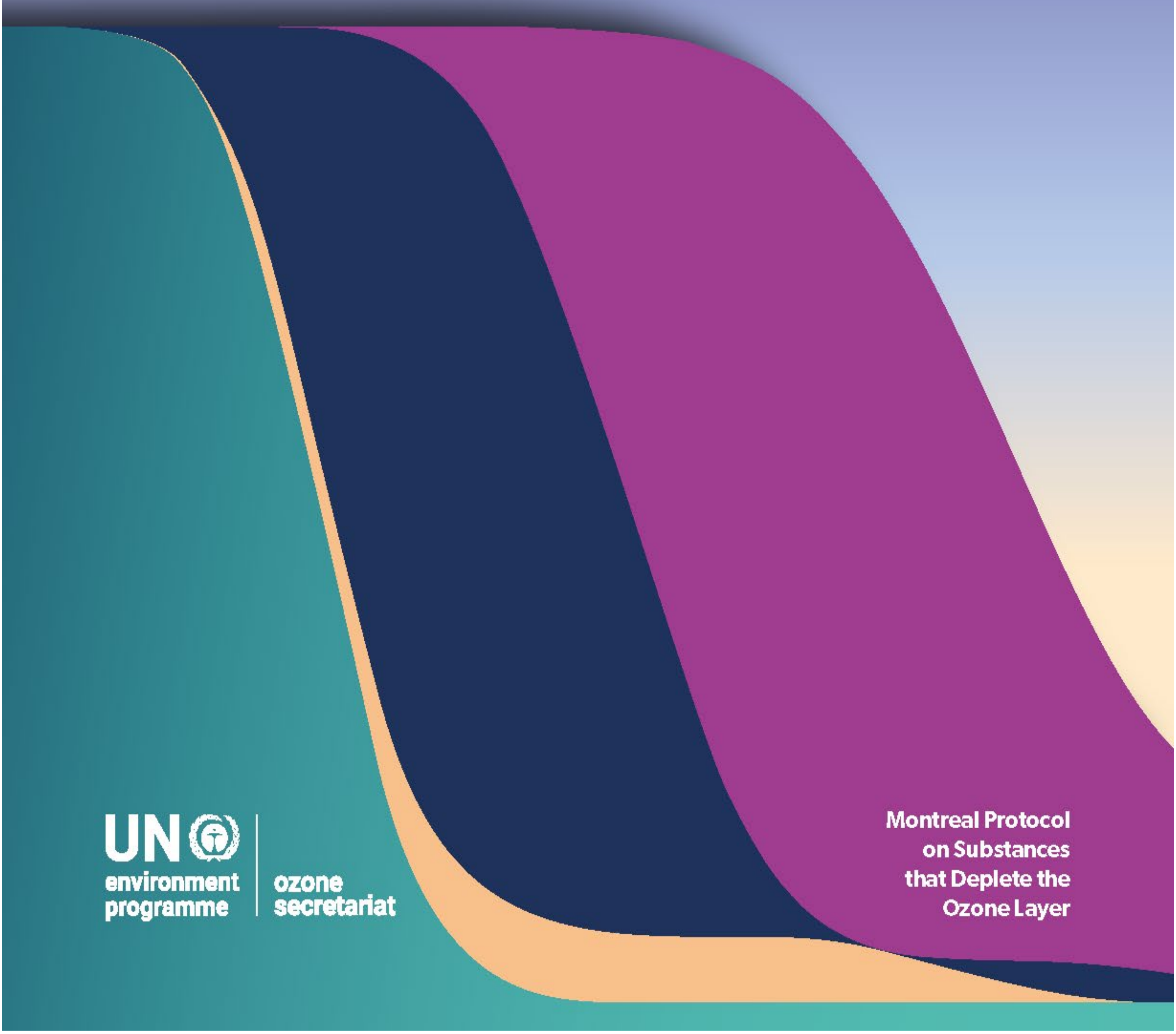
Medical and Chemical Technical Options Committee

2022 Assessment Report



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Montreal Protocol
on Substances
that Deplete the
Ozone Layer

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United Nations Environment Programme (UNEP)
Report of the Medical and Chemical Technical Options Committee

December 2022

2022 ASSESSMENT REPORT

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2022 REPORT OF THE MEDICAL AND CHEMICAL TECHNICAL OPTIONS COMMITTEE

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Executive Summary

Production, including Feedstocks

This chapter describes the production of controlled substances, including for feedstock uses, and a range of related issues, including by-production, production intermediates, estimated emissions for production, distribution and use of feedstocks, stocks, illegal trade, patents, regulatory issues, precursor substances to per- and polyfluoroalkyl substances (PFAS) and trifluoroacetic acid and its salts (TFA), carbon tetrachloride (CTC), ODS that are not controlled substances such as dichloromethane, chloroform, ethylene dichloride, trichloroethylene, perchloroethylene, and methyl chloride, and HFCs that are not listed in Annex F.

