.5% of production	- (no reduction possible)
Feedstock emissions	0.1% of feedstock use	- (no reduction possible)

[1] used in the maximum emission control scenarios in Chapter 6; - means no reduction possible; based on chapter 4 (Table 4-6); [2] method used in the no control scenarios in Chapter 6; based on AFEAS (1993), except for refrigeration and fire extinguishing, which is based on McCulloch (1992, 1994a,b); [3] assuming regular refilling.

6. GLOBAL EMISSIONS FOR THE PERIOD 1986-2100

6.1 INTRODUCTION

This chapter presents scenarios for global emissions for the period 1986 - 2100. The emissions presented reflect actual emissions, taking into account the delay between production and emission. Actual emissions are calculated from global use, as described in Chapter 5 (Table 5-1). Therefore, in 6.2 first worldwide *use* of halocarbons is estimated, assuming that the 1992 Copenhagen amendments to the Montreal Protocol are realized (Box 1). This is the reference scenario. Next, in 6.3 global emissions are presented for the reference scenario (i.e. a situation without further control) and for some other scenarios, assuming that additional levels of control are implemented. Summarizing, future emissions are estimated in this study as follows:

1. In 6.2.1 future demand for halocarbons and SF_6 is estimated as it would have been without the Montreal Protocol (so-called pre-Montreal demand).

2. In 6.2.2 first the amount of halocarbons to be replaced is estimated as the difference between the pre-Montreal demand and the envisaged use when the 1992 Copenhagen amendments to the Montreal Protocol will be realized.

3. For each halocarbon in each application it is estimated to what extent the halocarbon will be replaced by HCFCs, HFCs, PFCs, FICs or SF_6 (Table 3-9, Chapter 3). The resulting global use of halocarbons and SF_6 is considered as the reference scenario (6.2.3).

4. In 6.3 emissions are calculated for the reference scenario, assuming no further emission control. The method used to calculate emissions is described in 5.2.

5. Further, in 6.3 the effect of emission control is estimated, assuming (i) good housekeeping, maximum recycling and destruction of halocarbon waste, (ii) use in "closed applications" only and (iii) use of compounds or blends with low GWP only.

Box 1. Estimating future use of halocarbons and SF_6

$Use_{total} = Use_{regulated\ compounds} + Use_{substitute} + Use_{own\ market}$

$Use_{substitute} = PERC * (USE_{pre\text{-}MP\ regulated\ compounds} - USE_{regulated\ compounds})$

where

$Use_{regulated\ compounds}$ = use of compounds that are regulated under the Montreal Protocol (kg y^{-1})
$Use_{substitute}$ = use of compounds as substitute for regulated compounds (kg y^{-1})
$Use_{own\ market}$ = own market of not regulated compounds (kg y^{-1})
$USE_{pre\text{-}\ MP\ regulated\ compounds}$ = use of regulated compound if there were no Montreal Protocol (kg y^{-1})
PERC = fraction of regulated compounds that is replaced by the non-regulated compound considered (fraction of amount to be replaced)

6.2 USE OF HALOCARBONS

6.2.1 FUTURE USE OF HALOCARBONS IF THERE WERE NO MONTREAL PROTOCOL

The *pre-Montreal demand* for halocarbons is defined here as the future demand for halocarbons for a situation without the Montreal Protocol. In the reference scenario it is assumed that the pre-Montreal demand for halocarbons will not stabilize in the near future. The pre-Montreal demand is estimated assuming that in industrialized countries per capita pre-Montreal use stabilizes at the 1986 level. Total demand for halocarbons in 2000 and 2040 is based on Hammitt et al. (1987). For the period 2040 - 2100 it is assumed that per capita pre-Montreal demand in less developed countries linearly increases to the 1986 level of industrialized countries. Thus by 2100 the globally averaged pre-Montreal per capita use equals that of the 1986 level in industrialized countries (Table 6-1). This is in line with the assumed increase of GNP in less developed countries, as presented in the IPCC 1992 scenarios (Pepper et al., 1992). The world population is assumed to increase as in scenario IS92a of IPCC (Pepper et al., 1992).

Views about pre-Montreal demand

There are basically three views on trends in future pre-Montreal demand for halocarbons: demand could increase exponentially, linearly, or it could follow an S-curve (Fig. 6-1). Figure 6-1 shows that the differences between these three views increase in the second half of the next century. For the period up to 2040 the differences are much smaller.

An exponential increase was envisaged by Hammitt et al, (1987), who estimated use of CFCs and halons for the period 1985 - 2040, for a situation without regulations. These scenarios were based on detailed market analyses. Hammitt et al. (1987) concluded that from the year 2000 global use of CFCs and halons would increase by 2.4% per year. Similar growth rates were used as the basis for the IPCC 1992 scenarios (Pepper et al., 1992; Houghton et al., 1992), which were used by Den Elzen (1994), for instance.

A linear growth rate for the period 2040 - 2100, was assumed by Kroeze and Reijnders (1992). Their growth rates for the period up to 2040 were based on the study of Hammitt et al. (1987).

An S-curved growth was envisaged by McCulloch (1994a), who argued that most markets follow an S-curve rather than exponential growth.

Figure 6-2 shows some of the underlying consequences of the three extrapolations. The figure shows per capita use of CFC-12 as cooling agent in more and less developed regions of the world for the three projections shown in Fig. 6-1, assuming that (i) per capita use in industrialized countries stabilizes at the 1990 level, (ii) the world population stabilizes at 11.3 billion (Pepper et al., 1992) and (iii) that up to 1990, 95% of the CFC-12 was used in industrialized countries, based on the fact that 95% of all CFCs are used in the Northern Hemisphere (Fisher et al., 1994a). Industrialized regions include the OECD, Eastern Europe and the former USSR.

Figure 6-2 shows that the S-curved projections can only be realized if per capita CFC-12 use in present-day less developed countries remains at a low level. When assuming linear growth rates, per capita use could, by the end of the next century be the same for all world citizens. Exponential increase would allow per capita use to exceed 200 g y^{-1}, which is the 1990 level in industrialized countries. For comparison, in North America of 1986, about 250 - 350 g of CFC-12 was used per capita annually for mobile airconditioning. In the Netherlands, per capita use in stationary refrigeration amounted to about 55 g y^{-1} in 1986 (based on CFK Comissie, 1994).

From the above it may be concluded that an S-curved growth assuming short-term saturation underestimates future pre-Montreal demand for halocarbons. If the per capita use in industrialized countries stabilizes at the present level and increases in the less developed ones, demand for these compounds will continue to increase for some time to come. On the other hand it is unlikely that use will increase exponentially throughout the next century. Therefore, in the present study, it is assumed that per capita pre-Montreal demand will increase linearly, so that by 2100 the demand by each world citizen equals that of industrialized countries in 1986 (Tables 6-1 and 6-2).

6.2.2 HALOCARBONS TO BE REPLACED IN THE REFERENCE SCENARIO

The pre-Montreal demand for halocarbons increases throughout the next century (Table 6-2). Up to the early 1990s most of the demand was met by CFCs, halons and CH_3CCl_3. This will change dramatically as these compounds are to be phased out. In the reference scenario it is assumed that use of CFCs, halons and CH_3CCl_3 will be stopped before 2000 in industrialized countries and by 2005 in developing countries. It is furthermore assumed that use of HCFCs will be stopped in 2015 worldwide. The latter may be an optimistic assumption, since the Montreal Protocol allows use up to 2030. However, an earlier phase-out is envisaged by the industrial Alliance for Responsible Atmospheric Policy (Fay, 1995). As a result, the demand for alternatives by 2015 amounts to about 4000 kt in the reference scenario (Table 6-2). Most of this is assumed to be met by non-halocarbons (Table 3-10).

The breakdown in use per application in teh pre-Montreal situation is estimated assuming that the breakdown per gas per application will remain at the 1986 level as reported by AFEAS (1993, 1994), or if not presened by AFEAS, from Kroeze and Reijnders (1992). And it is assumed that 50% of the CFC-12 used as cooling agent is used in mobile airconditioning, that HCFC-22 is exclusively used for stationary refrigeration and CH_3CCl_3 for cleaning.

Table 6.1. Per capita use (g person^{-1} y^{-1})[1] of halocarbons in 1986 in industrialized countries (OECD, E. Europe and the former USSR)

CFC-11	CFC-12	CFC-113	CFC-114	CFC-115	HCFC-22	HCFC-142b	CH_3CCl_3	Halon 1301	Halon 1211
335	380	160	15	10	140	5.5	425	8.5	8.5

[1] population data are taken from UNEP (1993a) for the years up to 1980; from Pepper et al. (1992) from 1990; for 1986 and 2040 interpolated

Table 6-2. Pre-Montreal demand for CFCs, halons, CH_3CCl_3 and HCFCs (non-substitute use) and expected use when the 1992 Montreal Protocol is realized (reference scenario)

	CFCs, halons CH_3CCl_3		HCFC-22, HCFC-142b	
Year	Pre-Montreal demand	Reference scenario[5]	Pre-Montreal demand	Reference scenario[5]
1986[1]	1718	1718	189	189
2000[2]	2540	633	266	266
2005[3]	3037	0	298	177
2015[3]	4032	0	362	0
2040[2]	6520	0	521	0
2100[4]	15181	0	1646	0

[1] AFEAS, 1993, 1994 (non-feedstock consumption), non-reporting companies estimated by Olivier (personal communication); for gases not reported by AFEAS the 1985 data from Hammitt et al. (1987) are used [2] from Hammitt et al. (1987), except CFC-114 and CFC-115, which are from Kroeze and Reijnders (1992); for HCFC-22 and -142b the growth rate of CFCs is adopted, except HCFC-142b in 2000 = 1992 according to AFEAS (1993); [3] linearly interpolated; [4] based on global average per capita consumption as in 1986 in industrialized countries (see Table 6-1); [5] assuming that by 2000 use of CFCs, halons and CH_3CCl_3 is restricted to less developed countries, that no CFC-114 and -115 is used by 2000 and that HCFCs are phased out by 2015.

