

10

Non-Medical Aerosols, Solvents, and HFC 23

Coordinating Lead Authors

Sally Rand (USA), Masaaki Yamabe (Japan)

Lead Authors

Nick Campbell (United Kingdom), Jianxin Hu (China), Philip Lapin (USA), Archie McCulloch (United Kingdom), Abid Merchant (USA), Koichi Mizuno (Japan), John Owens (USA), Patrice Rollet (France)

Contributing Authors

Wolfgang Bloch (Germany)

Review Editors

Yuichi Fujimoto (Japan), José Pons (Venezuela)

Contents

EXECUTIVE SUMMARY	381	10.3 Solvents	387
10.1 Introduction	383	10.3.1 Current uses – HFCs, PFCs, HCFCs	388
10.2 Non-medical aerosols (including technical, safety, consumer and novelty aerosol products)	383	10.3.2 Projected consumption / emissions	390
10.2.1 Technical aerosols	384	10.3.3 Emissions reduction options	391
10.2.2 Safety aerosols	386	10.3.4 Emission reduction potential and abatement cost	393
10.2.3 Consumer aerosols (cosmetic and convenience aerosols)	386	10.4 HFC-23 from HCFC-22 production	394
10.2.4 Novelty products	386	10.4.1 Relevant practices during life cycle	396
10.2.5 Constraints on emission reduction potential	386	10.4.2 Emission reduction options	397
10.2.6 Emission reduction potential and abatement cost	387	10.4.3 Reduced emissions in the period prior to 2015 given current best practice	397
		10.5 Other miscellaneous uses	399
		References	399

EXECUTIVE SUMMARY

Non-medical aerosols

Prior to the Montreal Protocol, CFCs, particularly CFC-11 and CFC-12, were used extensively in non-medical aerosols as propellants or solvents. In developed countries today, more than 98% of non-medical aerosols now use non-ozone-depleting, low-GWP propellants (hydrocarbons, dimethylether, CO₂ or nitrogen). Some of the non-medical applications that previously used CFCs have also converted to not-in-kind technologies (spray pumps, rollers, etc.). These substitutions led to a total reduction of greenhouse-gas emissions of aerosol origin by over 99% between 1977 and 2001 (ADL, 2002; FEA, 2003). Although there are no technical barriers to the phase-out of CFCs, estimated consumption of CFCs in developing and CEIT countries was 4,300 tonnes in 2001 (UNEP, 2003a).

The remaining aerosol products use either HCFCs or HFCs because these propellants provide a safety, functional or health benefit for the users. In 2003, HFC use in aerosols represented total emissions of approximately 22.5 MtCO₂-eq. Both the US and European aerosol trade associations and the Japanese Ministry of Economy, Trade and Industry project low growth over the next decade.

Technical aerosols are a group of pressurized products used to clean, maintain, fix, test, manufacture, disinfect, or apply lubricant and mould release agents to various types of equipment. Technical aerosols are used in a number of industrial and commercial processes. In technical aerosols, HFCs are used most in dusters, where the substitution of HFC-134a by HFC-152a is a leading factor in reducing greenhouse-gas emissions. The substitution of HCFC-141b solvent by HFEs and HFCs with lower GWPs makes additional emission reductions possible in other technical aerosols.

Safety aerosols and insecticides for planes and restricted areas continue to rely on HFC-134a because of its non-flammability. Novelty aerosols generally use hydrocarbons, but some applications have been reformulated to HFC-134a in response to safety considerations. In consumer aerosols, the use of HFC-152a is likely to increase in the US due to regulations for the control of ground-level ozone formation caused by the emission of hydrocarbons from these products. However, on a global basis, such HFC-forcing regulation is not common.

Solvents

The primary ozone-depleting substances (ODSs) traditionally used in solvent applications are CFC-113, 1,1,1-trichloroethane and, to a lesser extent, CFC-11 and carbon tetrachloride. The ozone-depleting solvents have a variety of end uses. However, this report focuses on the largest application – cleaning – which includes precision, electronics and metal cleaning. It is estimated that 90% of ozone-depleting-solvent use had been reduced through conservation and substitution with not-in-kind technologies by 1999 (no-clean flux, aqueous or semi-aqueous clean-

ing, and hydrocarbon solvents). The remaining 10% of solvent uses are shared by several organic solvent alternatives.

The primary in-kind substitutes for 1,1,1-trichloroethane and carbon tetrachloride are non-ozone-depleting chlorinated solvents such as trichloroethylene, perchloroethylene and methylene chloride. More recently, n-propyl bromide has begun to be used in cleaning and adhesive applications, although there are concerns and uncertainties about its safety and ozone-depleting potential.

The in-kind substitutes for CFC-113 and CFC-11 are fluorinated alternatives such as hydrochlorofluorocarbons (HCFC-141b and HCFC-225ca/cb), perfluorocarbons (primarily C₆F₁₄), hydrofluorocarbons (HFC-43-10mee, HFC-365mfc and HFC-245fa, HFC-c447ef) and hydrofluoroethers (HFE-449s1, HFE-569sf2). These in-kind solvent substitutes cost more than the alternatives, and so they are primarily used in applications where safety, performance (such as compatibility, selective solvency and stability) or other environmental considerations are crucial. In most of the cleaning applications, the fluorinated solvents are used as blends with alcohols and/or chlorocarbons, thereby enhancing cleaning performance and reducing the overall cost of the solvents.

While HCFC-141b use in developed countries is rapidly decreasing, its use in developing countries and countries with economies in transition continues to increase due to low cost and widespread availability. HCFC-225ca/cb is currently used mainly in Japan and the US, but its use is expanding in developing countries.

PFC solvent use is constrained to a few high-performance niche applications due to its very limited solvency and high cost. Consumption is known to have decreased since the mid-1990s as a result of replacement with lower-GWP solvents.

Although HFCs are available in all regions, they have been used as solvents primarily in developed countries because of their high cost and the concentration of use in high-tech industries. With increasing concern about their GWP, uses tend to be focused in critical applications with no other substitutes. It is thought that use has now peaked at current levels and may even decline in the future.

Emission reduction options for solvent applications fall into two categories:

- (1) Improved containment in existing uses: New and retrofitted equipment can significantly reduce emissions of all solvents. Optimized equipment can reduce solvent consumption by as much as 80% in some applications. Due to their high cost and ease of recycling, the fluorinated solvents can be recovered and reused by the end-users or their suppliers.
- (2) Alternative fluids and technologies: A variety of organic solvents can replace HFCs/PFCs and ODSs in many applications. Caution is warranted prior to the adoption of any alternatives for which the toxicity profile is not complete. These alternative fluids include compounds with lower GWPs such as traditional chlorinated solvents, hydrofluoroethers (HFEs), and n-propyl bromide (nPB)

if its use continues to be allowed under the Montreal Protocol. The numerous not-in-kind technologies, including hydrocarbon and oxygenated solvents, are also viable alternatives in some applications. In a limited number of applications, no substitutes are available due to the unique performance characteristics of the HFC or PFC for those applications.

HFC-23 emissions from HCFC-22 production

Trifluoromethane (HFC-23 or CHF_3) is generated as a byproduct during the manufacture of chlorodifluoromethane (HCFC-22 or CHClF_2). HCFC-22 is used as a refrigerant in several different applications, as a blend component in foam blowing and as a chemical feedstock for manufacturing fluoropolymers such as polytetrafluoroethylene (PTFE). While the Montreal Protocol will eventually phase out the direct use of HCFC-22, its use as a feedstock will be permitted indefinitely because it does not involve the release of HCFC-22 to atmosphere.

HCFC-22 is produced in several developed and developing countries. The US, EU, Japan, China, India, and Korea are major producers of HCFC-22. HFC-23 is formed at the reactor stage of the manufacture of HCFC-22 as a result of over-fluorination. Its formation is dependent upon the conditions used in the manufacturing process and varies from 1.4 to 4.0 % of the production of HCFC-22 so that, while it is possible to reduce its formation by optimizing process conditions, it is not possible to eliminate the production of HFC-23. In a number of plants, HFC-23 is destroyed by thermal oxidation. The cost of reducing emissions varies significantly depending on the option used and will vary from plant to plant depending on the particular baseline situation.

Global emissions of HFC-23 increased by an estimated 12% between 1990 and 1995 as a result of a similar increase in global production of HCFC-22. However, due to the widespread implementation of process optimization and thermal destruction, this trend in HFC-23 emissions from developed countries has not continued and, since 1995, emissions have decreased as a proportion of production levels in those countries. On the other hand, HCFC-22 production has increased very rapidly in China and India in the last few years and global emissions of HFC-23 are still increasing.

Options for further emission reduction include:

- (1) Process optimization at additional facilities: In fully optimized processes, average HFC-23 generation can be reduced to as little as 1.4% of production. However, actual achievements vary for each facility and it is not possible to completely eliminate HFC-23 emissions by this means.
- (2) Capture and destruction: Thermal oxidation is an effective option for the abatement of HFC-23 byproduct emissions. Destruction efficiency can be >99.0% with measurements at one facility indicating the destruction of 99.9% of the HFC-23 but the impact of the “down-time” of thermal oxidation units on emissions needs to be taken into account. Several facilities in the EU, Japan and the US have already implemented this option.

Destruction of byproduct emissions of HFC-23 from HCFC-22 production has a reduction potential of up to 300 MtCO₂-eq per year by 2015 and specific costs below 0.2 US\$/tCO₂-eq according to two European studies in 2000. Reduction of HCFC-22 production due to market forces or national policies, or improvements in facility design and construction also could reduce HFC-23 emissions.

10.1 Introduction

Chapter 10 assesses the remaining or “miscellaneous” ODS-replacement applications where greenhouse-gas emissions have been identified. These applications are in the non-medical aerosols and solvents sectors. The majority of substitutes in these sectors are ozone- and climate-safe alternatives, except for some limited use of HFCs, HFEs and PFCs for technical or safety purposes. A few additional niche applications of ODSs with possible greenhouse-gas replacements are also identified but there is insufficient literature available to evaluate the global status of replacements, or of current or future emissions. Emissions from fluorocarbon production are considered, and a detailed evaluation is made of HFC-23 byproduct emissions from HCFC-22 production. The use of PFCs and SF₆ as ODS substitutes is also considered but the vast majority of emissions are found in sectors or applications that have never used ODSs.