Feedstocks

Total reported production of ODS since 2002 has increased, due to production for feedstock offsetting the decrease in calculated production for emissive uses. The proportion of HCFC-22 as a percentage of total reported ODS production increased significantly in the period 2002 to 2007, and is now over 50% of total ODS production, due to the increasing use of HCFC-22 as a feedstock.

Feedstocks are chemical building blocks that allow the cost-effective commercial synthesis of other chemicals. As raw materials, feedstocks are converted to other products, except for *de minimis* residues and emissions of unconverted raw material. Emissions from the use of feedstock consist of residual levels in the ultimate products, and fugitive leaks in the production, storage and/or transport processes. Significant investments and effort are spent to handle ODS and HFC feedstocks in a responsible, environmentally sensitive manner and, in most countries, are regulated through national pollution control measures.

There is no Montreal Protocol definition for production for use as feedstock. However, there is the definition of "controlled substances produced" in Article 1, paragraph 5, *"Controlled substances produced" as used in Article 1, paragraph 5 is the calculated level of controlled substances manufactured by a party. This excludes the calculated level of controlled substances entirely used as a feedstock in the manufacture of other chemicals…"*. The term "manufactured" is not defined; although a common-sense definition would be "to make or process (a raw material) into a finished product".

As revised in decision XXX/10 and Annex III to MOP-30, Article 7 data reporting instructions and guidelines require the reporting of feedstock uses for all controlled substances and, when calculating production, the Montreal Protocol allows countries to deduct amounts of controlled substances used for feedstock and amounts destroyed. When reporting production data, parties are not expected to deduct these figures from their data. The Secretariat makes the necessary deductions. All feedstock produced during a calendar year is reportable for that year, even if it has not been used.

In 2020, total ODS production and import reported for feedstock uses was 1,475,007 tonnes (554,116 ODP tonnes), a small decrease compared to 2019 (1,486,288 tonnes). The overall increase in ODS feedstock uses through the last decade has been mostly due to the increase in feedstock uses of Annex C1 HCFCs, particularly HCFC-22, while uptake of HFOs is driving a more recent increase in CTC feedstock use. It is highly likely that the COVID pandemic had an impact on feedstock production and consumption in 2020.

In 2020, the proportions of the largest ODS feedstocks were HCFC-22 (48% of the total mass quantity), CTC (20%), and HCFC-142b (11%). HCFC-22 is by a considerable margin the largest feedstock used, with 713,536 metric tonnes reported in 2020. HCFC-22 is mainly used to produce tetrafluoroethylene (TFE) and hexafluoropropylene (HFP), which can be used to make fluoropolymers, such as polytetrafluoroethylene, and some HFCs and HFOs. HCFC-142b is used to make polyvinylidene fluoride. The feedstock use of CTC has increased in recent years, due to growing demand for lower GWP HCFO/HFOs and perchloroethylene (PCE).

Following the entry into force of the Kigali Amendment, reporting of HFCs, including production and import for feedstock uses, is required for all parties that have ratified the amendment. The HFC feedstock data reported for 2020 and 2021 is incomplete due to the timing of reporting obligations, e.g., depending on when some parties ratified. The largest reported HFC feedstock is HFC-152a (thousands of tonnes).

Some HFC-23 generated as a by-product during the manufacture of HCFC-22 is recovered and used as a feedstock to produce Halon 1301 (bromotrifluoromethane), used as a feedstock for the manufacture of the pesticide fipronil and other chemicals. Further uses of HFC-23 as feedstock have recently been investigated. One particularly attractive process is the reaction of HFC-23 with chloroform, producing HCFC-22 and HCFC-21, using HFC-23 as a valuable feedstock, reducing waste, and improving the efficiency of the HCFC-22 manufacturing process.

By-production of controlled substances, including of HFC-23

By-production of controlled substances in other production processes occurs through over or under reaction enroute to the intended product (e.g., HFC-23 is an over fluorination of HCFC-22), the presence of impurities that undergo reaction, and unintended side reactions. Plants are designed to minimise by-production of controlled substances.