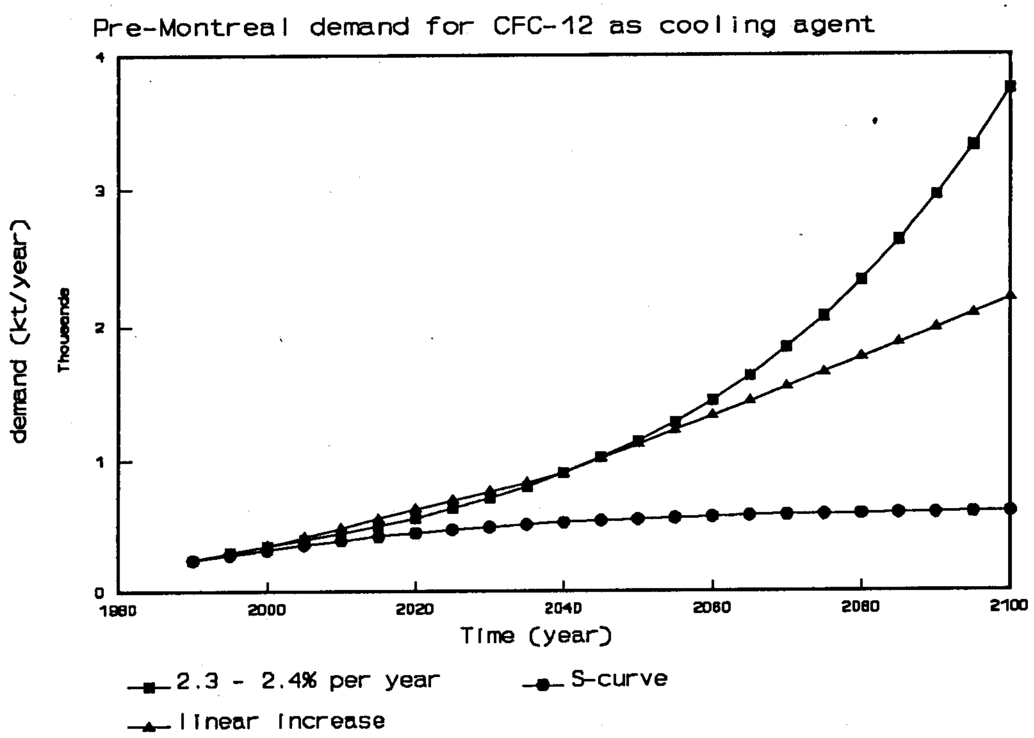

Fig. 6-1. Projected growth in global use of CFC-12 for cooling for the situation without Montreal Protocol: exponential growth based on Hammitt et al. (1987) extrapolated; S-curve of McCulloch et al. (1994a) and linear growth rate of Kroeze and Reijnders (1992)

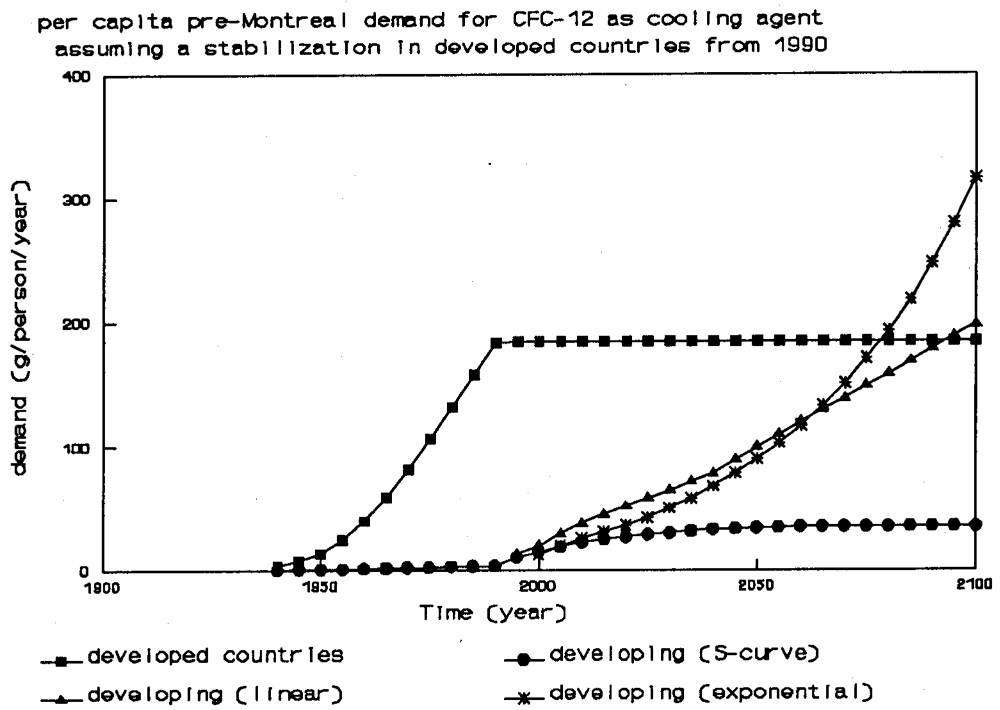

Fig. 6-2. Per capita halocarbon use for the three projections as shown in Fig. 6-1 in industrialized and less developed countries, assuming that in industrialized countries per capita use stabilizes from 1990.

6.2.3 USE OF HCFCs, HFCs, PFCs, FICs AND SF_6 IN THE REFERENCE SCENARIO

Table 6-3 shows the global use of HCFCs, HFCs, PFCs, FICs and SF_6 in the reference scenario, based on the amount to be replaced as shown in Table 6-2 and substitution rates as presented in Table 3-9 (Chapter 3). The reference scenario is described in 6.3.1.

Several of the compounds have been used for decades. By 1986 about 200 kt of HCFCs, PFCs and SF_6 had been used (so-called historical market, Table 6-3). It is tentatively assumed in the reference scenario that the historical use of PFCs and SF_6 doubles during the next century. For PFCs this may be an overestimation, because new HFC liquids in development may take over part of the market. The 2000 level is partly estimated from Ko et al. (1993).

Table 6-4 compares results of this study with other published estimates. In general, the results are in reasonable agreement. In 2000, about 645 kt of HCFCs and HFCs are used in the reference scenario, of which about 380 kt as substitute for phased-out compounds (Tables 6-4 and 6-5). This is in good agreement with the 625 kt as estimated by the industrial Alliance for Responsible Atmospheric Policy (Fay, 1995). The difference may be partly due to the fact that ARAP did not include substitution of CH_3CCl_3. Fay (1995) estimated use of HFCs and HCFCs in 2000 at 325 kt and 300 kt, respectively, as opposed to 240 and 405 kt presented in the reference scenario (Table 6-4). UNEP (1994b) estimated HCFC use in 2000 at 300 - 335 kt. Thus use of HCFCs in 2000 may be overestimated in the reference scenario and that of HFCs may be underestimated. The reference scenario assumes that a shift from HCFCs to HFCs will not start before 2000, while UNEP and ARAP seem to assume this will happen earlier. On the other hand, the reference scenario assumes a total phase-out of HCFCs by 2015, which may in fact happen later.

Annual use of HFCs increases from 920 kt in 2015 to 1440 kt in 2040 in the reference scenario. Again, this is in good agreement with the ARAP estimate of 1100 - 1400 kt for the year 2035 (Fay, 1995).

Use of HFC-134a in refrigeration increases to 340 kt in 2015 (Table 6-4). This is in reasonable agreement with the 300 kt by 2020, as envisaged by McCulloch (1994a). McCulloch's estimate of 90 kt of HFC-32 used as cooling agent by 2020 exceeds the 60 kt as envisaged in the reference scenario for 2015. These data show that the differences in the underlying assumptions between this study and McCulloch's (see 6.2.1), do not lead to large differences for the period up to 2040.

From Tables 6-2 and 6-3 can be deduced that HFCs, PFCs, FICs and SF_6 replace about 20% of the pre-Montreal demand for CFCs, halons and CH_3CCl_3 and 75% of the pre-Montreal demand for HCFC-22. The remaining substitutes are met by non-halocarbons and in refrigeration also by a reduction in the amount of cooling agents needed in refrigerators. Thus the reference scenario includes the currently observed trend that less refrigerant is needed per unit of cooling.

Table 6-5 presents a breakdown in use of halocarbons per application by 2040. Most important applications are cooling (60%), closed cell blowing (19%) and cleaning (8%). The most important halocarbon to be used is HFC-134a (40%). Second most important are HFC-125, HFC-143a and HFC-152a (each 7 - 9%).

Table 6-3. Use of HCFCs, HFCs, PFCs, FICs and SF_6 in the reference scenario 1986 - 2100 (non-feedstock use in kt y^{-1})

	HCFCs		HFCs	PFCs, FICs, SF_6		Total
Year	Historical use[2]	Use as substitute		Historical use	Use as substitute	
1986[1]	189	0	0	15	0	204
2000	266	140	241	15	9	671
2005	178	214	352	16	14	773
2015	0	0	918	17	50	985
2040	0	0	1439	21	80	1540
2100	0	0	4019	30	169	4218

[1] AFEAS, 1993, 1994 (non-feedstock consumption), non-reporting companies estimated by Olivier (pers.comm.); [2] data up to 1990 are from AFEAS, 1993; for future years based on Table 6-1; it is assumed that in 1970 the "stock" of unreleased HCFC-22 was 117 kt (based on AFEAS, 1993).

Table 6-4. Comparison of this study with other studies

Use of	Published estimate		This study (kt y^{-1})
	kt y^{-1}	Reference	
HFCs and HCFCs in 2000	625	Fay, 1995	645
HFCs in 2000	325	Fay, 1995	240
HCFCs in 2000	300 300 - 350	Fay, 1995 UNEP, 1994b	410
HFCs	1100 - 1400 in 2035	Fay, 1995	1440 in 2040
HFC-134a as cooling agent	300 in 2020	McCulloch, 1994a,b	340 in 2015
HFC-32 as cooling agent	90 in 2020	McCulloch, 1994a,b	60 in 2020
HCFCs as cooling agent	240 - 250 in 1994 and 200 in 2000	UNEP, 1994b	235 in 1995 and 250 in 2000
HCFC-22	230 in 1994 and 160-170 in 2000	UNEP, 1994b	235 in 1995 and 240 in 2000

Table 6-5. Use of HFCs, PFCs, FICs and SF_6 in the reference scenario in 2040 (non-feedstock use in kt y^{-1})

HFC-	23	32	125	134a	143a	152a	227ea	236fa	245ca	356	43-10mee	PFC	FIC	SF_6	Total
Aerosol				27		27	27								82
Cleaning											65	65			129
Open cell				2		2									4
Closed cell				19	37	19		75	75	75					299
Stationary cooling	17	86	86	240	86	86	17					11			630
Mobile airconditioning				301											301
Fire extinguishing	1		1	1			11					1	1	1	19
Other[1]			18	18			18					14		7	75
Total	18	86	106	608	124	134	73	75	75	75	65	91	1	8	1539

[1] including historical use of PFCs and SF_6; [2] PFCs may be replaced by HFC liquids in development

6.3 EMISSIONS OF HALOCARBONS

6.3.1 SCENARIO ASSUMPTIONS

Emissions are presented here for the **reference scenario** and for two other scenarios: (i) **closed applications only**, in which use of halocarbons and SF_6 is restricted to closed applications and (ii) **low GWP compounds only**, in which use of halocarbons is restricted to halocarbons with relatively low global warmimg potentials. These three scenarios are presented for two variations with and without emission control. In the **maximum emission control** variations, good housekeeping is realized and maximum recycling and destruction of halocarbon wastes. The assumptions in the scenarios, largely described earlier in this report, can be summarized as follows:

maximum emission control variants to scenarios

- This variant differs from the scenarios only in level of emission control by good housekeeping, recycling and destruction of halocarbon wastes. Thus in "reference case + maximum emission control" the use of halocarbons is not further restricted than in the 1992 Montreal Protocol, but emission reduction is maximized. The effect of emission control is also investigated for the closed applications only scenario and the low-GWP scenario (see above).