10.2 Non-medical aerosols (including technical, safety, consumer and novelty aerosol products)

Aerosol products use liquefied or compressed gas to propel active ingredients in liquid, paste or powder form in precise spray patterns with controlled droplet sizes and amounts. Some aerosol products use the propellant as the only active ingredient, an example being dusters. Typical products use an aerosol propellant that is a gas at atmospheric pressure but is a pressurized liquid in the can. The phase change from liquid to gas allows a high level of active ingredient per unit of propellant to be expelled from the aerosol can.

The first aerosol product was developed during World War II as a result of efforts to control tropical disease. Controlled-release aerosol products distributed DDT insecticide to small enclosed areas (e.g. rooms, tents, etc.) to control mosquitoes.

The aerosol sector grew extensively worldwide after 1945. In the 1960s and 1970s, the vast majority of these spray products used CFC-12 as a propellant or CFC-11 as a solvent. The publication of the Rowland-Molina theory in 1974, the banning of CFCs in most aerosols in the United States, Denmark, Sweden and Norway in the late 1970s and early 1980s, and the ratification and implementation of the Montreal Protocol have led to aerosol reformulations without CFCs. More than 10 billion aerosol products were used worldwide in 2001 (UNEP, 2003a).

In developed countries, more than 98% of the conversions of non-medical aerosols encouraged by the Montreal Protocol have been to ozone- and climate-safe propellants: hydrocarbons (HC), dimethylether (DME), CO₂, or nitrogen (N₂). (In the aerosol industry, the terms “hydrocarbons” or “HAPs” (hydrocarbon aerosol propellants) refer more specifically to the natural gas liquids: n-butane, propane, and iso-butane.) In addition, where this is feasible and where they are effective in use, many aerosol products have been replaced by not-in-kind substitutes. Over time, these have included finger or trigger spray pumps,

sticks (deodorants, insect repellents), rollers, brushes, and cloth. This substitution process led to a total reduction of greenhouse-gas emissions from aerosols by over 99% in the US between 1977 and 2001 (ADL, 2002), and the same reduction in Europe between 1988 and 2002 (FEA, 2003).

Those remaining products made with either HCFCs (in developing countries where the use of HCFC-22 and HCFC-142b is allowed until 2040) or HFCs (HFC-152a, -134a) are niche products where safety or other environmental considerations such as tropospheric ozone are a crucial issue. HCFC-22 and HCFC-141b, which were once considered to be replacements for CFCs, are in minimal use today in aerosol production (UNEP, 2003a). However, developing countries in general do not have prohibitions on the use of HCFCs in aerosols. HCFC-22 and HCFC-141b therefore have some limited applications in non-medical aerosol products requiring low flammable propellants or solvents. HCFC-22 is much cheaper than 134a. HCFC-141b, however, is a strong solvent so it is usually used in blends. Table 10.1 provides an overview of the non-medical aerosol propellant alternatives.

Although there are no technical barriers to the transition from CFCs to alternatives for non-medical aerosol products, the estimated consumption of CFCs in developing countries and countries with economies in transition was still 4,300 tonnes in 2001 (UNEP, 2003a).

Most of the remaining aerosol products use either HCFCs or HFCs because these propellants provide an important safety, functional, or health benefit for the users. The Code of Practice on HFC Use in Aerosols of the FEA (European Aerosol Federation) and the responsible use practices of the trade group for the US aerosol industry (the Consumer Specialty Products Association) insist that HFCs should only be used in aerosol applications where there are no other safe, practical, economic or environmentally acceptable alternatives. The use of HFCs in aerosols is also limited further by cost. HFCs are between five and eight times more expensive than HCs. Table 10.2 contains estimates of total current and projected use of HFCs by region.

In 2003, HFC use in non-medical aerosols represented total emissions in the range of around 22 MtCO₂-eq: approximately 9 MtCO₂-eq for the US, 6 MtCO₂-eq for the EU, and 2.5 MtCO₂-eq for Japan (ADL, 2002; FEA, 2003; METI, 2004). It is estimated that emissions in 2010 will be around 23 MtCO₂-eq (ADL, 2002; FEA, 2003; METI, 2004). Both American and European aerosol trade associations and the Japanese Ministry of Economy, Trade and Industry expect low levels of growth in overall GWP-weighted emissions as a result of the introduction of HFC-152a in a number of applications currently using HFC-134a. Banking is not an issue for the aerosol sector. Products are generally used within 2 years or less after filling.

Key products using HFCs and HCFCs are listed in the next section, with a discussion of each product’s efficacy, safety/health impact, volumes, growth pattern and substitution or reformulation potentials.

Table 10.1. Overview of non-medical aerosol propellant alternatives.

	HCFC-22	HFC-134a	HFC-152a	Dimethylether	Isobutane ⁽¹⁾
Substance characteristics					
Radiative efficiency (W m ⁻² ppb ⁻¹)	0.20	0.16	0.09	0.02	0.0047
Atmospheric lifetime (yr)	12	14	1.4	0.015	0.019
GWP (100-yr time horizon)					
- This report	1780	1410	122	1	n/a
- IPCC (1996)	1500	1300	140	1	
ODP	0.05	~0	-	-	-
Ground-level ozone impact					
- MIR ⁽²⁾ (g-O ₃ /g-substance)	<0.1	<0.1	<0.1	0.93	1.34
- POCP ⁽³⁾ (relative units)	0.1	0.1	1	17	31
Flammability (based on flashpoint)	None	None	Flammable	Flammable	Flammable
Technical data					
Stage of development	Commercial	Commercial	Commercial	Commercial	Commercial
Type of application:					
- Technical aerosols	X	X	X	X	X
- Safety aerosols	X	X			
- Consumer products	Phased out in industrialized countries		X	X	X
Emissions					
Use totally emissive in all cases					
Costs					
Additional investment costs			Special safety required at filling plant	Special safety required at filling plant	Special safety required at filling plant

⁽¹⁾ Listed values refer to isobutane only. Additional hydrocarbon propellants are used in non-medical aerosol applications as indicated in section 10.2.

⁽²⁾ Maximum Incremental Reactivity (See Chapter 2, Table 2.11 for more details)

⁽³⁾ Photochemical Ozone Creation Potential (See Chapter 2, Table 2.11 for more details)

Table 10.2. HFC use in aerosols (MtCO₂-eq).

Region	HFC use in aerosols (MtCO ₂ -eq)		
	2000	2003	2010
EU	6.0	6.25	5.8
Japan	2.8	2.5	2.5
US	9.9	9.0	8.6
Rest of World	3.2	4.8	6.5
Total	21.9	22.5	23.4

10.2.1 Technical aerosols

Technical aerosols are a group of pressurized products used to clean, maintain, fix, test, manufacture, disinfect, or apply lubricant and mould release agents to various equipment. They are also used in a number of industrial processes.

10.2.1.1 Dusters

Compressed gas “dusters” generate small jets of “clean” gas as a non-contact method for removing dust and other particulate

matter. Dusters are packaged in the same manner as aerosols, but the propellant is the only active ingredient in the can. As a result, there is usually considerably more gas in these items than in other aerosol products. Dusters are formulated in such a way that they leave no residue. The fact that there can be no flame suppression ingredients, e.g. water, increases the risk of ignition.

Dusters are used to clear dust and lint and other light particulate material from delicate surfaces (photographic negatives and lenses, substrates in semiconductor “chip” manufacture, computer/tv screens, high quality optics, specimens for electron microscopy) and difficult-to-reach places (the inside of Central Processing Unit “towers”, computer keyboards, the inside of cameras, photocopiers, ATMs). These products are used in laboratories, darkrooms, offices (both in homes and on the commercial scale) and workbenches. Dusters are very widely used by industrial entities for a wide range of applications. Dusters are also used by consumers in a similar broad set of applications in offices, homes and workshops.

Dusters have been reformulated in the US, Europe, and Japan, switching from CFC-12 to HCFC-22 (1989/1990) and later to HFC-134a or HFC-152a (1993/1994). In some coun-

tries, where its use as an aerosol propellant is not prohibited, a small amount of HCFC-22 is still used in dusters. It is estimated that dusters account for most HFC use in technical aerosols worldwide (excluding metered dose inhalers). The replacement of HFC-134a by HFC-152a, which has started in the US and is expected to develop in the EU and Japan, is a key factor in the stabilization of the reduction of the CO₂-eq emission level in 2010. In Japan, emissions of HFC-134a from dusters have decreased from 2,137 metric tonnes in 2000 to 1,851 metric tonnes in 2003 as a result of the introduction of HFC-152a. HFC-152a use increased from 18 metric tonnes in 2000 to 371 metric tonnes in 2003 (METI, 2004).

HFC-152a is far less ignitable than hydrocarbons (HCs) and can be used in less fire-sensitive applications. Generally, this use is acceptable in the office environment where usage would be characterized by short blasts emitting small amounts of gas, and where contact with ignition sources is very limited. When used in machinery or equipment where an ignition source is present, the power should be turned off. In the US, Consumer Products Safety Commission (CPSC) standards do not require HFC-152a in a duster to be labelled as flammable.

Reduction options for dusters

The expected decrease in emissions from HFCs in aerosols comes as a result of the replacement of HFC-134a by HFC-152a in a number of technical aerosol applications. In addition, there are some cases of substitution in Europe by HCs in these products. This is a recent development and it remains to be seen how the safety issues with these gases will develop.

Some reduction of greenhouse gas emissions can still be realized through the partial replacement of HFC-134a by HFC-152a or dimethyl ether. Mixtures of these propellants can have acceptable flammability characteristics for use in applications where flammability is of less concern.

Some potential exists for the use of carbon dioxide (CO₂) but this is very expensive. Compressed CO₂ has the disadvantage of providing fewer blasts per can and CO₂ products require expensive high-pressure canisters. The CO₂ systems in the market today use very small aerosol cans (less than 20 gr). According to a recent analysis entitled "Dustometer Study", it takes approximately twenty of the small CO₂ aerosol cans to replace the cleaning power of one HFC-152a-based aerosol can (12 oz/340 gr) (DuPont, 2004). The assumption is that the emissions from the energy use needed to make the steel CO₂ canisters would at least equal the inherent emissions from an HFC duster.

There is one not-in-kind solution for high-pressure industrial applications: electrical air compressors. They are used in large high-volume production environments. Their cost and total efficacy make these systems useful in only a small number of situations. Rubber bulb brushes, if kept clean, are an alternative to dusters for low-pressure applications such as dusting lenses and dislodging dust from camera interiors.

10.2.1.2 Other technical aerosols

This category of products accounts for considerably less HFC use and is unlikely to grow in the future.