Several production pathways use HCFC-22, tetrafluoroethylene (TFE) or hexafluoropropene (HFP) (both made from HCFC-22 feedstock) as feedstocks, including HFO-1234yf, HFC-125, HFC-227ea, HFC-32. The manufacture of HCFC-22 generates HFC-23 by-production and emissions.

HCFC-22 is by a considerable margin the largest feedstock used, with 713,536 tonnes reported production in 2020. About 97% of this is used to produce TFE and HFP, both used primarily to manufacture fluoropolymers. Article 2J of the MP, sets out destruction requirements for HFC-23 from HCFC-22 production. However, there are also significant high GWP by-products associated with production of TFE/HFP from HCFC-22, that if emitted contribute to global warming. The manufacture of TFE/HFP from HCFC-22 used as feedstock generates by-production and emissions of HFC-23 and very high GWP PFC-c-318 ($c\text{-}C_4F_8$). If unabated, these emissions as CO_2e are higher than the estimated emissions of HFC-23 from HCFC-22 production when applying the Executive Committee indicated maximum emission rate for HFC-23 from HCFC-22 production. Parties may wish to consider the significance of these potential emissions.

HFC-23 can also be formed as by-product during the production of HFC-32. Production processes of other fluorocarbons, such as for HFC-125, HFC-134a, HFC-143a, and possibly some steps of HFO production processes, can also result in by-production of HFC-23, among a range of other fluorochemical by-products, although preliminary data indicates at much lower rates than for HCFC-22 (2–4 % HFC-23 by weight) and HFC-32 (<0.1 % HFC-23 by weight) production. Depending on process conditions, electrochemical fluorination of alkanes can also generate fluorinated by-products, including HFC-23. HFC-125 production can also result in by-production of CFC-113, -114, -115.

Production of intermediates that are substances listed in Annexes A to F

In chemical production, intermediates are the chemical building blocks that raw materials go through when being chemically transformed into products. Intermediates are either isolated or not isolated within the same process prior to consumption to make the final product. A non-isolated intermediate formed in a chemical process is not considered as a finished product while it remains within the chemical process. As such, a non-isolated intermediate is not commonly reported under Article 7. For example, the formation of the intermediate HCFC-21 is not commonly reported as a feedstock in the process of manufacturing HCFC-22. Substances that are produced, isolated, and stored prior to being transferred to a separate process plant (even if within the same establishment) would be considered as a finished product, subject to reporting as production for feedstock use, and are not considered intermediates.

There will be a wide range of emission factors for intermediates from these processes. Intermediates that are formed and consumed almost immediately within a single vessel will have a much lower potential for emission, tending to insignificant, with an emission factor of near zero. An intermediate formed, processed, and potentially held between different reaction loops within the same process will have a higher potential for emission, although the emission rate could still be expected to be considerably lower, by one or more orders of magnitude, than emissions of the final product.

Production emissions and their mitigation

An emission is usually considered to be the release of a substance into the environment; although often used to describe gas releases to the atmosphere, they can also include substances released in solids or liquids that later transition to the atmosphere. In some processes, substances can be dissolved or entrained in some of the co-products and can then be released to the environment in the location where these co-products are subsequently stored and used, which is often remote from the plant that produced them. Most processes will employ a range of elements of good practice for minimising emissions.

Emissions during chemical manufacturing can result from products, co-products[1], intermediates, feedstock, or by-products; which of these are being emitted will have an important bearing on how the operation mitigates those emissions.

Emissions of products, co-products, intermediates, and feedstocks from processes are economically undesirable and the process operators will seek to minimise them, employing a range of good practices.

Emissions of unwanted by-products, and to a lesser extent low value co-products, is a different consideration. For financial reasons, a process will typically seek to minimise the formation of unwanted by-products. Nevertheless, in some cases an increase in the rate of production of the desired product at the expense of a higher production rate of by-product may be economically attractive. There would usually be a need to include additional equipment (such as destruction or separation and chemical transformation technologies), with further operating and maintenance costs to the process to mitigate these unwanted by-product emissions. However, the lack of a clear environmental, safety or economic drivers has often meant that, once produced, these unwanted by-products are emitted unabated. If there are no financial incentives, regulatory controls may be needed to ensure that the emissions of unwanted by-products produced by the process are minimised. Various techniques are possible to treat unwanted by-products to minimise their emission, typically end-of-pipe processes.

Estimated emissions of controlled substances from production, distribution, and feedstock use

Emissions of controlled substances during their production, distribution, and feedstock use contribute to overall global emissions.