- The effect of maximum emission control is described in Chapter 4 and summarized in 5.3. The general assumptions are that leakage is prevented as much as possible and 80% of the halocarbons and SF_6 that is available after use is recycled or destroyed. Such severe emission control will not happen without further regulation.

reference scenario

- The pre-Montreal demand for 2000 and 2040 is based on Hammitt et al. (1987). For the period 2040 - 2100 it is calculated assuming that per capita pre-Montreal demand gradually increases to the 1986 level in industrialized countries.

- The 1992 Montreal Protocol is realized (Copenhagen amendments). Thus use of CFCs in industrialized countries is stopped before 2000 and in the rest of the world in 2005. Use of HCFCs is assumed to increase unrestricted until 2000 and to be 0 from 2015 (changes between these years are all linear).

- About 20% of CFCs, halons and CH_3CCl_3 to be replaced and 75% of the historical use of HCFC-22 to be replaced are met by HFC, PFCs, FICs and SF_6. These percentages take into account the currently observed trend that less refrigerant is needed per unit cooling. It is furthermore assumed that substitution starts from 1995 and that 2.5% of the cooling agents are used for household appliances.

- Emissions are calculated as described in Chapter 5.2, assuming no additional emission control. Thus in the reference scenario, halocarbons are not recycled or destroyed after use and housekeeping is not further improved. The reference scenario ignores new markets for halocarbons.

- In "reference + MAX" emission control through better housekeeping, recycling and destruction of halocarbon wastes is maximized.

closed applications only

- This scenario differs from the reference scenario in that use of halocarbons is only allowed in "closed" applications. As described in Chapter 4, actual closed applications do not exist. Usually applications are considered closed when their annual leakage is low. Therefore, in this scenario halocarbons are only allowed in stationary refrigeration and closed foam blowing.

- In "closed applications only + MAX" emission control through better housekeeping, recycling and destruction of halocarbon wastes is maximized.

low GWP compounds only

- This scenario differs from the reference scenario in that only compounds or blends are used with a relatively low GWPs. Thus the total amount used per application is the same as in the reference scenario, but the substitutes used are pure or blended mixtures having a GWP less than 250. An average GWP of 250 is about 90% lower than the average GWP of halocarbons emitted in the reference scenario (Tables 6-6 and 6-7). This implies an assumption that for 90% of the halocarbons used, in the reference scenario low-GWP alternatives are available. These could include blends containing HFCs. In Chapter 3 is concluded that for most applications non-halocarbons could, in the near future, replace 90 - 100% of the demand for halocarbons. If, in addition, low-GWP HFCs are allowed, an upper limit of 250 would seem within reach. Appendix 6-1 also shows results for scenarios with a maximum GWP of 500 and 750. Halocarbons with a direct GWP less than 250 include HCFC-123, HCFC-225ca, HFC-152a and the FICs. The GWP of HFC-143 is in the range 250 - 500, and those of HFC-32 and -245ca in the range 500 - 750 (Appendix 2-1).

- In "low-GWP compounds only + MAX" emission control through better housekeeping, recycling and destruction of halocarbon wastes is maximized.

6.3.2 EMISSIONS OF HCFCs, HFCs, PFCs, FICs and SF_6; 2000 - 2100

Tables 6-6 and 6-7, Figs. 6-3 and 6-4 and Appendix 6-1 summarize global emissions for the period 1990 - 2100 in kt and expressed in CO_2-equivalents. For the latter the direct Global Warming Potentials over 100 years from IPCC (1994) were used. GWPs for HCFC-225ca/cb, HFC-356, PFCs, and FICs are assumed to be 350 (average of ca and cb), 1300 (as HFC-134a), 9400 (average of PFCs), and 10 (tentatively estimated as twice the GWP of CF_3I), respectively.

In 2000 at least two-thirds of the emissions (in kt) are HCFCs. However, their emissions decrease as a result of their phase-out.

In the reference scenario total emissions of HFCs, PFCs, FICs and SF_6 amount to about 165 kt by 2000, which is considerably less than the 265 kt used in that year (Table 6-3). This difference is caused by the delay between use and emissions. Since almost 80% of the HFCs are used in cooling and closed foam blowing, emissions lag behind use.

In the reference scenario without emission control global emissions of HFCs, PFCs, FICs and SF_6 increase to 3800 Mton of CO_2-equivalents by 2040. Maximum emission control could reduce these emissions by 40 - 45%. These emissions equal to 14% and 8% of the 1990 global CO_2 emission (27 Gt CO_2 y^{-1}; Houghton et al., 1992), respectively. Some recycling is being implemented presently. Therefore it can be concluded that without specific policy, fluorocarbon emissions may by 2040 equal to 8 - 14% of the 1990 global CO_2 emissions and may be at the higher end of this range because certainly not all of the potential emission control will be implemented without furter regulations. Stabilization of global CO_2 emissions at the 1990 level may be difficult to achieve. If global CO_2 emissions increase, the relative contribution of halocarbons to global warming would decrease.

Restricting use of halocarbons to closed applications could result in emissions that are 40 - 50% lower than in the reference scenario. This illustrates the fact that applications with low annual emissions may, when the equipment lifetime is long, emit large quantities of halocarbons. An "open" application like cleaning probably offer as much or more possibilities to reduce emissions than the "closed" applications considered here. Restricting use to closed applications is most effective when in addition emission control is maximized.

Using only compounds with a low GWP reduces emissions expressed in CO_2-equivalents by about 90% relative to the reference scenario. Most of the HFCs used in this scenario may be blended, which may make recycling difficult.

The average GWP of the mix of halocarbons emitted increases in most scenarios between the years 2000 and 2040 (Table 6-7). In the reference scenario without emission control the increase is about 25% and in the closed applications only scenario about 40%. This is mainly the result of the HCFC phase-out. The HFCs used have higher GWPs than the HCFCs they replace. Restricting use of halocarbons to stationary cooling and closed foam blowing reduces the average GWP by about 10 - 25% during the first decades of the next century.

Table 6-6. Global CO_2-equivalent emissions of HCFCs, HFCs, PFCs and SF_6 for the period 2000 - 2100 (Mt CO_2 equivalnts y^{-1})

	Reference scenario		Closed applications only		Low GWP compounds only (GWP < 250)	
Year	No Control	+ Max	No Control	+ Max	No Control	+ Max
HFCs, PFCs, FICs, SF_6						
2000	532	366	111	34	41	22
2005	829	529	241	86	74	42
2015	2077	1096	961	415	191	102
2040	3798	2166	2103	1172	356	209
2100	9382	5278	5906	3251	943	543
HCFCs						
2000	491	176	464	156	79	27
2005	550	254	503	211	94	41
2015	258	223	249	217	45	36
2040	0	3	0	3	0	1
2100	0	0	0	0	0	0

Table 6-7. Total CO_2-equivalent emissions, average GWP of the mix of HCFCs, HFCs, PFCs and SF_6 emitted and total CO_2-equivalent emissions expressed as % of the 1990 CO_2 emissions for the reference scenario (reference), closed applications only scenario (closed only) and low GWP compounds only scenario (GWP < 250); all three scenarios are presented for a situation without emission control (No control) and for a situation in which emission control by better housekeeping, recycling and destruction of halocarbon wastes is maximized (+ MAX)

	Total CO_2-eq. emission (Mt y^{-1})			Average GWP			% of 1990 global CO_2 emissions		
Year	reference	closed only	GWP < 250	reference	closed only	GWP < 250	reference	closed only	GWP < 250
	No control	No control	No control	No control	No control	No control	No control	No control	No control
2000	1022	575	120	2139	1798	250	4	2	<1
2005	1378	744	168	2048	1854	250	5	3	<1
2015	2335	1210	236	2474	2177	250	9	4	<1
2040	3798	2103	356	2671	2504	250	14	8	1
2100	9382	5906	943	2488	2437	250	35	22	3
	+ MAX	+ MAX	+ MAX	+ MAX	+ MAX	+ MAX	+ MAX	+ MAX	+ MAX
2000	541	190	50	2752	1808	250	2	1	<1
2005	783	308	83	2345	1836	250	3	1	<1
2015	1319	632	138	2390	2124	250	5	2	<1
2040	2169	1175	210	2587	2602	250	8	4	<1
2100	5278	3251	543	2432	2550	250	20	12	2