Freeze sprays are used to test the electrical conductivity of components on circuit boards. They are used for thermally locating intermittently operating electrical components. They are used in static-sensitive areas and therefore need to be non-flammable. Freeze sprays are like dusters in that they are cans filled with propellant only. These cannot be anything other than non-flammable propellants since they are mainly used to test electrically charged circuits that could ignite flammable gases.

Flux remover is a product used to clean excess flux and solder residue from circuit boards and other electronic components, especially in the repair of components and printed circuit boards. Since these are usually used near soldering irons or other sources of ignition, the formulations are made to be non-flammable in order to safeguard worker safety.

Mould release agents are used to release products moulded in plastic or synthetic fibre from their moulds without damage to the end product. These aerosols are in the process of being re-formulated due to the phase-out of HCFC-141b in all aerosol solvent uses in developed countries. The substitution of HFCs by HCs is technically feasible for some applications when appropriate consideration is given to flammability risks.

Electronic contact cleaners are used to dissolve and remove oil, grease, flux, condensation and other contaminants quickly from delicate electronic circuitry and expensive electronic instrumentation. Contact cleaners combine quick drying and high dielectric solvency for residue-free cleaning. They are used to clean switchboards or circuitry, magnetic tape, printed circuit boards, electronic relays, and security equipment. Contact cleaning needs a completely non-flammable formulation for use while equipment is in operation. It is therefore necessary to use pressurized cleaners containing non-flammable solvents as well as non-flammable propellants (in most cases HFC-134a).

Reduction options for other technical aerosols

For cleaners (contact cleaners, flux removers, etc.) and mould release agents, the substitution of the HCFC-141b solvent by hydrofluoroethers (HFEs) or HFCs with lower GWPs would reduce emissions without giving rise to substantial technical issues. The current cost of HFEs is higher than that of HFC-134a or HFC-152a. Mixes of HFC-152a, or dimethyl ether in smaller percentages, with HFC-134a are also a practical solution. Compressed gas is also an emission reduction option but with an important technical limitation. Compressed gas does not ensure constant pressure level within the can and its use is therefore impractical once two-thirds of the product has been expelled. Some not-in-kind solutions (manual or mechanical sprays) have been tested without success due to their reduced efficiency; new solutions like bag-on-bag containers appearing in Japan could be adapted for uses not requiring high-pressure sprays.

10.2.2 Safety aerosols

Tyre inflators

Tyre inflators are made with latex sealants, a solvent acting as a diluent, and propellant. They are a safe, effective, and a far less strenuous alternative to changing a flat tyre for people who cannot change a tyre or do not wish to risk doing so for safety reasons (e.g. busy traffic or personal safety late at night and on dark roads). Many of the tyre inflators on the market initially used dimethyl ether or HCs as the propellant. However, after a series of accidents and fatalities while repairing tyres containing HC in an enclosed garage, many manufacturers of these products choose to reformulate and switch to the more expensive HFC-134a and away from flammable propellants.

It is estimated that more than 80% of inflators have now been converted to HFC-134a because of its non-flammability, and sometimes because of local regulations.

Safety signal horns

These products are made and used for safety purposes such as signalling on boats, and signalling in industrial plants and offices for emergency evacuations. Performance requirements include portability, and easy and non-electrical operation. In the United States, horns designed to meet US Coast Guard (USCG) specifications must be audible one mile (1.6 kilometres) from the point of activation.

Insecticides for planes or restricted areas

The non-flammability requirement for products used in certain areas (planes, source of energized equipment like transformers etc.) leads to the use of HFC-134a, particularly for insecticides.

Reduction options for safety aerosols

Technically, HCs could be used to operate safety horns. However, because hydrocarbons are highly flammable, they constitute an additional risk element in emergency situations or where flame or ignition sources are frequently present. Whistles and mouth horns are substitutes but are not as loud as safety horns and therefore do not perform as well, especially in an emergency on the water or in burning buildings. Whistles and mouth horns can also be difficult to use in smoke-filled environments.

10.2.3 Consumer aerosols (cosmetic and convenience aerosols)

In the US, in response to mandates from the Federal Clean Air Amendments of 1990, state regulations in 16 states have been adopted to limit the content of volatile organic compounds (VOCs) in consumer products such as hair spray and deodorants. A comparatively small number of aerosol products (less than 2%) have needed to utilize HFC-152a in order to comply with these standards. Unlike hydrocarbons and dimethyl ether, HFC-134a and HFC-152a are exempt from VOC controls because they do not participate in the reaction to form ground-

level ozone.

While there will be an increase in the use of HFC-152a in US consumer aerosol products, overall the replacement of HFC-134a by HFC-152a in dusters will result in the net decrease in emissions shown in Table 10.2.

Currently, VOC controls in Europe do not exempt HFCs because of the broad definition of VOCs (boiling point < 250°C under standard pressure/temperature conditions). No transition from HCs to HFCs for consumer products is therefore expected in the EU. No other VOC regulations identified elsewhere in the world restrict the use of HCs in aerosols.

Reduction options for formulated consumer products

HFCs are only used in consumer aerosol products in the US where no other options exist to meet product safety or VOC regulatory needs. Reformulation options are therefore very limited. In addition, since the overall world market for aerosols involves only very limited HFC use (less than 2% of all aerosol products), such use represents only a very small fraction of total HFC use, limiting the potential for substitution.

10.2.4 Novelty products

Products in this category include artificial snow, silly string (spray of solid polymer material), and noise-makers. No data about global or regional HFC use are available for these applications. However, in the EU, this category could represent up to 25% of total HFC emissions for non-medical aerosols (Harnisch and Schwartz, 2003). Noise-makers are a variation of the safety horns discussed in section 10.1.2, but noise-makers are different in that they emit a less loud, deeper pitched sound. Additionally, the large majority (>80%) of horns marketed as noise-makers are made with HCs and not HFCs. Noise-makers with HFCs account for a very small percentage of the overall market. Artificial snow and string novelties were once marketed using flammable propellants but, after highly publicized safety incidents, were reformulated to HFC-134a in many developed countries. Conversions to lower-GWP propellant mixes or HC propellants should be considered where safety permits.

10.2.5 Constraints on emission reduction potential

In the US, in order to comply with limits on tropospheric ozone levels pursuant to the Federal Clean Air Act, some state-level VOC emission restrictions are leading to the reformulation of hydrocarbon-propellant aerosol products, e.g. consumer aerosols, to HFC-152a. In the EU, the recently proposed regulation on fluorinated gases has not restricted HFC use in technical or safety aerosols but has proposed a ban on use in novelty products (according to the definition of novelty in Directive 94/48/EC; for example artificial snow, silly string, decorative foams etc.).

10.2.6 Emission reduction potential and abatement cost

Three separate studies estimate that the potential reduction in HFC non-medical aerosol emissions ranges from 10% to 88% (see Table 10.3 for more details) depending on the country and substitution costs (Harnisch and Gluckman 2001; METI, 2004; US EPA, 2004b).

The abatement costs associated with using the HFC aerosol substitutes vary greatly from negative costs to over 150 US\$₂₀₀₂/tCO₂-eq depending upon the applications and the required level of final safety (flammability).

A European study covering only 15 EU member states was conducted by Harnisch and Gluckman (2001) and projects an emissions reduction in 2010 of 39% for a cost of less than below 23 US\$₂₀₀₂/tCO₂-eq/tCO₂-eq and an additional reduction of 39% for a cost of between 23 and 57 US\$₂₀₀₂/tCO₂-eq. Another European study by Harnisch and Schwartz (2003) is not referred to as it focuses only on novelty aerosols, which represent 25% of total HFC aerosol emissions in the EU.

The Japanese study by METI (2004) projects a 10% emission reduction potential for non-medical aerosols used in Japan, mainly as a result of the substitution of HFC-134a by HFC-152a. This study does not give any cost estimates.

The US EPA's emission-abatement report (2004) has estimated emission reduction potentials in 2020 in the US, non-US Annex I and non-Annex I countries. This study considered three abatement options:

- replacement of HFC-134 as a propellant by HFC-152a;
- substitution of HFCs by hydrocarbon propellants (with safety concerns being properly handled); and
- substitution by not-in-kind packaging such as triggers, pumps, or sticks.

These substitutions represent a 57% reduction potential of total emissions in 2020, with reductions of 37%, 10% and 10% for each category respectively.

10.3 Solvents

On an ozone-depletion-weighted basis, solvents constituted approximately 15% of the market for chemicals targeted for phase-out under the Montreal Protocol. In the case of the four ozone-depleting substances used as solvents – CFC-113, CFC-11, carbon tetrachloride and 1,1,1-trichloroethane (also known as methyl chloroform) – most use by far involved CFC-113 and 1,1,1-trichloroethane in industrial applications and in industrial cleaning equipment. Carbon tetrachloride was predominately for dry-cleaning textiles, or in hand or maintenance cleaning. The three main end uses of CFC-113 and 1,1,1-trichloroethane in the past were metal cleaning, electronics cleaning, and precision cleaning. Metal cleaning usually involves removing cutting oils and residual metal filings from metal surfaces, and the maintenance and repair of equipment and machinery. This sector relied principally on 1,1,1-trichloroethane. Precision and electronics cleaning mostly used CFC-113. Precision cleaning mainly involves products that require a high level of cleanliness and generally have complex shapes, small clearances, and other cleaning challenges (UNEP, 1998). Electronics cleaning, or defluxing, consists mainly of the removal of the flux residue left after a soldering operation on printed circuit boards and other contamination-sensitive electronics applications. Tables 10.4 and 10.5 provide an overview of CFC-113 and 1,1,1-trichloroethane solvent cleaning applications and market estimates.

The Solvent Technical Options Committee (STOC) of TEAP estimates that 90% of ozone-depleting solvent use (based on the peak consumption of 1994-95) has been reduced by switching to not-in-kind technologies (UNEP, 1998). The remaining 10% of the market for ozone-depleting substances is shared by several organic solvent alternatives. In developed countries, almost all ozone-depleting solvents (CFC-113, CFC-11, carbon tetrachloride and 1,1,1-trichloroethane) have been replaced by either not-in-kind technology (no-clean flux, aqueous, semi-aqueous or hydrocarbon solvents) or other organic solvents. HCFC use is declining and is expected to be

Table 10.3. Summary of emission reduction potential and abatement cost for non-medical aerosols applications.