MCTOC has reviewed and revised emission factors for production, distribution, and feedstock use of controlled substances in chemical manufacturing processes and outlined variables that can influence the applicability of these emission factors.

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[1] Associated products that have a commercial value but are not the main product of the process, e.g., in the case of controlled substances, hydrochloric acid (HCl aq.) is a common co-product with a low sales value relative to the cost of chlorine.

Global emissions of controlled substances during production, distribution and feedstock use are estimated using MCTOC's *most likely* emission factors. Distribution emissions depend on specific the supply chains and containers used, such as disposable cylinders. Distribution emissions from disposable cylinders are not considered in these estimates.

Table ES.1 Estimated emissions of controlled substances from production, distribution, and feedstock use

Reported Production 2020	Production Tonnes	Emission Factor (EF)				Emissions		
		Production	Distribution	Feedstock use	Total EF	Metric Tonnes	ODP Tonnes	MMT CO_2e
ODS feedstock use	1,475,007	2.50%	0.50%	0.60%	3.60%	53,100	19,948	
ODS non-feedstock	284,942	2.50%	0.80%		3.30%	9,403	672	
HFCs total production incl. feedstock use	779,644	2.50%	0.80%		3.30%	25,728		42.8

Notes: *ODS non-feedstock production is the calculated production [calcProd = Production - Feedstock uses - Destruction - QPS uses for MeBr], negative reports were excluded. HFC reported production in 2020 probably accounts for about 80% of total HFC production (due to the timing of reporting obligations). Excludes emissions due to the use of disposable cylinders.*

Patents

With the global implementation of Kigali amendment, the production and application of HFCs alternatives become crucial for successful phase-down of HFCs. Patents are increasingly becoming a cause for concern for both the chemical manufactures and equipment manufacturers related to those HFCs alternatives. The restriction of free access to patents has raised great concerns about the technology ability, as well as the availability of the alternatives, especially by Article 5 parties. Parties may wish to consider mechanisms to facilitate technology transfer to enable the most rapid global fulfilment of the Kigali Amendment.

Carbon tetrachloride

Production of carbon tetrachloride (CTC) has increased in recent years (to a recent peak of 318 ktonnes in 2019), due mainly to growing demand for CTC use as feedstock to HFCs and HFOs/HCFOs and to perchloroethylene. This trend is likely to continue due to expected increasing demand for HFO/HCFOs.

Based on Article 7 reported CTC production of 289 ktonnes for 2020, global CTC emissions are estimated as 17.8 ktonnes (7.1–28.1 ktonnes), of which 12.8 ktonnes (4.6–20.6 ktonnes) arise directly from CTC production, handling, supply chain, and use, and a further 5 ktonnes (2.5–7.5 ktonnes) from anthropogenic non-chloromethanes production, such as the vinyl chain production process. The production process of the vinyl chain (production of ethylene dichloride to vinyl chloride monomer to polyvinyl chloride) occurring on chlorine producing sites is identified as a new potential source of unreported CTC emissions.

Very short-lived substances

Many ozone-depleting substances not controlled under the Montreal Protocol that are being evaluated by atmospheric scientists are chlorinated hydrocarbons with a very low ODP, known as very short-lived substances (VSLS) because of their short atmospheric lifetimes. Chlorinated VSLS have a relatively small, but growing, contribution to total tropospheric chlorine, assessed at 4% in 2020.

Dichloromethane (DCM) production in 2020 is estimated at over 1,800 ktonnes. Feedstock use for HFC-32 manufacture exceeded 400 ktonnes in 2020. Solvent use and emissions in non-Article 5 parties peaked in the early 2000s and have now stabilised at around 200 ktonnes/year; solvent growth in Article 5 parties has led to calculated global emissions of greater than 1,400 ktonnes in 2020. New regulations in China will ban the use of DCM in foam blowing agent and public paint stripping applications by 2025, resulting in a possible usage reduction of about 300 ktonnes/year.

Chloroform (CFM) production exceeded 1,500 ktonnes in 2020, mostly used as feedstock for HCFC-22. HCFC-22 production for emissive uses is expected to decline sharply in 2025. However, growth of CFM as a feedstock for TFE/HFP production will likely result in maintenance of a similar level of global CFM production. Solvent uses are expected to account for some of the unexpectedly high emissions of chloroform.

Ethylene dichloride (EDC) production in 2020 was more than 62,000 ktonnes, with a great deal of global trade. EDC is used to make vinyl chloride monomer (VCM), which is then polymerised to make PVC. Emissions from production and feedstock use are estimated to be 60–105 ktonnes. Consumption for solvent use could amount to an additional 3–20 ktonnes of emissions globally.