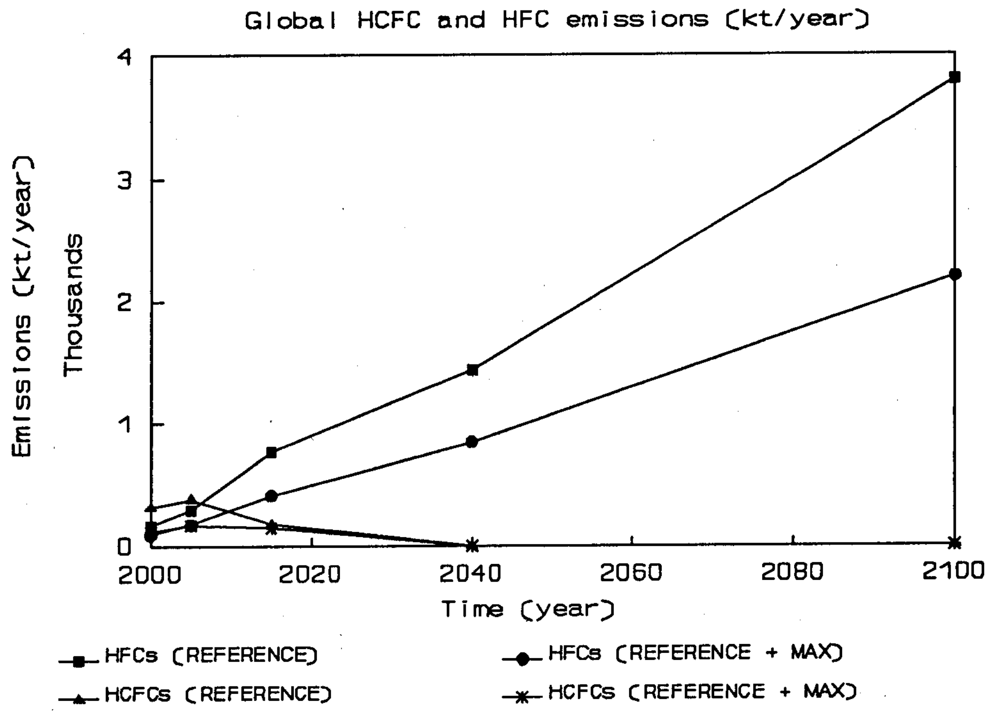

Fig. 6-3. Emissions of HCFCs and HFCs (including PFCs, FICs and SF_6) in the reference scenario and in the maximum emission control scenario in kt y^{-1}

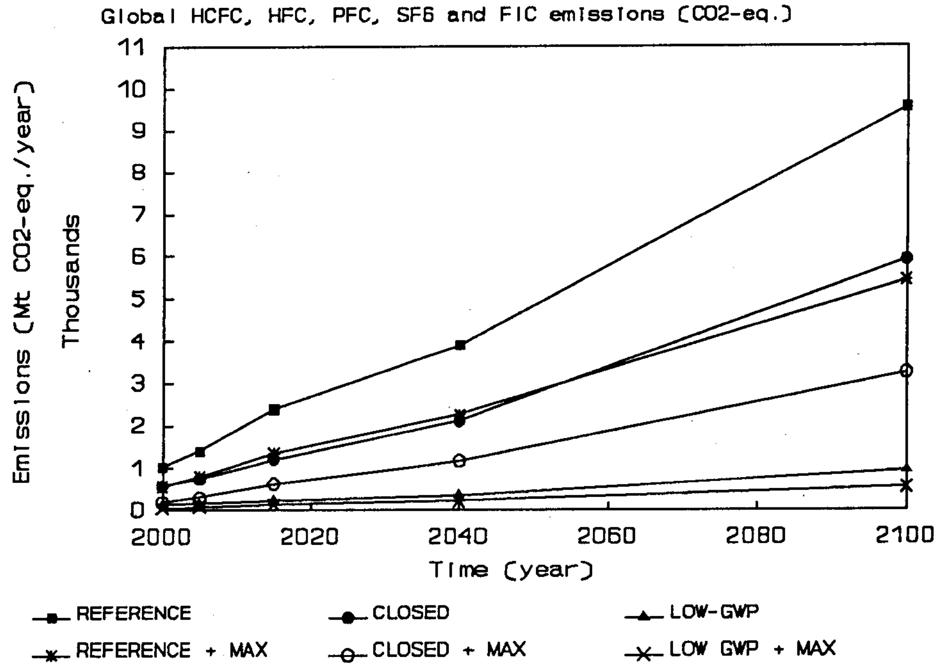

Fig. 6-4. Emissions of HCFCs, HFCs, PFCs, FICs and SF_6 in the reference scenario, closed applications only scenario and low GWP compounds only scenario, all three with (+ MAX) and without maximum emission control; in Mton CO_2-equivalents per year.

6.4 CONCLUSIONS

This chapter presents emissions of halocarbons for the period 1986 - 2100. Projections for future emissions largely depend on the underlying assumptions about market trends. It is shown here that although there are large differences in views on the future market, these differences become important only after the year 2040.

Emissions for several scenarios are presented here. The reference scenario reflects a situation without specific regulations for HFCs, PFCs, FICs and SF_6. In this scenario global use of HFCs inreases to about 920 kt in 2015 and 1440 kt in 2040. When CFCs and HCFCs are phased out, the most important halocarbon applications are stationary cooling (60%), closed foam (19%) and cleaning (8%). The most widely used halocarbon is HFC-134a (40%). Second most important are HFC-125, HFC-143a and HFC-152a (7 - 9% each).

Without specific policy, emissions of HFCs, PFCs, FICs and SF_6 may by 2040 equal to 8 - 14% of the 1990 global CO_2 emissions and may be at the higher end of this range because the lower end assumes maximum emission control, which will certainly not be fully implemented without further regulations. The results of this study are in general in good agreement with the earlier RIVM estimate of 7 - 17% (Kroeze, 1994).

Maximum emission control through better housekeeping, recycling and destruction of halocarbon wastes reduces CO_2-equivalent emissions by about 40 - 45% in the reference scenario.

The average GWP of the halocarbon mix emitted increases by about 25% between 2005 and 2040 in the reference scenario. This is mainly the result or the HCFC phase-out: the HFCs used have higher GWPs than the HCFCs they replace.

Restricting use to stationary cooling and closed foam blowing, which are applications with relatively low annual loss rates, decreases halocarbon emissions by about 40 - 50% relative to the reference scenario. Restricting use to closed applications is most effective when in addition emission control is maximized.

When only compounds are used with global warming potentials lower than 250, CO_2-equivalent emissions 90% lower than in the reference scenario.

7 CONCLUSIONS

This study surveys current knowledge on global emissions of several halocarbons and presents scenarios for future emissions (up to 2100). The compounds studied here are not regulated under the Montreal Protocol. These include HFCs, PFCs, FICs and SF_6 and are mainly used as substitutes for CFCs, halons, CH_3CCl_3 and HCFCs, which will be phased out when the Montreal Protocol on substances that deplete the ozone layer is implemented. The Global Warming Potentials (GWPs) of HFCs and PFCs vary widely. Some of them as well as SF_6 have GWPs exceeding the direct GWPs of CFCs. FICs, on the other hand, have much lower GWPs.

Halocarbons are used as aerosol, solvent, blowing agent, cooling agent, and fire extinguisher. When the Montreal Protocol will be implemented, halocarbons will to a considerable extent be replaced by non-halocarbons. It has been estimated in this study to what extent HFCs, PFCs, FICs and SF_6 replace the demand for CFCs, halons and CH_3CCl_3 as would have been the case without the Montreal Protocol. The most realistic substitution rates are estimated for aerosols (9-11%), cleaning (<5%), open-foam blowing (1-2%), closed-foam blowing (40-45%), stationary refrigeration (>50%), mobile airconditioning (<75%), fixed fire extinguishing (45-50%) and other (30%). In addition, it is assumed that 75% of the historical HCFC-22 market will be replaced by HFCs after an HCFC phase-out.

It is concluded that non-halocarbons are, or will become, available for all major applications in the near future. Some of these are toxic, flammable, less energy efficient or contribute to smog formation. However, in many cases this can be overcome by redesigning equipment or by a change in processing and servicing. The costs involved depend on the price of the compounds used, the costs of retrofitting or redesigning equipement and the costs of servicing. For users of halocarbons, the costs of a phase-out can be kept low if the timing is such that early replacement of equipment is not necessary.

Options for emission control include better housekeeping and recycling and destruction of halocarbon wastes. For each application it is investigated to what extent emissions can be reduced. It is concluded that perfectly closed systems do not exist. Even when maximum emission control is implemented, considerable amounts of halocarbons are emitted unavoidably.

Actual emissions differ from the annual use. For a number of applications emissions occur almost immediately. However, when compounds are used as cooling or blowing agents, emissions may be delayed by many years. In this study the method for estimating actual emissions is mainly based on AFEAS (1993).

For a situation without specific regulations, use of HFCs may increase to about 1440 kt y^{-1} in 2040 (reference scenario). This is in good agreement with an estimate of the industrial Alliance of Responsible Atmospheric Policy, that estimated the use of HFCs by 2035 to be 1100 - 1400 kt y^{-1} (Fay, 1995). When CFCs and HCFCs are phased out, the most important halocarbon applications are stationary cooling (60%), closed foam (19%) and cleaning (8%). The most widely used halocarbon is HFC-134a (40%). Second most important are HFC-125, HFC-143a, and HFC-152a (7 - 9% each).

Emission control by better housekeeping, recycling and destruction of halocarbon wastes reduces CO_2-equivalent emissions by 40 - 45% in the reference scenario (reference + MAX). Part of this reduction may be achieved without additional policy.

The CO_2-equivalent emissions of HFCs, PFCs, FICs and SF_6 are 8 - 14% of the 1990 global CO_2 emissions in the scenarios without HFC policy by 2040 (reference and reference + MAX), and are probably at the higher end of this range. The lower end of the range assumes maximum emission control through better housekeeping, recycling and destruction of halocarbon wastes, which will not be realized without additional regulations. These results are within the range of 7 - 17% as published earlier by RIVM.

An HCFC phase-out may increase the average GWP of the halocarbon mix emitted. In the reference scenario, the average GWP increases by about 25% between 2005 and 2040. This because HFCs have on average higher GWPs than the HCFCs they replace. The average GWP of the mix used in the reference scenario is 2000 - 2700, which is higher than the ARAP estimate of 1300 (Fay, 1995).

Restricting use to stationary cooling and closed-foam blowing, which are applications with the lowest annual loss rates, decrease halocarbon emissions by about 40 - 50% relative to the reference scenario. Restricting use to closed applications is most effective when emission control is simultaneously maximized.

It is concluded that CO_2-equivalent emissions are reduced most in the scenario where compounds are selected based on the Global Warming Potentials. When only compounds with global warming potentials lower than 250 are used, CO_2-equivalent emissions are 90% lower than in the reference scenario. An average GWP of 250 is 90% lower than the average GWP in the reference scenario. This implies an assumption that for 90% of the fluorocarbons to be used low-GWP alternatives are be available. It is concluded here this may be achievable in the near future.

REFERENCES

AFEAS, 1993. Production, sales and atmopsheric release of fluorocarbons through 1992.

AFEAS, 1994. Historic production, sales and atmospheric release of HCFC-142b.

Allied Signal, 1989. AccuDriSF$_6$. Technical Bulletin/Sulphur Hexafluoride. Allied-Signal INC. 524-999 9/89 2M, Morristown, NJ 07962-1139, USA

Aluminium Delfzijl, 1992. Polyfluorinated compounds. Bijdrage aan het broeikaseffect. Alumiun Delfzijl BV, Delfzijl, The Netherlands. 5 pp.