Reference	Harnisch and Gluckman (2001)	US EPA (2004)		METI (2004)
		USA 2020	non-USA 2020	Japan 2010
Region	European Union			
Year	2010			
Total emission projection (MtCO ₂ -eq)	5.1 (2010)	4.0 (2020)	6.7 (2020)	2.5 (2010)
Emission abatement (MtCO ₂ -eq)	a) 2.0 b) 2.0 c) 0.5	2.3	3.8	0.3
Abatement cost (US\$ ₂₀₀₂ /tCO ₂ -eq)	a) <23 b) 23 to 57 c) 57 to 170	-25 to 2.5	-25 to 2.5	n/a

Table 10.4. CFC-113 uses.

Applications	Electronics cleaning	Metal cleaning	Drying	Particle removal	Carrier fluid	Dielectric fluid	Medical	Misc.
Percentage	40	30	8	4	4	2	3	9

Table 10.5. 1,1,1-trichloroethane uses.

Applications	Electronics cold cleaning	Degreasing and	Adhesives	Aerosols	Coating	Chemical process intermediate
Distribution	4%	53%	13%	13%	10%	7%

eliminated by 2015. In developing countries and countries with economies in transition, the use of ozone-depleting solvents, especially HCFC-141b, continues. Although many of the larger international firms with operating facilities located in those countries have switched to non-ozone-depleting technology, few small or medium enterprises have completed the transition.

The primary in-kind substitutes for 1,1,1-trichloroethane have been the chlorocarbon alternatives such as trichloroethylene, perchloroethylene and methylene chloride. These substitutes have very low (0.005-0.007) ozone-depletion potential, and similar cleaning properties (UNEP, 1998). These chemicals were widely used for cleaning in the past until toxicity concerns resulted in switches to ozone-depleting substances. In addition, a brominated solvent – n-propyl bromide – was recently introduced. It has similar properties and has acquired a definite market share of organic solvents for defluxing, general cleaning and adhesives applications.

The in-kind substitutes for CFC-113 and CFC-11 are fluorinated alternatives such as hydrochlorofluorocarbons (HCFC-141b and HCFC-225ca/cb), perfluorocarbons (primarily C₆F₁₄), hydrofluorocarbons (HFC-43-10mee, HFC-365mfc and HFC-245fa, HFC-c447ef) and hydrofluoroethers (HFE-449s1, HFE-569sf2). HCFC-141b and HCFC-225ca/cb have properties similar to CFC-113 and CFC-11 and have therefore been preferred as alternatives where in-kind alternatives are required. In particular, the low cost and good solvency of HCFC-141b initially allowed it to capture a significant market share of CFC solvents. However, HCFCs are transitional substances due to their ozone-depleting potential. Their use is declining in developed countries but still increasing in developing countries (UNEP-TEAP, 2003).

Most of the electronic cleaning market converted to not-in-kind alternatives such as no-clean processes, aqueous and semi-aqueous cleaning. Oxygenated solvents (e.g. alcohols, glycols, ethyl lactate) have also replaced CFC-113 in some portions of the electronics cleaning market. A very small segment of the market went to the HCFC alternatives and their azeotropic blends. Some of the metal-cleaning, particulate removal, medical and miscellaneous applications also switched to

aqueous, semi-aqueous, HCFC and chlorocarbon alternatives. Recently, some of these applications have moved to a newer brominated solvent – normal propyl bromide (nPB) – an ozone-depleting substance not yet controlled by the Montreal protocol. However, uncertainty about the toxicity of nPB has limited its development in certain countries. Most of the displacement drying applications switched to either hot-air drying or alcohol drying systems. Some of the drying applications also switched to HCFCs. The cleaning applications (electronics, metal and particulate removal) and carrier solvents are the focus of this section.

In the late 1980s and early 1990s, PFCs (primarily C₆F₁₄) entered into some of the CFC-113 markets, with limited use in precision and electronics cleaning applications. Use was mostly limited to high-performance, precision-engineered applications where no other alternatives were technically feasible due to performance or safety requirements. Other alternatives such as HFCs and HFEs have been developed with better cleaning performance, significantly lower global warming potential and comparable cost. PFCs are no longer considered technically necessary for most applications.

In the long-term, HFCs and PFCs are expected to acquire a very small share of the ozone-depleting-solvent market. The IPCC's TAR has produced projections indicating that less than 3% of the possible CFC solvent demand will be replaced by HFCs and PFCs (IPCC, 2001b). Some of the reasons for these low uses are the higher cost of HFCs and PFCs, the ready availability of other low cost and acceptable alternatives, and the limited solvency of the common soils in these solvents. Because of this limited use of HFC and other fluorinated alternatives, the EU Commission did not include any restriction on HFC solvent use in its recent proposed regulation on certain fluorinated gases (CEC, 2003).

10.3.1 Current uses – HFCs, PFCs, HCFCs

The solvent applications that currently employ HCFCs, HFCs, and PFCs are shown in Table 10.6, together with an overview of the environmental and technical data for each substance.

Table 10.6. Overview of HFCs, PFCs and HCFCs in solvent applications.

	HCFC-141b	HCFC-225ca/cb	HFC-43-10mee	HFC-365mfc (C ₆ F ₁₄)	PFC-51-14
Substance characteristics					
Radiative efficiency (W m ⁻² ppb ⁻¹)	0.14	0.2/0.32	0.4	0.21	0.49
Atmospheric lifetime (yr)	9.3	1.9/5.8	15.9	8.6	3,200
GWP (100-yr time horizon)					
- This report	713	120/586	1,610	782	9,140
- IPCC (1996, 2001a)	600	180/620	1,300	890	7,400
ODP	0.12	0.02/0.03	-	-	-
Ground-level ozone impact					
- MIR ⁽¹⁾ (g-O ₃ /g-substance)	<0.1	<0.1	n/a	n/a	n/a
- POCP ⁽²⁾ (relative units)	0.1	0.2/0.1	n/a	n/a	n/a
Ground-level ozone impact	None	None	None	None	None
Flammability (based on flashpoint)	None	None	None	Flammable	None
Technical data					
Stage of development	Commercial	Commercial	Commercial	Commercial	Commercial
Type of application:					
- Electronics cleaning	X	X	X		
- Precision cleaning	X	X	X	X	X
- Metal cleaning	X	X	X		
- Drying	X	X	X	X	
- Carrier solvent	X	X	X		X

⁽¹⁾ Maximum Incremental Reactivity (See Chapter 2, Table 2.11 for more details)

⁽²⁾ Photochemical Ozone Creation Potential (See Chapter 2, Table 2.11 for more details)

10.3.1.1 HFCs

Two HFC solvent alternatives are available commercially: HFC-43-10mee (C₅H₂F₁₀) and HFC-c447ef (heptafluorocyclopentane; C₅H₃F₇). Two other HFCs are coming onto the solvent markets.

HFC-43-10mee is a non-flammable, non-VOC (US definition) solvent with low toxicity (US EPA, 1998). The atmospheric life of HFC-43-10mee is 15.9 years; it has a GWP of 1610 (Chapter 2, Table 2.6). HFC-43-10mee readily forms azeotropes with many desirable alcohols, chlorocarbons and hydrocarbons to give blends enhanced cleaning properties (Merchant, 2001). It has better solvent properties than PFCs. The neat material is used as a carrier fluid, and in particulate removal and other miscellaneous applications. The blends are used in applications such as precision cleaning, defluxing flip chips and printed wiring board (PWB), and oxygen system cleaning.

HFC-c447ef (C₅H₃F₇) is a non-flammable, non-VOC solvent (US definition) with a boiling point of 82°C (Zeon Corporation, 2004). Its atmospheric lifetime is reported to be 3.4 years with a GWP of 250 (UNEP-TEAP, 2003)¹. This is lower than most HFCs and some HFEs. However, because of its high freezing point (21.5°C), its neat use is limited. Some azeotropic mix-

tures with alcohol and ketone, or mixtures with terpenes, are provided for the degreasing metal parts and flux cleaning of PWBs. The levels of use of this solvent are low and most current users are in Japan, but marketing has started in the US.

Two other HFC candidates, although primarily developed for foam-blowing applications, have been promoted in some solvent applications. They are HFC-365mfc (pentafluorobutane) (Solvay, 2005) and HFC-245fa (pentafluoropropane) (Honeywell, 2004).

HFC-365mfc is a non-VOC solvent (US definition) with an atmospheric life of 8.6 years, a GWP of 782 (Table 2.6) and very low toxicity (exposure guide of 500 ppm). The manufacturer's data sheet (Solvay, 2005) indicates that it is flammable (flashpoint of -27°C) and it is therefore used primarily in blends with other non-flammable HFCs or HFEs to suppress its flammability. The current cost of HFC-365mfc is lower than that of other HFCs and HFEs and so it is being increasingly used in low-cost non-flammable blends (with HFCs and HFEs) for some applications.

HFC-245fa has a relatively low boiling point (15°C) and this limits its use in conventional degreasers. At present, its use has been limited to aerosol blends; its use in cold cleaning is also envisaged, though this is also limited due to the rapid evaporation rate.

Although HFCs are available in all regions, they have been primarily used in developed countries due to their relatively

¹ Note that HFC-c447ef is not included in the assessment of literature on chemical and radiative effects in this report (in chapter 2).

high cost and the concentration of use in high-tech industries. In addition, given the increasing concern about their GWPs, they now tend to be used in critical applications with no other substitute. Growth is therefore expected to be minimal (Merchant, 2001).

10.3.1.2 PFCs

PFC solvents such as C_6F_{14} (PFC-5-1-14) have physical properties similar to CFC-113. The atmospheric lifetimes and GWPs of PFCs are very high (C_6F_{14} has an atmospheric lifetime of 3200 years and a GWP of 9140 (Table 2.6)). However, the very limited solubility of organic soils in these materials has restricted their use in cleaning to particulate removal and the cleaning of fluorinated oils and greases (Agopovich, 2001). Due to the high cost, the availability of substitutes, and regulations restricting or banning use, PFC use has been limited primarily to niche applications in developed countries (Japan, US and Western Europe) with virtually no use in developing countries or countries with economies in transition (IPCC/TEAP, 1999). For example, in the US, PFC use is restricted to only those applications where no other alternative meets performance or safety requirements. In Germany, the use of CFCs, HCFCs, HFCs and PFCs is prohibited in solvents, except the pertinent authority can allow for high-quality applications provided negative environmental impacts and impacts on the climate are not expected and only if state-of-the-art technology does not allow the use of any fluorine-free solvent (Germany, 1990).