Trichloroethylene (TCE) production and use in non-Article 5 parties are in decline; however, TCE production for feedstock is expected to continue at close to current global levels until the impact of the Kigali Amendment leads to declining production of HFC-134a. The use of TCE as feedstock to HFC-134a has continued to grow and was an estimated 360–380 ktonnes in 2020. TCE consumption as an emissive solvent has dropped by 40% globally since 2000 to around 110 ktonnes/year in 2020. TCE emissions are widespread from its main solvents markets in South and East Asia.

Perchloroethylene (PCE)— The largest use of PCE, currently close to 400 ktonnes/year, is as feedstock to several fluorocarbons, including CFC-113 and CFC-113a, used as feedstock for other fluorocarbons. Some of this PCE feedstock usage is expected to decline with implementation of the Kigali Amendment. Solvent use, for dry-cleaning and metal cleaning, has declined to around 175 ktonnes/year in recent years. Absent regulations, it is expected that perchloroethylene consumption as solvent will remain close to present levels. Solvent emissions of 160–170 ktonnes/year dwarf emissions from feedstock production and use, which are expected to be in the range of 8–16 ktonnes.

Methyl chloride (MeCl) is produced and used almost exclusively as feedstock for two main families of products: chloromethanes and organic silicone compounds. From the limited available data, production is estimated to be in the range 4,500–5,000 ktonnes/year. Emissions from production and feedstock uses are estimated to be in the range 5–8 ktonnes. Global emissions originate largely from natural sources.

Response to decision XXIX/12: HFCs not listed in Annex F

Decision XXIX/12 requests "*the assessment panels...to provide…information on the consumption and production of hydrofluorocarbons not listed in Annex F of the Protocol which have global warming potential no less than the lowest global warming potential of the hydrofluorocarbons listed in Annex F…*". Annex F references 100-year GWP values from IPCC Assessment Report 4 (AR4), which is interpreted here as the basis for the GWP threshold mentioned in decision XXIX/12 as the lowest GWP of Annex F HFCs, i.e., GWP 53 for HFC-152 listed in Annex F.

Some of the HFCs listed in Annex F have not had significant commercial use (to date), including HFC-134, HFC-143, HFC-236cb, HFC-245ca, and HFC-152.

There is no definition for "hydrofluorocarbons" in the Montreal Protocol. SAP 2018[2], Appendix A, separates saturated HFCs (i.e., those included in Annex F) from unsaturated HFCs (generally known commercially as HFOs). The Montreal Protocol's Annex F references 100-year GWP values from

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[2] WMO (World Meteorological Organization), 2018, *Scientific Assessment of Ozone Depletion: 2018*, Global Ozone Research and Monitoring Project–Report No. 58, 588 pp., Geneva, Switzerland, 2018.

AR4 (Table 2.14 (errata))[3]. IPCC AR6[4] (AR6) provides 100-year GWPs for a greater number of HFCs (HFCs and HFOs) compared to AR4, which did not include any HFOs. AR6 groups saturated HFCs and unsaturated HFCs together as hydrofluorocarbons. Even if unsaturated HFCs (the HFOs) are included within the scope of hydrofluorocarbons, most would have GWPs that are lower than the GWP threshold of 53 defined through decision XXIX/12.

The AR6 list of HFC substances has been used to identify additional HFCs that have 100-year GWPs exceeding the defined threshold of 53 and available information about their commercial use. 100-year GWP values are not listed in AR4 Table 2.14 (errata) for these substances, which therefore requires AR6 GWP values to be used to determine if they exceed the defined threshold of GWP 53 (HFC-152). The comparison of AR4 and AR6 GWPs shows significant differences for some HFCs, including for existing Annex F HFCs, in part due to changes in how GWPs are calculated. AR6 GWP for HFC-152 is 21.5 compared with AR4 GWP for HFC-152 of 53, which is the GWP threshold defined in the decision. Those HFCs that are not included in Annex F and that have GWPs above the threshold of 53 are included in Table 2.19.

Parties may wish to consider any actions that they might want to take concerning those HFCs not listed in Annex F with GWPs above 53 with known commercial use (HFC-245cb, HFC-245eb, HFC-52-13p, HFC-76-13sf, HFC-c447ef, *cis*-1,1,2,2,3,4-hexafluorocyclobutane).