Annema J.A., 1989. Zwavelhexafluoride. Toepassingen, electrtechniek, ontledingsprodukten, giftigheid, milieu-risico's. Stichting Natuur en Milieu, Utrecht, The Netherlands. 31 pp.

Austin J., N. Butchart and K.P. Shine, 1992. Possibility of an Arctic ozone hole in a doubled-CO$_2$ climate. Nature 360, 221-225.

Brühl C. and R. Hennig, 1989. Umweltsfirshungen des Bundesministers des innern Zwischenbericht zun FE-Vorhaben 104 02 521. Assessment of models for predicting of changes in the ozone content of the atmosphere. 113 pp.

CFK Commissie, 1994. CFK Aktieprogramma. Jaarrapportage 1993. Projektburo CFK, Tilburg, The Netherlands.

Cohen S. and A. Pickaver (eds), 1992. Climbing out of the ozone hole. A preliminary survey of alternatives to ozone-depleting chemicals. Greenpeace International.

Den Elzen M., 1994. Global environmental change. An integrated modelling approach. PhD Thesis, 253 pp.

Devotta S., S. Gopichand and V.R. Pendyala, 1993. Assessment of HFCs, fluorinated ethers and amine as alternatives to CFC-12. Int.J.Refrig. 16 (2), 84-90.

Dieckmann, J.T., J. Bentley and A. Varone, 1991. Non-inert refrigerant study for automotive applications. Arthur S. Little, Inc. 20 Acorn Park, Cambridge, MA. 02140. U.S. Department of Transportation, Transportation Systems Center, Kendall Square, Cambridge, MA 02142.

Dishart K.T. and M.C. Wolff, 1990. Advantages and process options of hydrocarbon nased formulations in semi-aqueous cleaning. E.I. Du Pont de Nemoure & Company, Inc. Paper presented at the NEPCON West 90, February 26, 1990, CA.

Dupont, 1988. Safety of Dupont DYMEL propellants. E-95693 (5/88). E.I. du Pont de Nemours & Co. (Inc.) FREON Products division, Wilmington, Delaware 19898, USA.

Dupont, 1990a. FE-25 for total flooding agent applications. DuPont de Nemours International S.A., Geneva, Switzerland. 1 pp.

Dupont, 1990b. FE-232 streaming agent for portable applications. DuPont de Nemours International S.A., Geneva, Switzerland. 1 pp.

Dupont, 1993. HCFC AEL incraesed to 30 oom. Dupont Press information. September 1993. Du Pont de Nemours International S.A., Le-Grand-Saconnex, Switzerland.

Dupont, 1994. Information presented at the tenth meeting of the International Negotiating Committee, Geneva, 27 August 1994. Dupont USA.

Enquete Comission, 1994. Responsibility for the future. Options for sustainable management of substance chains and material flows; interim report. Enquete Comission of the German Bundestag on the "Protection of Humanity and the Environment" (ed.). Submitted by the 12th German Bundestag's Enquete Commission on the "Protection of Humanity and Sound Product Cycles in Industrial Society". Economica Verl., Bonn. ISBN 3-87081-044-4.

EPA, 1994a. Federal Register, Part II, Environmental Protection Agency, 40 CFR Parts 9 and 82, Protection of stratospheric ozone; Final rule. Friday March 18, 1994. Washington, USA.

EPA, 1994b. Inventory of U.S. greenhouse gas emissions and sinks: 1990-1993. United States Environmental Protection Agency, EPA 230-R-94-014. September 1994. Washinton D.C., U.S.A.

Fay K.J., 1995. Critique of articles by C. Kroeze concerning potential effect of HFC policy on global greenhouse gas emissions. Alliance for Responsible Atmospheric Policy and the International Climate Change Partnership. Arlington, Virginia, USA.

Fisher D.A. and P.M. Midgley, 1993. Production and release to the atmosphere of chlorodifluoromethane (HCFC-22). Atmospheric environment 27, 2215-2223.

Fisher D.A., T. Duafala, P.M. Midgley, C. Niemi, A. Makhijani and S. Seidel, 1994a. Production and emission of CFCs, halons and related molecules. In: Kaye J.A., S.A. Penkett and F.M. Ormond (eds.), Report on concentrations, lifetimes, and trends of CFCs, halons, and related species. NASA Reference Publication 1339. NASA office of mission to planet earth, Washington, D.C., USA.

Fisher S.K., J.J. Tomlinsen and P.J. Hughes, 1994b. Energy and global warming impacts of not-in-kind and next generation CFC and HCFC alternatives. Oak Ridge National Laboratory, Oak Ridge, USA.

Frehn B., 1994. Hydrocarbons as alternative refrigerants for heat pumps - initial operational experience. RWE Energie, Essen, Germany.

Gamlen P.H., B.C. Lane, P.M. Midgley and J.M. Steed, 1986. The production and release to the atmosphere of CCl_3F and CCl_2F_2 (chlorofluorocarbons CFC 11 and CFC 12). Atm.Environ. 20 (6), 1077-1085.

GECR, 1994. British firm to produce hydrocarbon refrigerants. Global Environmental Change Report Vol. VI, No. 13, 8 july 1994, 6-7. Cutter Information Cooperation, 37 Braodway Arlington, MA 02174-5539, USA.

Geuzendam C and W. Gilijamse, 1994. Assessment of energy efficient techmologies for and-use in the residential and the commercial sectors. IVAM Environmental Research. Report no. 94-15. Amsterdam, The Netherlands.

Great Lakes, 1994. FM-200. The new solution for fire protection. Great Lakes Chemical Corporation, Ellesmere Port, UK.

Gribbin J., 1992. CFCs active. Nature 357, 272.

Hammitt J.K., F. Camm, P.S. Connell, W.E. Mooz, K.A. Wolf, D.J. Wuebbles and A. Bamezai, 1987. Future emission scenarios for chemical sthat may deplete stratospheric ozone. Nature '330, 771-716.

Heat Transfer Holland, 1994. DEC luchtkoeling, klimaatbeheersing zonder CFK's. Heat Transfer Holland BV, Hasselt, The Netherlands. 15 pp.

Houghton J.T., B.A. Callander, and S.K. Varney (eds.), 1992. Climate change 1992. The supplementary report to the IPCC scientific assessment. Published for the Intergovernmental Panel on Climate Change, Cambridge University Press.

IPCC, 1994. Radiative forcing of climate change. The 1994 report of the scientific assessment working group of IPCC. Summary for policy makers. Intergovernmental Panel on Climate Change. 28 pp.

IKON, 1994. Recent toxicity data on fluoroiodocarbons, DRAFT, White paper, October 29, 1994. 7 pp. The Ikon Corporation, Albuqueruqe, USA.

Isaksen I.S.A., 1994. Dual effects of ozone reduction. Nature 372, 322-323.

James R.W. and H.F. Missenden, 1992. The use of propane in domestic refrigerators. Rev.Int.Froid, Vol. 15 (2), 95-100.

Ko M.K.W., N.D. Sze, W.C. Wang, G. Shia, A. Goldman, F.J. Murcray, D.G. Murcray and C.P. Rinsland, 1993. Atmospheric sulphur hexafluoride: sources, sinks and greenhouse warming. J.Geophys.Res. 98 (D6), 10499-10507.

Kranz P.B., T. Gardner-Clayson, K.C. Malinowski, T.D. Schaab, J.E. Stadelmaier and P.M. Randall, 1994. Ultrasonic cleaning as a replacement for a chlorofluorocarbon-based system. Project summary. U.S. EPA, Research and Development, Risk Reduction Engineering Laboratory, Cincinatti, OH 45268. EPA/600/SR-93/223.

Kroeze C. and L. Reijnders, 1992. Halocarbons and global warming II and III. Science of the Total Environment 112, 269 - 314.

Kroeze C., 1994. Potential effect of HFC policy on global greenhouse gas emissions in 2035. RIVM report no. 773001002. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands.

Lermond D.S., R.B. Ramsey Jr. and J. Yellow, 1989. New HCFC blend for metal cleaning. E.I. DuPont de Nemours & Co. Inc. Wilmington, DE. Paper presented at the International Conference on CFC & halon alternatives. October 10-11, 1989, Washington DC.

Liu B.Y., M.-L. Tomasek and R. Radermarcher, 1994. Experimental results with hydrocarbon mixtures in domestic refrigerants/freezers. Center for Environmental Energy Engineering (CEEE), University of Maryland, College Park, Maryland, USA.

Maclaine-cross I.L., 1994. Fireball, a brief report on pilot experiments to measure the insurance risk of hydrocarbons in motor-cars. School of Mechanical and Manufacturing Enginieering, the University of New South Wales, Australia.

McCarthy, R.L., F.A. Bower and J.P. Jesson, 1977. The fluorocarbon-ozone theory-I. Production and release-world production and release of CCl_3F and CCl_2F_2 (fluorocarbons 11 and 12) through 1975. Atmospheric environment 11, 491-497.

McCulloch, A., 1992. Global production and emissions of bromochlorofluorodifluoromethane and bromotrifluoromethane (Halons 1211 and 1301). Atmospheric environment 26, 1325-1329.

McCulloch A., 1994a. Sources of hydrochlorofluorocarbons, hydrofluorocarbons and fluorocarbons and their potential emissions during the next twenty five years. Environmental Monitoring and Assessment 31, 167-174.

McCulloch A., 1994b. Sources of hydrochlorofluorocarbons, hydrofluorocarbons and fluorocarbons and their potential emissions during the next twenty five years. Maastricht 1993.

Midgley P.M., 1989. The production and release to the atmosphere of 1,1,1-trichloroethane (methyl chloroform). Atm.Environ. 23, 2663-2665.

Midgley P.M. and D.A. Fischer, 1993. The Production and release to the atmosphere of CFCs 113, 114 and 115. Atm.Environ. 27, 271-276.

Nimitz J., 1994a. Refrigerants containing fluoroiodocarbons (FICs). Paper accepted for presentation at the 1994 ASHRAE International Compressor Engineering Conference, Purdue University, W. Lafayette, IN, July 19-22, 1994.

Nimitz J., 1994b. New foam blowing agents containing fluoroiodocarbons. Paper accepted for presentation at teh SPI Polyurethanes Conference, Boston, MA, October 10-12, 1994.

Nimitz J., 1994c. Current status of fluoroiodocarbons as CFC and halon replacements. Part 1. Submitted for the First North American Conference & Exhibition: Emerging Clean Air Technologies & Business Opportunities. Toronto, Canada, September 26-30, 1994.