The published data about the consumption of C_6F_{14} are limited. Volumes are known to have decreased since the mid-1990s due to replacement with lower-GWP compounds (IPCC/TEAP, 1999).

10.3.1.3 HCFCs

The only HCFC solvents used are HCFC-141b and HCFC-225ca/cb, with ODPs of 0.12 and 0.02/0.03 (Chapter 1, Table 1.2) and GWPs of 713 and 120/586 respectively (Chapter 2, Table 2.6). HCFC-141b is mainly used in foam blowing, with use as a solvent representing less than 10% of global use in 2002 (UNEP-TEAP, 2003).

The use of HCFC-141b as a solvent is widely banned in developed countries, with a few derogations for technical reasons. Use from existing stockpiles is, however, allowed in the US.

In developing countries, the use of HCFC-141b is still

increasing, especially in China, India, and Brazil. As economic growth rates are high, use could have exceeded 5000 tonnes in 2002, even with process containment and recycling (AFEAS, 2001). HCFC-141b is often the most cost-effective replacement for 1,1,1-trichloroethane or CFC-113. The decrease in developed countries, especially as use for foam blowing is phased out, will lead to production restructuring which could create shortages in 2010–2015 (UNEP-TEAP, 2003).

HCFC-225ca/cb use has always focused on niche applications in precision cleaning and use as a carrier solvent because of its ozone-depleting potential and phase-out schedule; it is being gradually replaced by HFC, HFE and not-in-kind alternatives. Most sales are in Japan and the US (around 4,000 tonnes in 2002); sales are increasing in developing countries (2,000 tonnes in 2002) (UNEP-TEAP, 2003).

The HCFC total consumption phase-out for developing countries is scheduled for 1 January 2040, with a freeze in consumption in 2015. But some countries are accelerating this schedule, especially for solvents (e.g., Malaysia, Thailand). Most of the uses of HCFC-141b and HCFC-225ca/cb can be technically replaced by partly introducing zero-ODP HFC or HFE, with a lengthy qualification transition time for complex and crucial applications and sometimes at a high cost.

10.3.2 Projected consumption / emissions

Most solvent uses are emissive in nature, with a short inventory period of a few months to two years (IPCC, 2000). Although used solvents can and are distilled and recycled on site, all quantities sold are eventually emitted. The IPCC Good Practice Guidance recommends a default emission factor of 50% of the initial solvent charge per year (IPCC, 2000). A report by the US Environmental Protection Agency (US EPA) assumes that 90% of the solvent consumed annually is emitted to the atmosphere (US EPA, 2004a). Consequently, the distinction between consumption and emission is typically not significant for these applications.

The US EPA has projected global emissions of HFCs and PFCs from solvent uses as shown in Table 10.7 (US EPA, 2004a). PFC emissions are assumed to decline linearly until they are essentially no longer used in solvent applications in 2025.

Table 10.7. Projected HFC and PFC emissions from solvent uses (MtCO₂-eq) (US EPA, 2004).

Region	HFC and PFC emissions from solvent use (MtCO ₂ -eq)			
	2005	2010	2015	2020
United States	1.65	1.80	1.91	2.09
Developed countries (non-US)	2.05	2.09	2.09	2.13
Developing countries	0.22	0.33	0.37	0.44
Total	3.92	4.18	4.40	4.62

Note: Totals may not tally due to independent rounding-off.

10.3.3 Emissions reduction options

Most of the new solvent handling equipment is designed to ensure very low emissions, partly because of the higher cost of the HFC, PFC and HCFC solvents and partly due to increased environmental awareness and regulations in some countries for all solvents requiring zero or low emissions. The new tight machines generally have higher freeboards, dual temperature cooling coils, automated work transport facilities, welded pipe joints, hoods or sliding doors, and superheated vapour drying systems. Likewise, it is possible to reduce emissions to a minimal level by implementing good handling practices, such as reducing drag-out losses of solvent from the system by keeping the workload in the vapour zone long enough to drain and drop any entrapped or remaining solvent (UNEP, 1998). It is also possible to minimize evaporative losses by improving the design of solvent bath enclosures and of vapour-recovery condensing systems (March, 1998).

10.3.3.1 HFCs, PFCs, HCFCs emission reduction

In tests with both new degreasers and retrofitted degreasers with specified enhancement features, measurements of HFC, PFC and HCFC solvent emissions showed that there was a decrease of as much as 80% (Ramsey, 1996). Another study indicated that retrofitting a vapour degreaser with an open-top area of 3.6 meters square (13 square feet) can, in combination with proper maintenance, reduce emissions from a solvent process by 46 to 70 percent, depending on the specific retrofit methods chosen (Durkee, 1997). With higher-cost fluorinated solvents, the pay-off from upgrading an old degreaser to a new degreaser standard is estimated to be > 62% (rate of return with break-even in less than 2 years) (Ramsey, 1996).

10.3.3.2 Alternative fluids (chlorinated solvents, HFE-449s1, HFE-569sf2 HFE-347pcf, n-propyl bromide)

In some cleaning applications, lower-GWP solvents can be used to replace higher-GWP solvents. These options include the use of lower-GWP HFCs to replace the use of PFCs and higher-GWP HFCs. Similarly, with very few exceptions, the non-ozone-depleting solvents can be used as alternatives to HCFCs.

Cleaning processes using halogenated alternative fluids, with the exception of n-propyl bromide (due to the higher vaporization temperature compared to chlorocarbons), are typically similar to the processes they replace with respect to energy use (ADL, 2002). Consequently, these aspects are not assessed for each option.

Fluids that are alternatives to both HFCs/PFCs and ODSs include:

Chlorinated solvents

Chlorinated solvents such as dichloromethane (methylene chloride), trichloroethene (trichloroethylene) and tetrachloroethene (perchloroethylene) have been used for decades in cleaning applications (Risotto, 2001). The implementation of the Montreal

Protocol motivated a return to the use of these traditional solvents. Chlorinated solvents are used as replacements for CFCs, 1,1,1-trichloroethane and HCFCs in a variety of cleaning applications due to their high solvency. While the higher boiling points of trichloroethene (87°C) and tetrachloroethene (121°C) limit their use in some applications, they also provide an advantage in cleaning some soils such as resins and waxes (Risotto, 2001). However, in some instances, the solvent strength of the chlorinated solvents may cause incompatibility with the components to be cleaned.

Direct greenhouse-gas emissions from the use of chlorinated solvents are much lower than those from the products they replace due to their very low GWPs.

Chlorinated solvents are non-flammable but have toxicological profiles that require low exposure guidelines. The 8-hour exposure guidelines for dichloromethane, trichloroethene and tetrachloroethene are 50 ppm, 50 ppm and 25 ppm respectively (Risotto, 2001). Worker exposure to these solvents needs to be minimized in order to use them safely. Many regions have placed restrictions on the handling, use and disposal of chlorinated solvents (Risotto, 2001). The EU has reclassified trichloroethylene as carcinogenic (OJ, 2003).

Chlorinated solvents are among the lowest-cost solvents and are widely available in virtually all regions (UNEP, 2003b).

Hydrofluoroethers

HFE-449s1, HFE-569sf2, HFE-449s1 and HFE-569sf2 are segregated hydrofluoroethers with the ether oxygen separating a fully fluorinated and a fully hydrogenated alkyl group. Both of these compounds are used as replacements for CFCs and HCFCs. The pure HFEs are limited in utility in cleaning applications due to their mild solvent strength. However, HFEs are also used in azeotropic blends with other solvents (such as alcohols and trans-1,2-dichloroethylene) and in co-solvent cleaning processes, giving them broader cleaning efficacy (Owens, 2001).

As a result of the low GWPs of these HFEs, the direct greenhouse-gas emissions from them are significantly reduced compared to the products they replace (GWP of 56 and 397 for HFE-569sf2 and HFE-449s1 respectively; see Table 2.6 in Chapter 2).

HFE-449s1 and HFE-569sf2 are non-flammable and have relatively high exposure guidelines (750 ppm and 200 ppm respectively), allowing them to be used safely in many cleaning applications (Owens, 2001).

These HFE compounds are available in most regions. The relatively high cost of these materials limits their use compared to lower-cost solvents such as the chlorinated solvents and hydrocarbons (UNEP, 2003b).

HFE-347pcf

This compound is a non-segregated hydrofluoroether with oxygen separating two partially fluorinated alkyl groups. The material is a new compound and has only recently become commercially available. Very little information is available regarding the performance of this material in cleaning applications.

Normal-propyl bromide

Normal-propyl bromide (nPB) is a non-flammable, brominated alkane. Its high solvent strength makes it effective in a variety of cleaning applications, including both vapour degreasing and cold cleaning (Shubkin, 2001). In some instances, n-propyl bromide may be incompatible with the components to be cleaned (Shubkin, 2001).

The direct greenhouse-gas emissions from n-propyl bromide are very low due to its very low GWP. The ODP of n-propyl bromide varies depending upon the latitude at which it is emitted. The current calculations indicate a range of ODPs from 0.013 to 0.105 (WMO, 2002).

Normal-propyl bromide has low acute toxicity but its complete toxicological profile necessitates a low exposure guideline. Current exposure guidelines set by n-propyl bromide manufacturers range from 5 to 100 ppm (US EPA, 2003b). However, recent toxicological studies continue to raise concerns regarding its chronic toxicity (both reproductive and central nervous system effects), causing some organizations to suggest that even lower exposure guidelines are required to protect workers (CDHS, 2003). The EU has decided to reclassify its toxicity as altering fertility and dangerous for the foetus (OJ, 2004).

Normal-propyl bromide is available in most regions, including Asia, with local production in China (UNEP, 2003b). World production capacity for the manufacture of nPB is increasing, although consumption is currently stable. This is resulting in a lowering of bulk prices to a level comparable to the upper range of chlorinated solvents (UNEP, 2003b).

10.3.3.3 Not-in-kind options

These are numerous, and include no-clean, aqueous, hydrocarbon and oxygenated solvents, and they correspond to the fragmented market with a large number of small users in very diverse industries. Each presents “trade-offs” between effectiveness in use, cost, safety, and environmental properties.

No-clean applications

The use of no-clean flux is the preferred option in electronics cleaning and can be used for practically all types of printed circuit boards, even for most applications in the aerospace, aeronautics and military sectors (given the crucial reliability and safety issues). It is even used in the vast majority of high-tech printed circuit boards for automotive controls (>70%). But this approach requires very tight control of incoming materials, adapted chemicals for soldering and skilled operators to master the process. Overall, industry experts report 85% of printed circuit boards are assembled with a no-clean process, in developed as well as in developing countries. Total process costs are reduced and environmental impact is very low with no direct greenhouse-gas emissions.