HFEs used as solvent replacements for controlled substances have GWPs (AR4 values) between 59 and 580. HFE solvents are most likely used in equipment where emissions are minimised to avoid losses. Some fluorinated ethers with GWPs greater than 53 are used as inhalation anaesthetics where emissions are more likely to occur. Reported production and consumption could be a valuable data set for anaesthetics that could be correlated with related emissions of substances, either from their production, use, or with the expected impact of emission abatement measures. Several halogenated ethers with GWPs greater than 53 are in commercial use, including as solvent replacements for controlled substances. The primary use is as anaesthetic gases, which are not historically related to controlled substances under the Montreal Protocol, some are also ozone-depleting substances. Anaesthetic gases are estimated to contribute up to 0.1 % of total greenhouse gas emissions and account for around 5 % of total healthcare emissions.

Parties may wish to consider any actions that they might want to take concerning anaesthetics that are halogenated ethers and other halogenated ethers with known commercial use with GWPs (IPCC AR6) greater than 53.

Process agents

Process agents have been characterised as controlled substances that, because of their unique chemical and/or physical properties, facilitate an intended chemical reaction and/or inhibit an unintended (undesired) chemical reaction. Process agent uses can be differentiated from feedstock uses, where controlled substances undergo transformation in processes in which they are converted from their original compositions except for insignificant trace emissions.

Parties have made a range of decisions relating to the use of controlled substances as process agents. Decision X/14 established that: the term “process agents” should be understood to mean the use of controlled substances for applications listed in Table A in that decision; and to treat process agents in

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[3] IPCC, 2012, *AR4 Climate Change 2007, The Physical Science Basis*, *The Working Group I Contribution to the IPCC Fourth Assessment Report Summary for Policymakers*, Technical Summary and Frequently Asked Questions, Table 2.14 (Errata), 15 June 2012.

[4] IPCC, 2021, *Climate Change 2021, The Physical Science Basis*, *Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, Chapter 7 Supplementary Material, Table 7.SM.7, contains metrics for substances including greenhouse gas lifetimes, radiative efficiencies and Global Warming Potentials (GWPs).

a manner similar to feedstock and not to include them in the calculation of production and consumption provided that emissions from these processes were reduced to insignificant levels, as defined by Table B. Subsequent decisions have updated Tables A and B with new information.

The process agent uses first defined in Table A of decision X/14 included 25 applications of ODS including CTC, CFC-113, CFC-11, and CFC-12. In subsequent decisions, Table A grew to more than 40 applications, adding Halon 1011 (bromochloromethane, BCM) to the group of controlled substances used in these applications. From 2010 onwards, Article 5 parties were included in the measures for process agent uses. By 2019, when Tables A and B were last updated by decision XXXI/6, the number of process agent applications had reduced to 10 across 4 parties, and maximum emissions limits were 509 tonnes for 4,327.5 tonnes of make-up or consumption.

Most of the process agent uses are long-standing processes, where the ODS are used as solvents to create unique yields, selectivity and/or resistance to harsh chemical environments, with the result that production is achieved with high efficiency. Legacy processes built around these properties make it difficult or impossible to convert to alternatives in a cost effective and timely manner, and only a few examples are known. In this regard, the process agent uses have much in common with feedstock uses.

Most of the removals of process agents from Table A have resulted from plant closures, rather than substitution of other substances for the ODS process agent. For some of the remaining applications, no alternatives are available to date. The lifetime of a chemical production plant could be up to 50 years. If the product is important enough to warrant continued production, and the plant is maintained in good condition, then the large investment required to put into operation a new ODS-free process is unlikely to be justified.

A suite of measures exist that can be applied to minimise make-up/consumption and emissions and each one needs to be considered by an operator. These measures include limiting make-up/consumption to the essential minimum, ensuring tight systems (no leaking valves and joints); evacuation and purging with recovery, prior to opening equipment; closed-loop transfer systems; proximity of production and use of the ODS; monitoring sensors at potential leak locations to provide alerts for prompt repair; use of absorbents such as activated charcoal on vents; and destruction of vent gases.

Solvents

The main applications of HCFC and HFC solvents are metal cleaning, where metal working oil, grease, pitch wax, etc., are cleaned from metals, electronics cleaning, where flux is cleaned, precision cleaning, where particulate or dust is cleaned from precision parts (e.g., military equipment and aerospace components), and coating deposition, where coatings are dissolved in solvent to deposit onto surfaces e.g., medical devices such as syringe needles.