Nimitz J., 1994d. Trifluoromethyl iodide and its blends as high-performance, environmentally sound halon 1301 replacements. In: Proceedings of the 1994 halon options technical working conference, University of New Mexico, Albuquerque, NM, May 3-5 1994.

Olivier J.G.J. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands. Personal communication.

OORG, 1994. Minutes of the sixth Ozone Operations Resource Group (OORG) meeting, October 27, 1994. Worldbank, Washington, USA.

PRI, 1994. Problems in the TEWI argument. A discussion paper by People's Research Institute on Energy & Environment, Tokyo. For Greenpeace, Japan. 7 pp.

Pepper W., J. Leggett, R. Swart, J. Wasson, J. Edmonds, I. Mintzer, 1992. Emission scenarios for the IPCC. An update.

Ramanathan V., L. Callis, R. Cess, J. Hansen, I. Isaksen, W. Kuhn, A. Lacis, F. Luther, J. Mahlman, R. Reck and M. Schlesinger, 1987. Climate-chemical interactions and effects of changing atmospheric trace gases. Rev.Geophys. 25 (7), 1441-1482.

Ramaswamy V., M.D. Swarzkopf, and K.P. Shine, 1992. Radiative forcing of climate from halocarbon-induced global stratospheroc ozone loss. Nature 355, 810-812.

Ravishankara A.R., A.A. Turnipseed, N.R. Jensen, S. Barone, M. Mills, C.J. Howard and S. Solomon, 1994. Do hydrofluorocarbons destroy stratospheric ozone? Science 263, 71-75.

Richardson R.N. (1994). Performance comparison of R12, R134a, R290 (propane) and R290/R600a (propane/isobutane) mixtures in a fully instrumented hermetic test circuit. Insitute of Cryogenicx, University of Southampton, Southampton, SO9 5NH. 7 pp.

Ros J.P.M., 1994. Du Pont de Nemours. Samwerkingsproject Procesbeschrijvingen Industrie Nederland. RIVM Report no. 773006169. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands.

Rusch G.M., 1994. Toxicity of trifluoroacetic acid. In: Workshop on teh environmental fate of trifluoroacetic acid, 3-4 March 1994. Miami Beach, Florida, USA. AFEAS, Washington.

Solomon A., J.B. Burkholder, A.R. Ravishankara and R.R. Garcia, 1994. Ozone depletion and global warming potentials of CF_3I. J.Geophys.Res. 99, 20929-20935.

Stamp M. Great Lakes Chemical Europe, South Wirral, UK. Personal communication.

Strong D., 1994. Natural refrigerants: the next revolution? Refrigeration and air conditioning, August 1994, 26-27.

Thompson A.M., 1991. New ozone hole phenomenon. Nature 352, 282-283.

Toumi R., S. Bekki and K.S. Law, 1994. Indirect influence of ozone depletion on climate forcing by clouds. Nature 372, 348-351.

Treadwell D.W., 1994. Application of propane (R290) to a single packages unitary air-conditioning product. Lennox Industries Inc. 5 pp.

UNEP, 1987. The Montreal Protocol on substances that deplete the ozone layer. Final Act, Na.87-6106. Ozone secretariat, Nairobi, Kenya.

UNEP, 1991. Handbook for the Montreal Protocol on substances that deplete the ozone layer. Second edition. Ozone secretariat, Nairobi, Kenya.

UNEP, 1992. Report of the fourth meeting of the parties to the Montreal Protocol on substances that deplete the ozone layer. Na.92-6155. Ozone secretariat, Nairobi, Kenya.

UNEP, 1993a. Environmental data report 1993-94. United Nations Environmental Programme.

UNEP, 1993b. Halons. A special supplement of OzonAction. UNEP IE/PAC, Imprimerie Rozay, Vincennes, France, 4 pp.

UNEP, 1994a. Montreal Protocol an substances that deplete the ozone layer. 1994 Report of the technology and economic assessment panel. UNEP, Nairobi, Kenya.

UNEP, 1994b. Montreal Protocol an substances that deplete the ozone layer. 1994 Report of the refrigeration, air conditioning and heat pumps technical options committee. UNEP, Nairobi, Kenya.

UNEP IE, 1994. Non-fluorocarbon alternatives for refrigeration and air conditioning. OzonAction Special Supplement no. 2. September 1994, ISSN 1020-1602. United Nations Environmental Programme, Industry and Environment, Paris, France.

Van Amstel A.R., R.A.W. Albers, C. Kroeze, A.C. Matthijsen, J.G.J. Olivier, and J. Spakman, 1994. Greenhouse gas emissions in the Netherlands 1990, 1991, 1992 and projections for 1990-2000. A background report for the National

Communications of the Netherlands for the Climate Convention. RIVM report no. 773001003. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands.

Van Gerwen R.J.M. and C.M.A. Jansen (1994). Risk assessment of flammable refrigerants. Paper presented at the IIR-IIF Conference, Commission B1, B1, E1, E2, Hannover, May 1994. Netherlands Organisation for Applied Scientific Research TNO, Apeldoorn, The Netherlands.

APPENDIX 1-1. LIST OF ABBREVIATIONS AND DEFINITIONS

AFEAS	Alternative Fluorocarbon Environmental Acceptability Study
ARAP	Alliance for Responsible Atmospheric Policy
Azeotrope mixture	Mixture of compounds having similar boiling points
CCl_4	Carbon tetrachloride
CH_3CCl_3	1,1,1 Trichloroethane, or methyl chloroform (MCF)
CFC	Chlorofluorocarbon
Drop-in substitute	Compound that can be used instead of currently used compound without equipment modification, or with minor retrofitting of equipment
FIC	Fluoroiodocarbon
Fluorocarbons	Halocarbons containing one or more fluoride atoms, including CFCs, HCFCs, HFCs, PFCs and FICs
GWP	Global Warming Potential, defined by IPCC as the time-integrated commitment to climate forcing from the instantaneous release of 1 kg of a trace gase expressed relative to that from 1 kg of carbon dioxide (Houghton et al., 1992).
Halons	Chlorobromocarbons
Halocarbons	Chlorinated, fluorinated, brominated and/or iodated carbon compounds, including CFCs, HCFCs, HFCs, PFCs, FICs, CH_3CCl_3, CCl_4 and halons
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
Historical market	Applications in which HCFCs, PFCs or SF_6 were used before the Montreal Protocol (i.e. before 1987).
MAC	Mobile airconditioning
Montreal Protocol	International agreement to protect the ozone layer. First signed in 1987 in Montreal (UNEP, 1987). Strengthened in 1990 in London (UNEP, 1991) and in 1992 in Copenhagen (UNEP, 1992).
ODP	Ozone Depleting Potential
PFC	Perfluorocarbon

Pre-Montreal demand	Future demand for a compound as it would have been without the Montreal Protcol
Production	Industrial manufacture of new, not recycled, compounds
SF_6	Sulfur hexafluoride
TEWI	Total Equivalent Warming Impact (including direct warming of compounds emitted from a system and energy-related emissions of CO_2)
Use	End use of a compound (non-feedstock use)

APPENDIX 2-1. OVERVIEW OF DIFFERENT COMPOUNDS

Table A-1. Chemical formulas, atmospheric lifetimes, direct GWPs over 100 years and systematic names of several compounds considered in this study

Compound	Chemical formula	Atmospheric lifetime (y)[1]	Direct GWP (CO_2 = 1)[1]	Systematic name
Chlorofluorocarbons (CFCs)				
CFC-11	$CFCl_3$	50±5	4000	trichlorofluoromethane
CFC-12	CF_2Cl_2	102	8500	dichlorodifluoromethane
CFC-13	CF_3Cl	640	11700	chlorotrifluoromethane
CFC-111	C_2FCl_5			pentachlorofluoroethane
CFC-112	$C_2F_2Cl_4$			tetrachlorodifluoroethane
CFC-113	$C_2F_3Cl_3$	85	5000	trichlorotrifluoroethane
CFC-114	$C_2F_4Cl_2$	300	9300	dichlorotetrafluoroethane
CFC-115	C_2F_5Cl	1700	9300	chloropentafluoroethane
CFC-211	C_3FCl_7			septochlorofluoropropane
CFC-212	$C_3F_2Cl_6$			hexachlorodifluoropropane
CFC-213	$C_3F_3Cl_5$			pentachlorotrifluoropropane
CFC-214	$C_3F_4Cl_4$			tetrachlorotetrafluoropropane
CFC-215	$C_3F_5Cl_3$			trichloropentafluoropropane
CFC-216	$C_3F_6Cl_2$			trichlorohexafluoropropane
CFC-217	C_3F_7Cl			dichloroseptofluoropropane
Chlorobromocarbons (halons)				
halon 1211	CF_2ClBr			chlorobromodifluoromethane
halon 1301	CF_3Br	65	5600	bromotrifluoromethane
halon 2402	$C_2F_4Br_2$			dibromotetrafluoroethane

Table A-1. Chemical formulas, atmospheric lifetimes, direct GWPs over 100 years and systematic names of several compounds considered in this study