Hydrocarbon solvent cleaning

This process has proven a good solution with paraffin hydrocarbon formulations; cleaning is efficient but the non-volatile

or less-volatile residue can be incompatible with some downstream manufacturing or finishes. Some cases of materials incompatibility are also known. Environmental impact is low (low GWP, no ODP) but these solvents are generally classified as VOCs. Their toxicity is also low. Due to their flammability (flashpoint > 55°C), they have to be used in open tank equipment at a temperature at least 15°C below their flashpoint. After cleaning, rinsing has to be done using fresh solvent. To reduce solvent consumption, on-site recycling with vacuum distillation is recommended. In some cases, safety considerations and emissions reduction require a closed machine with a vacuum system. This is not always compatible with high-throughput processes. Use in precision mechanics (injectors, bearings etc.) has developed in the last 3 years, but it involves a drastic change of process, and a medium to high investment, as well as good operator training.

Oxygenated solvent cleaning

Oxygenated organic solvents are compounds based on hydrocarbons containing appendant oxygen (alcohols and ketones), integral oxygens (ethers), or both (esters). These substances have been used for many years in diverse cleaning applications. Their cost and environmental impact are low (low GWP, no ODP), except they are classified as VOCs and may contribute to ground-level ozone pollution. Some of the oxygenated compounds are flammable as neat product or the mixture may become flammable in use. Precautions for handling flammables must therefore be considered, e.g. explosion-proof equipment.

Aqueous cleaning

These processes can be good substitutes for metal degreasing or even precision cleaning when corrosion of the materials is not an issue. For some tasks, where finish is a crucial issue, the number of required washing and rinsing baths, and the quality of the water, might be a deterrent. The availability of good-quality water and water disposal issues need to be addressed from the outset of process design. Aqueous cleaning processes have low environmental impact (not VOCs, low GWP, and no ODP) and low toxicity. The total TEWI can be equivalent to low-GWP solvent processes, as energy for drying has to be included in the total evaluation (ADL, 2002). It should be noted that a change from solvent to water cleaning does require good training of the workforce. The process is generally not forgiving; any error in operation or maintenance could result in corrosion and other quality problems. Investment costs can be high but operating costs are generally lower than those with solvent alternatives.

Table 10.8 provides an overview of the alternative fluids and not-in-kind technologies, including environmental and technical data.

Like other solvents, the hydrocarbon and oxygenated solvents lead to emissions that vary with the equipment used as well as with storing, handling and recovery procedures. The emission rate (per kg of parts cleaned for example) can decrease from 10 to 1 if containment in the equipment (upgrading or new

Table 10.8. Overview of alternative fluids and not-in-kind technologies in solvent applications.

	CH ₂ Cl ₂ ⁽¹⁾	HFE-449s1 ⁽²⁾	n-propyl bromide	No Clean	Hydro-carbon / oxygenated	Aqueous / semi-aqueous
Substance characteristics						
Radiative efficiency (W m ⁻² ppb ⁻¹)	0.03	0.31	0.3	n/a		n/a
Atmospheric lifetime (yr)	0.38	5	0.04	n/a		n/a
GWP (100-yr time horizon)						
- This report	10	397	n/a	n/a		n/a
- IPCC (1996)	9	not given				
ODP	-	-	-	-	-	-
Ground-level ozone impact						
- MIR ⁽³⁾ (g-O ₃ /g-substance)	0.07	n/a	n/a			
- POCP ⁽⁴⁾ (relative units)	7	n/a	n/a			
Ground-level ozone impact	Low to moderate	None	Low to moderate	None	Low to moderate	None
Flammability (based on flashpoint)	None	None	None	n/a	Flammable	n/a
Technical data						
Stage of development	Commercial	Commercial	Commercial	Commercial	Commercial	Commercial
Type of application:						
- Electronics cleaning		X	X	X	X	X
- Precision cleaning		X	X		X	X
- Metal cleaning	X	X	X		X	X
- Drying					X	
- Carrier solvent	X	X	X		X	

⁽¹⁾ Listed values refer to CH₂Cl₂ only. Additional chlorinated solvents are used in these applications as indicated in section 10.3.3.2.

⁽²⁾ Listed values refer to HFE-449s1 only. Additional HFE solvents are used in these applications as indicated in section 10.3.3.2.

⁽³⁾ Maximum Incremental Reactivity (See Chapter 2, Table 2.11 for more details.)

⁽⁴⁾ Photochemical Ozone Creation Potential (See Chapter 2, Table 2.11 for more details.)

installation) is optimized and if care is exercised throughout the implementation of the process.

The flammability of oxygenated and, to a lesser extent, hydrocarbon solvents generally requires the use of higher-containment, flammable-rated equipment, which leads to reduced emissions. In the case of hydrocarbons, the high boiling point induces lower volatility at the normal use temperature and, accordingly, low emissions. In many countries, environmental and VOC regulations have further pushed the emissions reduction from all solvent use and in particular from cleaning with organic or hydrocarbons solvents.²

No-clean and aqueous cleaning processes do not emit any volatile compounds; however, for aqueous cleaning, total energy consumption (heating and drying) is a source of CO₂ emissions (ADL, 2002).

10.3.4 Emission reduction potential and abatement cost

Reduction potential

Four separate studies (two European, one Japanese and one

from the US EPA) state a range for the potential reduction in HFC/PFC solvent emissions of 0% to 67%. See Table 10.9 for more details. The two European studies, which covered EU countries, were conducted by Harnisch and Gluckman (2001) and Harnisch and Schwartz (2003). The first study stated an estimate for solvent emission reductions of 0.3 to 0.5 MtCO₂-eq (15% to 25%) depending upon the level of investment (abatement cost). The estimate in the second study was a solvent emission reduction potential of 60% (0.3 MtCO₂-eq) by 2010 using substitution with lower-GWP solvents. For Japan, a recent study concludes there is no emission reduction potential for solvent uses below projected business as usual quantities (METI, 2004).

The US EPA's recently published emission-abatement report (2004) has estimated emission reduction potentials in 2020 in the US, non-US Annex I and non-Annex I countries. This study looked at several abatement options and concluded that the global reduction potential was 58% (2.7 MtCO₂-eq in 2020). Based on these abatement options, the reduction potentials are:

Retrofit	0% to 10.5%
Conversion to low-GWP solvents such as HFE	21% to 50%
Conversion to not-in-kind semi-aqueous	5%-10%
Conversion to not-in-kind aqueous	10%-20%

² For example EU Directive 1999/13/EC on industrial solvent cleaning (OJ, 1999).

Table 10.9. Summary of emission reduction potential and abatement cost for solvent applications.

Reference	Harnisch and Gluckman (2001) European Union 2010	Harnisch and Schwartz (2003) European Union 2010	US EPA (2004)		METI (2004)
			USA 2020	non-USA 2020	Japan 2010
Region Year					
Total emission projection (MtCO ₂ -eq)	2.0	0.5	2.1	2.6	3.6
Emission abatement (MtCO ₂ -eq)	a) 0.3 b) 0.5 c) 0.5	0.3	1.4	1.3	0
Abatement cost (US\$ ₂₀₀₂ /tCO ₂ -eq)	a) <23 b) 23 to 57 c) 57 to 170	0	-37 to 2	-37 to 2	n/a

Abatement costs

The abatement costs associated with using the solvent alternatives vary greatly: from increased costs for adopting a new technology to cost savings due to reduced solvent consumption. Some options are cost-neutral.

Harnisch and Gluckman (2001) assumed that abatement costs could range from <20 €₁₉₉₉ (23 US\$₂₀₀₂) to a range of 50 to 150 €₁₉₉₉ (57 to 170 US\$₂₀₀₂), depending on the level of abatement achieved.

Harnisch and Schwartz (2003) estimate abatement costs for HFC/PFC solvent emission reduction in the EU to be cost-neutral based upon substitution with lower GWP solvents (0€₂₀₀₀/tCO₂-eq [0 US\$₂₀₀₂/tCO₂-eq] using a ten-year depreciation period and 10% discount rate).

The US EPA (2004) has estimated the abatement costs for several alternatives using a 4% discount rate:

Equipment Retrofit

-36 US\$₂₀₀₀/tCO₂-eq [-37 US\$₂₀₀₂/tCO₂-eq]

Conversion to lower GWP solvents such as HFE

0 US\$₂₀₀₀/tCO₂-eq [0 US\$₂₀₀₂/tCO₂-eq]

Conversion to not-in-kind semi-aqueous

0.2 US\$₂₀₀₀/tCO₂-eq [0.2 US\$₂₀₀₂/tCO₂-eq]

Conversion to not-in-kind aqueous

2 US\$₂₀₀₀/tCO₂-eq [2 US\$₂₀₀₂/tCO₂-eq]

10.4 HFC-23 from HCFC-22 production

In addition to emissions of a chemical during its use and distribution, there may also be emissions of the material that is being produced, the so-called “fugitive emission” or emissions of other byproduct chemicals generated during the production of a related chemical (e.g. HFC-23 from HCFC-22). Emissions from fluorocarbon production processes have been estimated at approximately 0.5% of the total production of each compound (AFEAS, 2004). Emissions may vary because of the process used or destruction technology employed. However, because manufacturers have an incentive to minimize lost product, and emission rates are already reported to be very low, fugitive

emissions are assumed to be insignificant compared to emissions from consumption. In contrast, byproduct emissions of HFC-23 from HCFC-22 are significant and well documented.

Trifluoromethane (HFC-23 or CHF₃) is generated as a byproduct during the manufacture of chlorodifluoromethane (HCFC-22 or CHClF₂). HCFC-22 is used as a refrigerant in several different applications, as a blend component in foam blowing and as a chemical feedstock for manufacturing synthetic polymers. In developed countries, the phase-out of HCFC-22 consumption scheduled under the Montreal Protocol will occur by 2020 because of its stratospheric ozone-depleting properties. Feedstock production, however, will be allowed to continue indefinitely because it does not involve the release of HCFC-22 to atmosphere in the same way as the dispersive uses. Consumption in developing countries will be phased out over a longer time period, using consumption (and production) in the year 2015 as a baseline.