Solvents using HCFCs and HFCs have been used in several different industries, for example, in aerospace, micro-mechanical part manufacturing, plating, aerosol cleaners, circuit flushing, electronics defluxing/cleaning, oxygen service cleaning and the medical industry in coating deposition.

HFCs are commonly used as azeotropic mixtures, which are mixtures of two or more liquids that have the same mixture concentration in liquid and vapour phases. Fluorinated solvents, like HFC-43-10-mee, HFC-365mfc, and HFC-245fa (a solvent used in aerosols), have poorer solvency than chlorinated solvents because of the lower dipole of the fluorine-carbon covalent bond compared with the chlorine-carbon bond. As a result, HFCs are often mixed with chlorinated chemicals to boost the solvency.

Many alternative solvents and technologies developed as ODS alternatives are also the candidates for alternatives to HCFCs and high-GWP HFCs. These include not-in-kind technologies, such as aqueous cleaning, semi-aqueous cleaning, hydrocarbon and oxygenated solvents, and in-kind solvents, such as chlorinated solvents and fluorinated solvents, including high-GWP HFCs not listed in Annex F and low-GWP HFOs, HCFOs and HFEs, with various levels of acceptance. Alternatives are being used for electronics defluxing/cleaning and precision cleaning in several industries automotive, aerospace, medical device, and optical components where high levels of cleanliness are required. Industries have their own set of specific solvent requirements and associated test procedures, e.g., to ensure cleaned parts are acceptable for use.

Several blends of HFEs, HCFOs and HFOs are available as HFC and HCFC alternatives. These blends take advantage of key properties of the solvent alternatives, for example, blending a non-flammable solvent with one that has high solvency while also reducing the cost. The major trend in the development of solvents is the introduction of substances with unsaturated molecules, and thus short atmospheric lifetimes, near zero-ODP and low-GWP, such as HFOs, HCFOs, CFOs and hydrobromofluoroolefins (HBFOs).

Medical grade HFC-134a is used in relatively minor quantities in sub-critical liquid solvent extraction (under pressure) of bio-organics from biomass in the production of food flavours, fragrances, cannabinoids, and other bio-organics. Alternative solvent extractants include super-critical carbon dioxide, ethanol, hexane, and butane, which, compared with HFC-134a, are considered disadvantageous.

Solvent end users work to control emissions to every extent possible since this directly affects their operating costs. Solvent cleaning systems (often referred to as vapor degreasers) will contain primary cooling coils for condensation of the boiling solvent and secondary coils operated at much lower temperature to reduce solvent vapor concentrations and emissions. Many users will also recycle solvent for reuse. Only the largest solvent equipment installations would typically find the use of additional solvent capture and recovery equipment, such as carbon adsorption, to mitigate fugitive emissions to be cost effective.

n-Propyl bromide

n-Propyl bromide is used as an electrical cleaning agent, degreaser, or carrier solvent, as an intermediate in chemical manufacture, in spray adhesives, dry cleaning, insulation for building and construction material, and as a refrigerant flushing agent. Consumer uses include degreasers, cleaners, adhesives, sealants, and automotive care products. *n*-Propyl bromide is also used in consumer aerosol products for electronics cleaning and degreasing, dusters, adhesives, textile spot removers, and paintable mould release agents. Alternatives to *n*-propyl bromide are the same as, or similar to, other solvent alternatives to controlled substances.

n-Propyl bromide is not a controlled substance under the Montreal Protocol. There are concerns regarding its use based both on its potential for ozone depletion and its toxicity. *n*-Propyl bromide may also contribute to photochemical smog and is regulated as a volatile organic compound.

Primarily due to health and safety risk characterisations for *n*-propyl bromide, several countries regulate its use. The relatively low workplace exposure standards indicate that use of *n*-propyl bromide in solvent applications is likely to be problematic, and its use will likely be limited to applications where worker exposure is controlled and will require significant emission control. Nevertheless, *n*-propyl bromide continues to appear as a marketed solvent at trade exhibitions with demand in several markets (e.g., China, Japan, and the United States).

Semiconductor and other electronics manufacturing

In semiconductor and other electronics manufacturing, fluorinated gases/liquids such as HFCs are used for dry etching (to form circuit patterns on wafers), chamber cleaning (to remove deposited silicon materials from chamber walls), and as a heat transfer fluid (to control etching performance).