Compound	Chemical formula	Atmospheric lifetime (y)[1]	Direct GWP (CO_2 = 1)[1]	Systematic name
Hydrochlorofluorocarbons (HCFCs)				
HCFC-21	$CHFCl_2$			dichlorofluoromethane
HCFC-22	CHF_2Cl	13.3	1700	chlorodifluoromethane
HCFC-31	CH_2FCl			chlorofluoromethane
HCFC-121	C_2HFCl_4			tetrachlorofloroethane
HCFC-122	$C_2HF_2Cl_3$			trichlorodifloroethane
HCFC-123	$C_2HF_3Cl_2$	1.4	93	dichlorotrifloroethane
HCFC-124	C_2HF_4Cl	5.9	480	chlorotetrefloroethane
HCFC-131	$C_2H_2FCl_3$			trichlorofluoroethane
HCFC-132b	$C_2H_2F_2Cl_2$			dichlorodifluoroethane
HCFC-133a	$C_2H_2F_3Cl$			chlorotrifluoroethane
HCFC-141b	$C_2H_3FCl_2$	9.4	630	dichlorofluoroethane
HCFC-142b	$C_2H_3F_2Cl$	19.5	2000	chlorodifluoroethane
HCFC-221	C_3HFCl_6			hexachlorofluoropropane
HCFC-222	$C_3HF_2Cl_5$			pentachlorodifluoropropane
HCFC-223	$C_3HF_3Cl_4$			tetrachlorotrifluoropropane
HCFC-224	$C_3HF_4Cl_3$			trichlorotetrafluoropropane
HCFC-225ca	$C_3HF_5Cl_2$	2.5	170	dichloropentafluoropropane
HCFC-225cb	$C_3HF_5Cl_2$	6.6	530	dichloropentafluoropropane
HCFC-226	C_3HF_6Cl			chlorohexafluoropropane
HCFC-231	$C_3H_2FCl_5$			pentachlorofluoropropane
HCFC-232	$C_3H_2F_2Cl_4$			tetrachlorodifluoropropane
HCFC-233	$C_3H_2F_3Cl_3$			trichlorotrifluoropropane
HCFC-234	$C_3H_2F_4Cl_2$			dichlorotetrafluoropropane
HCFC-235	$C_3H_2F_5Cl$			chloropentafluoropropane
HCFC-241	$C_3H_3FCl_4$			tetrachlorofluoropropane
HCFC-242	$C_3H_3F_2Cl_3$			trichlorodifluoropropane
HCFC-243	$C_3H_3F_3Cl_2$			dichlorotrifluoropropane
HCFC-244	$C_3H_3F_4Cl$			chlorotetrafluoropropane
HCFC-251	$C_3H_4FCl_3$			trichlorofluoropropane
HCFC-252	$C_3H_4F_2Cl_2$			dichlorodifluoropropane
HCFC-253	$C_3H_4F_3Cl$			chlorotrifluoropropane
HCFC-261	$C_3H_5FCl_2$			dichlorofluoropropane
HCFC-262	$C_3H_5F_2Cl$			chlorodifluoropropane
HCFC-271	C_3H_6FCl			chlorofluoropropane
carbon tetrachloride	CCl_4	42	1400	tetrachloromethane
methyl chloroform (MCF)	CH_3CCl_3	5.4±0.6	110	1,1,1 trichloroethane
Hydrocluorcarbons (HFCs)				
HFC-23	CHF_3	250	12100	trifluoromethane
HFC-32	CH_2F_2	6	580	difluoromethane
HFC-43-10mee	$C_4H_2F_{10}$	2.8	1600	decafluorobutane
HFC-125	C_2HF_5	36	3200	pentafluoroethane
HFC-134	CHF_2CHF_2	11.9	1200	tetrafluoroethane
HFC-134a	CH_2FCF_3	14	1300	tetrafluoroethane
HFC-152a	$C_2H_4F_2$	1.5	140	difluoroethane
HFC-143	CHF_2CH_2F	3.5	290	trifluoroethane
HFC-143a	CF_3CH_3	55	4400	trifluoroethane
HFC-227ea	C_3HF_7	41	3300	septofluoropropane
HFC-236fa	$C_3H_2F_6$	250	8000	hexaflouoropropane
HFC-245ca	$C_3H_3F_5$	7	610	pentafluoropropane

Table A-1. Chemical formulas, atmospheric lifetimes, direct GWPs over 100 years and systematic names of several compounds considered in this study

Compound	Chemical formula	Atmospheric lifetime (y)[1]	Direct GWP ($CO_2 = 1$)[1]	Systematic name
Perfluorocarbons (PFCs)				
perflorormethane	CF_4	50000	6300	tetraflouormethane
perfluoroethane	C_2F_6	10000	12500	haxefluoroethane
perfluorocyclo-butane	$c\text{-}C_4F_8$	3200	9100	octafluorobutane
perfluorohexane	C_6F_{14}	3200	6800	perfluorohexane
Fluoroiodocarbons (FICs)				
	CF_3I	<<1	5	trifluoromethyl iodine
	CF_3CF_2I			pentafluoroethyl iodine
	$CF_3(CF_2)_2I$			heptafluoropropyl iodine
	$CF_3(CF_2)_3I$			nonafluorobutyl iodine
dimethyl ether	CH_3OCH_3			dimethyl ether
propane	C_3H_8			propane
butane	C_4H_{10}			butane
sulfur hexafluoride	SF_6	3200	24900	sulfur hexafluoride

[1] IPCC, 1994; Solomon et al. (1994) for trifloroiodomethane; blanks: no data available

APPENDIX 5-1. OVERVIEW OF METHODS TO ESTIMATE EMISSIONS

A number of methods to estimate actual emissions in a certain year are presented in the literature, as shown in Boxes 1 - 8.

One of the first studies on halocarbon emission was published by McCarthy et al. (1977), who developed a method for estimating actual emissions of CFC-11 and -12 (Box 1). As shown in Boxes 2 - 8 most studies adopted, or modified their method to estimate actual emissions.

Gamlen et al. (1986) estimate emissions of CFC-11 and -12 from sales (Box 2). They distingish aerosols, two types of refrigerants and three types of foams, but do not include solvents, fire extinguishers and emissions during the production of halocarbons.

Brühl and Hennig (1989) calculate emissions from the annual production (Box 3) and included halons. For applications with a short delay, emissions are calculated as a percentage of the production. When longer delays occur, the emissions are estimated as a percentage of the halocarbon bank. For refrigeration they only consider the cooling agent produced for replacement.

Kroeze and Reijnders (1992) consider three delay times for each application: before use, during use, and after use (box 4). In addition, they distinguished the following types of emissions: (i) emissions that are avoidable by better housekeeping, for instance, spilling of cooling agent while filling a refrigerant, (ii) emissions that are essentially unavoidable, for instance, the annual leakage of blowing agent from insulation foam, and (iii) emissions that are avoidable by recycling or destruction of halocarbon wastes. All three emissions have different delay times.

Fisher and Midgley (1993) and Midgley and Fisher (1993) assessed emissions of CFC-113, -114, -115, and HCFC-22 (boxes 5 and 6).

Fisher et al. (1994a) distinguish five types of emissions, ranging from no delay to a 20-year delay (Box 7). As shown, halocarbons from most applications are released within one year. The only exceptions are emissions from refrigerants and closed foams. The method does not consider emissions during the production of halocarbons, unless these are assigned to the end-use category. Also, fire extinguishers are not included.

McCulloch (1992, 1994a,b) considers halon emissions and three emission categories for CFCs with short-term, medium-term and long-term emissions. He gives some examples per category, and also estimates for some applications to what extent emissions could be reduced.

Summarizing, the methods generally agree that delays between use and emissions are most pronounced for refrigeration, closed foams and fire extinguishers. All methods aim at simulating a delay between use and actual emissions. Some consider formation of halocarbon banks. The methods differ in level of detail.

Box 1. Release of CFC-11 and CFC-12 according to McCarthy et al., 1977

Aerosol, open-foam blowing, solvents, cleaning agents	6 months release delay
Hermetically sealed refrigeration	2% initial filling loss, mean lifetime of 12 ± 4 years
Non-hermetically sealed refrigeration	2.25% initial filling loss, average life to discharge of the unit of 4 ± 2 years
Closed-foam blowing	10% loss during foam manufacture, followed by uniform loss rate of 4.5% per year over 20 years

Box 2. Release of CFC-11 and CFC-12 according to Gamlen et al. (1986)

Total production P_t ($kg\ y^{-1}$) is calculated as:

$$P_t = R(F)_t + S(A)_t + S(LR)_t + S(SR)_t + S(OC)_t + S(CC)_t + S(O)_t + (SA)_t$$

For refrigeration:

$S(LR)_t = 0.08S(TR)_t$ for CFC-12
$S(LR)_t = S(TR)_t$ for CFC-11

P = production
R = release
S = sales and the end-use
F = fugitive emissions (during production and filling)
A = aerosol
LR = long lived refrigeration
SR = short lived refrigeration
TR = total refrigeration (LR + TR)
OC = open-cell foam
CC = closed-cell foam
O = other
SA = stock adjustments where $\sum\limits_{t}(SA) \rightarrow 0$
t = year

Release from applications R_t ($kg\ y^{-1}$) is calculated as:

Aerosols	$R(A)_t = 0.5\ S(A)_t + 0.5\ S(A)_{(t-1)}$
Long-lived refrigerants	2% during filling, 98% after 12 years
Short-lived refrigerants	100% within 4 years
Open cell foam	$R(OC)_t = 0.83\ S(A)_t + 0.17\ S(A)_{(t-1)}$
Closed cell foam (CFC-12)[1]	$R(CC)_t = 0.83\ S(CC)_t + 0.17\ S(CC)_{(t-1)}$
Closed cell foam (CFC-11)	10% during foam blowing and 4.5% per year for 20 years; after 20 years, 5% of the remainder is incinerated, 75% released immediately and 20% continues leaking at a rate of 4.5% per year
Other (sterilant gas, solvents)	as aerosols

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[1] mainly polyolefin (since this is a prompt release application, it is sometimes considered an open foam).

Box 3. Release of halocarbons according to Brühl and Hennig (1989)

Annual emissions E in the year "t" are calculated from the annual production $P(t_i)$ in kg y^{-1}

Aerosols	$E_{aerosol}(t_i) = P_{aerosol}(t_i)$
Open cell foams	$E_{open\ foam}(t_i) = 5/6P_{open\ foam}(t_i) + 1/6P_{open\ foam}(t_{i-1})$
Refrigeration	$E_{refrigeration}(t_i) = P_{refrigeration}(t_i)$ (replacement)
Closed cell foams	$E_{closed\ foam}(t_i) = 10\%\ P_{closed\ foam}(t_i) + 4.5\% \sum_{j=1}^{20} P_{closed\ foam}(t_{i-j})$
Miscellaneous	$E_{mis}(t_i) = 0.5\ P_{mis}(t_i) + 0.5\ P_{mis}(t_{i-1})$
Fugitive	$E_{fugitive}(t_i) = 2\%\ P_{total}(t_i)$
Halon 1211	$E(t_i) = 5/18\ (Bank(t_{i-1}) + P(t_i))$ $Bank(t_i) = 13/18\ (Bank(t_{i-1}) + P(t_i))$
Halon 1301	$E(t_i) = 1/7\ (Bank(t_{i-1}) + P(t_i))$ $Bank(t_i) = 6/7\ (Bank(t_{i-1}) + P(t_i))$

Box 4. Release of halocarbons according to Kroeze and Reijnders (1992)

	Type of emission[1]	Time of emission	Delay time[2] (years)	Relative contribution[3] (% of annual use)
Aerosol	avoidable	-	-	0
	not avoidable	year of production	0	100
	recyclable	-	-	0
Open foam	avoidable	year of production	0	10
	not avoidable	year of production	0	35
	recyclable	after use	<1	55
Closed foam	avoidable	year of production	0	10
	not avoidable	during use	10	45
	recyclable	after use	25	45
Cleaning	avoidable	year of production	0	80
	not avoidable	during use	0	10
	recyclable	after use	<1	10
Refigeration (excl. mobile airco)	avoidable	year of production	0	15
	not avoidable	during use	7.5	50
	recyclable	after use	15	35
Mobile airconditioning	avoidable	during use	2	10
	not avoidable	during use	2	65
	recyclable	after use	15	25
Fire extinguisher	avoidable	year of production	0	50
	not avoidable	year of production	0	25
	recyclable	after use	10	25
Other	avoidable	year of production	0	100
	not avoidable	-	-	0
	recyclable	-	-	0

[1] Three types of emissions are distinguished: **avoidable** by better housekeeping; essentially **not avoidable**; and **recyclable**; [2] delay between use and emission; [3] estimates refer to 1990 situation.