HCFC-22 is produced in several developed and developing countries. The USA is a major world producer of HCFC-22, with three plants and approximately one-third of all developed-country production. There are ten manufacturing plants for HCFC-22 in the EU, with total capacity estimated at 184,000 metric tonnes; the reported levels of production are very close to this capacity (Irving and Branscombe, 2000; EFCTC, 2001; UNEP, 2002). Japan is another large producer of HCFC-22, with a reported production of 77,310 metric tonnes in 2003, and production in other Asian countries (notably China, India and Korea) has increased dramatically in recent years. There are now 19 HCFC-22 producers in China with a total capacity of 200,000 metric tonnes. They produced 177,000 metric tonnes in 2003 (CAOFSMI, 2003). Table 10.10 shows the historic and projected time series for global HCFC-22 production.

Trifluoromethane (HFC-23) is formed at the reactor stage of the manufacture of chloro-difluoromethane (HCFC-22) as a result of over-fluorination. Its formation depends upon the conditions used in the manufacturing process and varies from 1.4% to 4.0% of the production of HCFC-22 so that, while it is possible to reduce its formation by optimizing process conditions, it is not possible to eliminate the production of HFC-23.

Table 10.10. Business-as-usual and reduced emissions forecasts for HFC-23 (given current best practice).

Year	HCFC-22	HFC-23 emissions			Emission	
	Production	BAU		Current best practice	reduction	
	BAU	ktonnes	MtCO ₂ -eq	ktonnes	potential	
	ktonnes	ktonnes	MtCO ₂ -eq	ktonnes	MtCO ₂ -eq	
1990	341	6.4	92	6.4	92	
1991	373	7.0	100	7.0	100	
1992	385	7.3	104	7.3	104	
1993	382	7.2	103	7.2	103	
1994	387	7.2	103	7.2	103	
1995	385	7.3	104	7.3	104	
1996	430	8.6	123	8.6	123	
1997	408	8.4	120	8.4	120	
1998	448	9.7	139	9.7	139	
1999	458	10.4	149	10.4	149	
2000	491	11.5	165	11.5	165	
2001	521	12.6	180	12.6	180	
2002	551	13.6	195	13.6	195	
2003	581	14.7	210	14.7	210	
2004	520	14.1	202	14.1	202	
2005	550	15.2	218	13.8	197	20
2006	580	16.2	232	13.3	190	41
2007	610	17.3	248	12.6	180	67
2008	640	18.4	263	11.8	169	94
2009	670	19.4	278	10.7	153	124
2010	622	19.0	272	8.8	126	146
2011	652	20.1	288	7.4	106	182
2012	682	21.2	303	5.9	84	219
2013	712	22.3	319	4.2	60	259
2014	742	23.3	333	2.3	33	301
2015	707	23.2	332	2.3	33	299

In a number of plants, HFC-23 is destroyed by thermal oxidation, and emission tests have shown this to be highly effective (Irving and Branscombe, 2000). The cost of reducing emissions varies significantly depending on the option used and will vary from plant to plant depending on the particular situation.

Business-as-usual emissions prior to 2015

Global emissions of HFC-23 increased by an estimated 12% between 1990 and 1995, due to a similar increase in global production of HCFC-22 (Oram *et al.*, 1998). However, the widespread implementation of process optimization and thermal destruction has brought an end to this trend in HFC-23 emissions and, since 1995, the emission trend has fallen below the increase in production (US EPA, 2003a).

While such abatement measures serve to reduce or eliminate emissions, the quantity of HFC-23 actually produced is directly related to the production of HCFC-22 and so emission projections require a scenario for future HCFC-22 production volumes. These will depend on the consumption of HCFC-22 in developed countries, which is declining, and the consumption in developing countries and global demand for fluoropolymers feedstock (UNEP-TEAP, 2003), both of which are increasing.

The introduction in developed countries of additional controls on HCFC production after 2005 (over and above the required freeze) may have a neutral effect on production globally because it might stimulate investment plans for further HCFC-22 capacity in developing countries (UNEP-TEAP, 2003).

Consumption in developed countries is expected to decrease as a consequence of increasingly stringent national and regional regulations. However, a scenario that followed the requirements of the Montreal Protocol exactly in these countries was adopted as the best estimate (business-as-usual case) in the most recent Scientific Assessment of Ozone Depletion (Fraser, Montzka *et al.*, 2003). This envisages that, by 2015, consumption of HCFC-22 in these countries will have fallen by a factor of 10 from the level in 2000-2003.

In the same region, over the 1990s, growth in demand for fluoropolymer feedstock increased linearly at a rate of 5800 tonnes yr⁻¹, with a coefficient of variance (R²) of 0.84 (Cefic, 2003; SRI, 1998). In the absence of other influences, this rate of increase could continue, leading to a doubling of feedstock demand for HCFC-22 in developed countries by 2015.

In the remaining countries of the world, production of HCFC-22 for both dispersive and feedstock uses has grown

rapidly in recent years. Over the period 1997 to 2001, production for dispersive uses grew linearly at 20,000 tonnes yr⁻¹, with a coefficient of variance (R^2) of 0.95, and feedstock use increased by 4100 tonnes yr⁻¹ (R^2 equal to 0.99) (Bingfeng *et al.*, 2000; CCR, 2002; UNEP, 2002; UNEP-TEAP, 2003). Projected at these rates until 2015, the total global requirement for HCFC-22 could become about 710,000 tonnes yr⁻¹, about 40% of which would be for feedstock, compared with a total of 490,000 tonnes yr⁻¹ in the year 2000.

Up to 1995, records of atmospheric concentrations of HFC-23 (Oram *et al.*, 1998) and global HCFC-22 production (McCulloch *et al.*, 2003) indicate an emission intensity for HFC-23 of 20 kg per tonne of HCFC-22 production, or 2%. This suggests that there was substantial abatement of HFC-23 emissions at that time, either by process optimization or by destruction; unabated emissions would be expected to be of the order of 4% (Irving and Branscome, 2000). In the “business-as-usual” case for the period prior to 2015, it has been assumed that emissions from existing capacity will continue at 2% of HCFC-22 production and that new capacity will emit HFC-23 at a rate of 4%. Consequently, emissions of HFC-23 could increase by 60% between now and 2015, from about 15,000 tonnes yr⁻¹ in 2003 to 23,000 tonnes yr⁻¹.

10.4.1 Relevant practices during life cycle

In the most commonly used process, chlorodifluoromethane (HCFC-22) is produced by the reaction of chloroform (CHCl_3) and anhydrous hydrogen fluoride (HF) in the presence of an antimony pentachloride (SbCl_5) catalyst. The reaction takes place in a continuous-flow reactor full of boiling liquid, products being removed from the reaction system as vapours. Two molecules of HF react with one molecule of chloroform to yield chlorodifluoromethane, and reaction conditions are maintained to optimize HCFC-22 production but overfluorination (reaction of HCFC-22 with HF) can occur, yielding HFC-23 (CHF_3). Consequently, the vapour stream leaving the reactor contains, in addition to HCFC-22 (CHClF_2), HCFC-21 (CHCl_2F), CHCl_3 , HF and some entrained catalyst (which are recycled to the reactor) and also HFC-23 (CHF_3) and HCl. Separation of the hydrocarbon compounds is facilitated by the differences in volatility, which makes it possible to condense the chloroform and HCFC-21 for recycling and conversion to HCFC-22. It is technically feasible but not economical to convert HFC-23, once formed, back into HCFC-22 (Merchant, 2001). Most of the HFC-23 produced is released from the reaction system at the control valve used to maintain the system pressure (the “condenser vent”) and, unless separated for collection, is then emitted to the atmosphere.

This production process is relatively old (over 30 years) and has been extensively researched. However, the optimum operating conditions dictated by business economics are not necessarily the conditions required to minimize HFC-23 production. The upper limit for HFC-23 emissions is of the order of 3 to 4 percent of HCFC-22 production but the actual quantity of

HFC-23 produced depends in part on how the process is operated and the degree of process optimization. There are a number of factors that affect halogen exchange of chlorine to fluorine and thus affect the generation of HFC-23 in the reactor, and a significant reduction in HFC-23 formation can be achieved by adjusting process operating conditions, including modifying process equipment.

One variation on the liquid phase process is the so-called “swing” plant, designed to be capable of manufacturing either CFC-12 or -11 from carbon tetrachloride feedstock or HCFC-22 from chloroform. Reactor designs for the two products are basically very similar, with differences only in operating pressure, operating temperature and heat load. However, the chemical engineering design of the whole plant is, of necessity, a compromise between the ideals for the two products and, consequently, optimization of the process to minimize HFC-23 production when producing HCFC-22 is intrinsically more difficult than in a plant designed for HCFC-22 specifically. It is to be expected that swing plants will operate at the higher end of the HFC-23 production range (say 3 to 4% of HCFC-22 by mass).

The major exit point for HFC-23 from the reaction system in the HCFC-22 production process is the condenser vent, whence it can be discharged to the atmosphere after separation from useful products (HCFC-22 and HCl). There are four additional sources of HFC-23 emissions, three of which are inconsequential:

- Fugitive emissions from leaking compressors, valves and flanges. Because the process is maintained under relatively high pressures, there is a potential for fugitive emissions from leaking equipment. However, there is a strong incentive to prevent leaks because of the noxious nature of the reactor contents and the potential for loss of valuable product (HCFC-22). Any leaks can usually be identified and repaired quickly and effectively. Fugitive emissions are a minor source; in two plants where they were measured, the HCFC-22 lost in this way amounted to less than 0.1% of plant production (Irving and Branscombe, 2000).
- Removal with the HCFC-22 product and subsequent emission. Industry standard specifications limit the concentration of HFC-23 allowed in the product to a small fraction of a percent. Consequently, removal with the product also accounts for only a very small portion of the HFC-23 that is generated.
- Vents from product storage. These are not significant sources, even when plants capture HFC-23 (by condensation at high pressures and low temperatures) and subsequently store it as pure material. The storage tanks are enclosed vessels, not normally venting to atmosphere, and only a very small fraction of the plants producing HCFC-22 recover HFC-23. This is clear from the small quantity of HFC-23 that is sold.

- The most important of the additional loss routes is in the aqueous phases from caustic and water scrubbers used in the process. These may yield useful product, such as hydrochloric acid (aqueous HCl), or be destined for waste treatment, but in any case volatile organics in such aqueous streams are readily emitted when the streams are subsequently managed in open systems, such as wastewater treatment processes. HFC-23 concentrations in the aqueous effluent streams are only a few ppm at the most but the concentration in aqueous HCl can be several hundred ppm and this can represent an important release vector if the acid is used untreated. However, compared to the condenser vent, the aqueous HCl source is minor. Furthermore, the HFC-23 can be removed from the aqueous HCl by air-stripping for subsequent treatment in the thermal oxidizer.

10.4.2 Emission reduction options

Process optimization

In fully optimized processes, the likely range of emissions is about 1.5 to 3 percent of production, with 2 percent being a reasonable average estimate. Actual emissions depend on the age and design of the facility as well as the process management techniques applied. However, it is not possible to eliminate HFC-23 production completely by this means.

Capture and destruction

Further reductions in emissions beyond what is technically achievable through process optimization require additional equipment and, given that there is one main outlet for HFC-23 from the process, the most favourable option for eliminating emissions is to collect and treat the vent gases. Thermal oxidation is an effective treatment but the system must be designed to cope with, and render harmless, the halogen acids (HF and HCl) produced as a result of combustion. Depending on cost and availability, treatment can be on- or off-site. Emission tests at one plant showed that thermal oxidation destroys over 99.996 percent of the HFC-23 (Irving and Branscombe, 2000), making this a highly effective treatment option. However, the impact of the down-time of thermal oxidation units on the emissions of HFC-23 needs to be considered (EFCTC, 2001).

In the EU, thermal destruction was available from mid-2000 onwards, either on- or off-site, for six of the ten HCFC-22 manufacturing facilities. These facilities make up approximately 80% of EU HCFC-22 production but manufacturing plants in Spain (2), UK (1) and Greece (1) remain without such facilities. The cost of a typical unit is 3 million (about US\$4 million) to destroy 200 metric tonnes of HFC-23 per year, plus 200,000 yr⁻¹ (US\$250,000) in operating costs (EFCTC, 2001; Harnisch and Hendriks, 2000). Assuming a technological lifetime of 15 years, it is possible to calculate that specific abatement costs will be <0.2 US\$/tCO₂-eq.

In 1995, European emissions amounted to 3,150 metric tonnes. The potential emission in the year 2000 could have been up to 7,340 tonnes per annum, depending upon the rate of for-

mation in the individual manufacturing plants, but these were reduced to actual emissions of less than 2,025 metric tonnes (EFCTC, 2001).

The US EPA estimates that US emissions of HFC-23 in 2002 amounted to 1,690 metric tonnes of gas. Annual emissions have fluctuated since 1990, before dropping by 45 percent/tonne of HCFC-22 produced in 2002 (US EPA, 2004b).

In Japan, the production of HCFC-22 was reported at 72,787 metric tonnes for 2002, with the byproduction of 1,124 tonnes of HFC-23, of which 253 tonnes were destroyed. In 2003, 77,310 tonnes of HCFC-22 were produced, with the byproduction of 1,277 tonnes of HFC-23, 367 tonnes of which were destroyed (METI, 2004).

10.4.3 Reduced emissions in the period prior to 2015 given current best practice

It is apparent from historical trends, as described in *Business-as-usual emissions prior to 2015* above, that the amount of HFC-23 co-produced with HCFC-22 in the developed world will be reduced by approximately half. There is at present no published information about current HFC-23 global emissions and, for the reduced emissions case, it is assumed that destruction technology will be progressively introduced for all new and non-abated existing capacity from 2005 onwards. Destruction technology is assumed to be 100% efficient and to operate for 90% of the on-line time of the HCFC-22 plant.

Reduced emissions were calculated for the same activity (in the form of assumed future HCFC-22 production) as in the business-as-usual case. The difference between the two HFC-23 forecasts is therefore solely due to the extent of the deployment of destruction technology. The forecasts represent potential extreme cases and future changes in activity will tend to increase the probability of one or the other. Table 10.10 lists values for the forecasts and the HCFC-22 production on which they are based.

Implications of HCFC-22 production phase-out

In view of the uncertainties of scenario generation, the business-as-usual scenario uses consumption forecasts based on adherence to the Montreal Protocol, with no further controls. This is a fixed scenario (for the developed world) and amounts to a 90% reduction in the production and consumption of HCFCs for non-feedstock uses there by 2015, although many countries already have, or are planning, more stringent regulations. In 2010 in the US, the production and imports of HCFC-22 will be banned under the US Clean Air Act (US EPA, 1993), except for use in equipment manufactured before 2010. Within the EU, it is estimated that levels of HCFC-22 production for non-feedstock uses will decrease by 30% by the year 2010 under EU Regulation 2037/2000 on Substances that Deplete the Ozone Layer (EFCTC, 2001). Such legislation is well documented and the current effect on production of HCFC-22 is recorded in the data reported by AFEAS (2003), which shows a fall of 54,000 tonnes yr⁻¹ by the year 2001 from the peak production

of 271,000 tonnes yr⁻¹ that occurred in 1996. Potential dispersive consumption in the developed world is therefore already substantially below that in the business-as-usual scenario and will fall faster, skewing the probability of HFC-23 emissions towards the reduced emissions case.

Under the Montreal Protocol, the baseline year for developing countries is 2015, so that the regulatory maximum has yet to be established and production must be extrapolated from prior trends. In China, the production of HCFC-22 for dispersive use grew over the four years from 1998 to 2001 at a linear rate of 18,100 tonnes yr⁻¹ ($R^2 = 0.95$), or 26% in the year 2000 (CCR, 2002). When the other producers from developing countries and countries with economies in transition are included in the calculation, the growth rate reaches 20,000 tonnes yr⁻¹ and this rate has been assumed for both business-as-usual and reduced emissions cases. Any changes made to the assumed production rates will have a direct effect on the forecast HFC-23 emissions.

Use of HCFC-22 as feedstock

Historically, the demand for HCFC-22 in fluoropolymers has been growing linearly in the developed world at a rate that approximated to 3% in the year 2000, or absolute growth rates of 2200 tonnes yr⁻¹ in the US, 1600 tonnes yr⁻¹ in Japan and 2000 tonnes yr⁻¹ in the EU (Cefic, 2003; SRI, 1998). In 2001 in China, the demand for HCFC-22 in the production of fluoropolymers was 20,300 metric tonnes and the linear growth rate was 4100 tonnes yr⁻¹, with an R^2 value of 0.99 over four years (CCR,

2002). There is every reason to expect that this demand will continue to grow and there is no evidence for a future change in the growth rate. Hence, for both cases, demand for HCFC-22 in fluoropolymers was extrapolated using linear growth at these rates. Any changes made to the assumed production rates will have a direct effect on the forecast HFC-23 emissions.

Alternative processes for HCFC-22 production

Although it is technically feasible to manufacture HCFC-22 in a reaction involving chloroform and HF in the vapour phase over a solid catalyst, most, if not all, modern processes use the liquid-phase route described above (Hoechst, 1962). Furthermore, it is intrinsically more difficult to control a vapour-phase process for minimizing the formation of HFC-23 than to control a liquid-phase process. In the latter, conditions can be adjusted so that the boiling liquid in the reactor contains little HCFC-22, therefore minimizing the possibilities of fluorinating it to produce HFC-23. In the vapour phase, on the other hand, all HCFC-22 that is produced co-exists towards the exit of the catalyst with the excess of HF. In a vapour-phase process it is not impossible to adjust conditions to minimize HFC-23; it is only more difficult to do so than in the liquid phase.

Emission reduction potential

Table 10.10 shows the emissions under the mitigation scenario of this report, assuming implementation of current best practices. Destruction of byproduct emissions of HFC-23 from HCFC-22 production has a reduction potential of up to 300

Table 10.11. Niche applications of ozone-depleting substances with greenhouse-gas replacements.

Application	Comment
CFC-11 as a flushing agent for refrigerant and air-conditioning systems	Refrigeration and air-conditioning systems suffer occasional failures that result in contamination. The most common failure is a compressor burnout. Flushing systems with CFC-11 were effective, fast and safe. Alternatives include HCFC-141b, HCFs, terpenes, glycols and hydrocarbons. Flammability and system compatibility must be addressed.
CFC-11, CFC-113 for non-mechanical heat transfer	Cooling systems that rely on convection to remove heat from an area, rather than relying on mechanical refrigeration. A broad range of alternatives including not-in-kinds, HFCs and HFEs have been identified for retrofits and new systems. However, for applications where no other alternatives are technically feasible, PFCs are used. Most are used in closed systems with minimal emissions. Other applications have evaporative losses. For example, the electronics industry employs PFCs for cooling certain process equipment, during testing of packaged semiconductor devices and during vapour-phase reflow soldering of electronic components to circuit boards.
CFC-11 as an extraction solvent for perfumes, flavours, decaffeinated coffee	Used in a closed system. HFC-134a and not-in-kind replacements.
CFC-11, CFC-113 for cold cleaning and degreasing, hand cleaning	CFC used in buckets, as a wipe or spray to degrease parts, wash down equipment, clean oil spills, etc. No technical need for CFCs, HFCs or PFCs, but CFC use may continue if permitted by local regulation and if it is low cost and readily available.
CFC-114 for uranium isotope separation	This process requires operation of a heat transfer cycle to cool uranium isotope separation. Substitutes must meet an extremely rigorous set of criteria to be applicable to this end use. PFCs are used as a substitute.

MtCO₂-eq per year by 2015 and specific costs below 0.2 US\$/tCO₂-eq according to two European studies in 2000. Reduction of HCFC-22 production due to market forces or national policies, or improvements in facility design and construction also could reduce HFC-23 emissions.

10.5 Other miscellaneous uses

A few additional niche applications of ODSs with possible HFC, PFC or other greenhouse-gas replacements were identified. ODS use at the time of the Montreal Protocol was very low and there is insufficient literature available to evaluate the status of replacements, current or future emissions. It may also be the case that ODS use continues in some of these applications, especially where the source of the ODS is a common use such as a refrigerant and is redirected for convenience to an application such as cold cleaning or flushing. The consumption of ODSs or replacements in these applications is generally assumed to be insignificant but documentation does not exist. Although not comprehensive, Table 10.11 lists applications identified through expert judgment.

At the time of the Montreal Protocol, CFCs, PFCs and SF₆ were used simultaneously in a few applications, including wind tunnel tests, military dielectric applications, adiabatic applications, leak detection and tracer gases. Although there is little published information, consumption and emissions are not currently significant and not expected to grow significantly in the future.

Finally, other significant global sources of emissions of PFCs and SF₆ were considered and found to be from processes that never used ODSs or for new applications that would not have used ODSs. This includes PFCs from primary aluminium production, and semiconductor manufacture, and SF₆ used in high-voltage electrical equipment.

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