Box 5. Release of CFC-113, -114 and -115 according to Fisher and Midgley (1993)

Fugitive	1% during production 0.3% during packaging
Aerosols, cleaning, blowing of polyolefin foam, "other"	6 month release delay[1] (as Gamlen et al., 1986)
Blowing of phenolic foam	average release delay of 12 years (as closed foams in Gamlen et al., 1986)
Short-lived refrigeration, dielectric	4 ± 2 year lifetime
Long-lived refrigeration, heat transfer fluid	12 ± 4 year lifetime

[1] 95% of the use of CH_3CCl_3 may fall in this range too (Midgley, 1989)

Box 6. Release of HCFC-22 according to Midgley and Fisher (1993)

Fugitive	2.5% of the gorss manufactured volume 1% of the amount used as intermediate
Aerosols, open-foam blowing	6 month release delay (as Gamlen et al., 1986)
Closed-foam blowing	5% released immediately during foam manufacture and the remaining 95% is released in a linear fashion over the next 50 years
Refrigeration	3 - 10 year release delay
Other uses	distributed over inidvidual categories

Box 7. Release of halocarbons according to Fisher et al. (1994a)

Average delay between sale/production and release:

No delay	fugutive emissions
6 months	aerosol propellants, open cell blowing (including polyolefin foams), cleaning, drying, dry cleaning
4 years	short-lived refrigerants (all but houshold refrigerants)
12 years	long-lived refrigerants (household refrigerants and freezers)
4.5% per year over 20 years	closed cell blowing

Box 8. Release of halocarbons according to McCulloch (1992 and 1994a,b)

Three emission categories for CFCs and their substitutes:

short term	e.g. mobile airconditioning systems with annual current leakage rates of about 33% of the charge, potentially falling to 10%
medium term	e.g. large-scale refrigeration and airconditioning systems which are generally not hermetically sealed; annual leakage currently 17% of the deployed stock, potentially falling to 3%
long term	hermetically sealed systems such as domestic airconditioning and refrigeration; 40% of the original charge 15 years later plus 1% per year

Halons

1969 - 1980	66 and 36% of the amount of Halon 1211 and 1301 produced, respectively
1981 - 1985	69 and 52% of the amount of Halon 1211 and 1301 produced, respectively
1986 - 1992	58 and 33% of the amount of Halon 1211 and 1301 produced, respectively

APPENDIX 6-1. EMISSIONS OF HALOCARBONS IN 2040

Table A-1. Emissions of HFCs, PFCs, FICs and SF_6 in the reference scenario in 2040 (kt y^{-1}); no emission control through better housekeeping, recycling, and destruction of halocarbon wastes

HFC-	23	32	125	134a	143a	152a	227ea	236fa	245ca	356	43-10mee	PFC	FIC	SF_6	Total
Aerosol				27		27	27								81
Cleaning											64	64[2]			129
Open cell				2		2									4
Closed cell				16	32	16		65	65	65					260
Stationary cooling	16	77	77	221	77	77	16					11			574
Mobile airconditioning				286											286
Fire extinguishing	<1		<1	<1			4					<1	<1	<1	7
Other[1]			19	21	1	1	18					14		7	83
Total (kt)	17	78	96	574	111	123	65	65	65	65	65	90	<1	7	1422
Total (Mt CO_2-eq.)	200	45	308	746	486	17	215	522	40	85	103	844	0	186	3798

[1] including fugitive emissions, and emissions from historical use of PFCs and SF_6; [2] PFCs may be replaced by HFC liquids in development

Table A-2. Emissions of HFCs, PFCs, FICs and SF_6 in the reference scenario + maximum emission control in 2040 (kt y^{-1})

HFC-	23	32	125	134a	143a	152a	227ea	236fa	245ca	356	43-10mee	PFC	FIC	SF_6	Total
Aerosol				27		27	27								81
Cleaning											13	13[2]			26
Open cell				1		1									2
Closed cell				12	24	12		48	48	48					194
Stationary cooling	7	34	34	97	34	34	7					5			252
Mobile airconditioning				199											199
Fire extinguishing	<1		<1	<1			2					<1	<1	<1	3
Other[1]			18	19			18					14		7	78
Total (kt)	7	34	53	356	59	75	54	49	49	49	13	32	<1	7	835
Total (Mt CO_2-eq.)	87	20	168	463	258	10	178	388	30	63	21	300	0	207	2169

[1] including fugitive emissions, and emissions from historical use of PFCs and SF_6; [2] PFCs may be replaced by HFC liquids in development

Table A-3. Emissions of HFCs, PFCs, FICs and SF_6 in the closed applications only scenario in 2040 (kt y^{-1}); no emission control through better housekeeping, recycling, and destruction of halocarbon wastes

HFC-	23	32	125	134a	143a	152a	227ea	236fa	245ca	356	43-10mee	PFC	FIC	SF_6	Total
Aerosol															0
Cleaning															0
Open cell															0
Closed cell				16	32	16		65	65	65					260
Stationary cooling	16	77	77	222	77	77	16					11			574
Mobile airconditioning															0
Fire extinguishing															0
Other[1]															0
Total (kt)	16	78	78	241	111	94	16	65	65	65	0	11	0	0	841
Total (Mt CO_2-eq.)	194	45	250	312	487	13	54	521	40	85	0	103	0	0	2103

[1] including fugitive emissions and emissions from historical use of PFCs and SF_6

Table A-4. Emissions of HFCs, PFCs, FICs and SF_6 in the closed applications only scenario + maximum emission control in 2040 (kt y^{-1})

HFC-	23	32	125	134a	143a	152a	227ea	236fa	245ca	356	43-10mee	PFC	FIC	SF_6	Total
Aerosol															0
Cleaning															0
Open cell															0
Closed cell				12	24	12		48	48	48					194
Stationary cooling	7	34	34	97	34	34	7					5			252
Mobile airconditioning															0
Fire extinguishing															0
Other[1]															0
Total (kt)	7	34	34	111	59	47	7	49	49	49	0	5	0	0	450
Total (Mt CO_2-eq.)	85	20	111	143	258	7	23	388	30	63	0	45	0	0	1175

[1] including fugitive emissons and emissions from historical use of PFCs and SF_6

Table A-5 shows emissions in the low-GWP scenario. In this scenario only compounds are used with relatively low GWPs. The Table shows the emissions of low-GWP compounds that are needed to substitute HFCs, PFCs, FICs and SF_6 in kt (upper part of Table A-5), and in CO_2-equivalents (lower part of Table).

Table A-5. Emissions of substitutes, including low-GWP fluorocarbon blends, for of HFCs, PFCs, FICs and SF_6 in the low GWP scenario in 2040 (kt y^{-1} and CO_2-equivalents y^{-1}); no emission control through better housekeeping, recycling, and destruction of halocarbon wastes

Substitute[3] for HFC-	23	32	125	134a	143a	152a	227ea	236fa	245ca	356	43-10mee	PFC	FIC	SF_6	Total
Aerosol				27		27	27								81
Cleaning											64	64[2]			129
Open cell				2		2									4
Closed cell				16	32	16		65	65	65					260
Stationary cooling	16	77	77	222	77	77	16					11			574
Mobile airconditioning				286											286
Fire extinguishing	<1		<1	<1			4					<1	<1	<1	7
Other[1]			19	21	1	1	18					14		7	83
Total (kt)[3]	17	78	96	574	111	123	65	65	65	65	65	90	<1	7	1422
Total (Mt CO_2-eq.)															
- GWP < 250	4	19	24	143	28	31	16	16	16	16	16	22	<1	2	356
- GWP < 500	8	39	48	287	55	62	32	33	33	33	33	45	<1	4	711
- GWP < 750	12	58	72	430	83	93	46	49	49	49	49	67	<1	6	1067

[1] including fugitive emissions and emissions from historical use of PFCs and SF_6; [2] PFCs may be replaced by HFC liquids in development; [3] substitutes include pure fluorocarbons or blends containing fluorocarbons with low GWPs

Table A-6 shows emissions in the low-GWP scenario. In this scenario only compounds are used with relatively low GWPs. The Table shows the emissions of low-GWP compounds that are needed to substitute HFCs, PFCs, FICs and SF_6 in kt (upper part of Table A-5), and in CO_2-equivalents (lower part of Table).

Table A-6. Emissions of substitutes, including low-GWP fluorocarbon blends, for of HFCs, PFCs, FICs and SF_6 in the low GWP scenario in 2040 + maximum emission control in 2040 (kt y^{-1} and CO_2-equivalents y^{-1})

Substitute[3] for HFC-	23	32	125	134a	143a	152a	227ea	236fa	245ca	356	43-10mee	PFC	FIC	SF_6	Total
Aerosol				27		27	27								81
Cleaning											13	13[2]			26
Open cell				1		1									2
Closed cell				12	24	12		48	48	48					194
Stationary cooling	7	34	34	97	34	34	7					5			252
Mobile airconditioning				199											199
Fire extinguishing	<1		<1	<1			2					<1	<1	<1	3
Other[1]			18	19			18					14		7	78
Total (kt)	7	34	53	356	59	75	54	49	49	49	13	32	<1	7	835
Total (Mt CO_2-eq.)															
- GWP < 250	2	9	13	89	15	19	13	12	12	12	3	8	<1	2	210
- GWP < 500	4	17	26	178	29	37	27	24	24	24	6	16	<1	4	419
- GWP < 750	5	26	39	267	44	56	40	36	36	36	10	24	<1	5	629

[1] including fugitive emissions and emissions from historical use of PFCs and SF_6; [2] PFCs may be replaced by HFC liquids in development; [3] substitutes include pure fluorocarbons or blends containing fluorocarbons with low GWPs