Dry etching utilises plasma-generated fluorine radicals and other reactive fluorine-containing ions that react with the substrate or thin-film to be etched. The fluorinated gases used in dry etching include PFCs, HFCs, sulphur hexafluoride (SF_6) and nitrogen trifluoride (NF_3). PFCs such as PFC-14 (CF_4), PFC-c318 (cyclic C_4F_8) are used. The most commonly used HFCs for dry etching are HFC-23 (CHF_3), HFC-32 (CH_2F_2) and HFC-41 (CH_3F).

HFC-23 is commonly used for selective etching of silicon dioxide (SiO_2) and silicon nitride (SiN). PFC-c318, HFC-32, HFC-41 and C_4F_6 (perfluoro-1,3-butadiene) are utilised in high aspect hole etching. PFC-c318, perfluorobuta-1,3-diene, and HFC-32 are also used to form polymer films (CF_x) to protect the sidewalls during high aspect hole etching.

Not all the fluorinated gas breaks down, or is consumed, in the plasma. Radicals and molecules can also recombine in the plasma. Unreacted gas (or recombined molecules) accounts for most emissions of fluorinated gases from electronics manufacturing. A small fraction of the gas will also be converted into fluorinated by-products.

The walls of the chemical vapour deposition chamber, electrodes, and chamber hardware are cleaned using fluorinated chemicals. Plasma-generated fluorine radicals and other reactive fluorine-containing ions are used to remove the build-up of silicon materials on the chamber walls and tools. PFC-116 (C_2F_6), SF_6 and NF_3 are the most commonly used gases for chamber cleaning. HFCs are only minimally used for chamber cleaning.

Fluorinated heat transfer fluids are used for thermal management. PFCs, perfluoroalkyl amine, hydrofluoroether, and perfluoropolyether are commonly used fluorinated chemicals used as heat transfer fluids. Fluorinated heat transfer fluids are used for thermal management. PFCs, perfluoroalkyl amine, hydrofluoroether, and perfluoropolyether are commonly used fluorinated chemicals used as heat transfer fluids. HFCs are not commonly used as heat transfer fluids.

Global consumption of HFCs (HFC-23, HFC-32, HFC-41) for electronics manufacturing has increased significantly over the last decade. With an average annual growth rate of 15% since 2013, total global consumption of HFC-23 for semiconductor manufacturing (etching and chamber cleaning) is estimated at 720 tonnes in 2020. Historically, HFC-41 and HFC-32 have been consumed in much smaller quantities, although consumption is growing. While disaggregated data was not available, HFC-32 is expected to be about 300 to 500 tonnes, and likely more, in 2020. Consumption of all three HFCs are expected to increase with increasing semiconductor production and the increasing complexity of semiconductor devices. The global consumption of HFC-32 and HFC-41 are also expected to continue to increase at a high rate due to their use in high aspect hole etching.

Future demand for HFCs used as heat transfer fluids is expected to remain limited or decrease, as countries move to phase out non-essential uses of HFCs.

Like semiconductor manufacturing, etching and chamber cleaning are the key processes that use fluorinated chemicals in other electronics manufacturing, i.e., flat panel display (includes use of HFC-23), photovoltaics (HFCs not commonly used) and microelectromechanical systems (includes use of HFC-23).

HFC emissions from electronics manufacturing consist of the unutilised portion of the process gas and gases formed as a by-product during the process from other process gases. Some facilities have implemented emissions control technologies that significantly reduce emissions of HFCs and other fluorinated gases during semiconductor manufacturing. Abatement and scrubbing of process emissions is considered best practice. Pollutant emissions are required to meet local regulatory standards.

For etching and chamber cleaning, alternatives to HFC use in semiconductor manufacturing include other fluorinated gases, such as saturated PFCs, SF_6 and NF_3, many of which have higher GWPs and lower utilization rates than HFCs, such as HFC-32 and HFC-41.

Some parties appear to treat production and consumption of HFCs in semiconductor manufacturing in the same way as other emissive uses; while other parties appear to treat the production and consumption of HFCs for semiconductors as feedstock use, excluding the portion that results in emissions of HFCs in the process.

Parties may wish to consider how to treat HFC production and consumption for semiconductor uses for the purposes of Article 7 data reporting.

Magnesium production

Cover gases are used in magnesium production, casting processes, and recycling to prevent oxidation and combustion of molten magnesium. Without protection, molten magnesium will oxidise and ignite in the presence of air and form magnesium oxide (MgO) deposits that greatly reduce the quality and strength of the final product.

Sulfur hexafluoride (SF_6), with a very high GWP of 22,800, is the most widely used cover gas. Several gases with lower GWPs are used as alternatives to SF_6, including HFC-134a (GWP of 1,430) and a fluoroketone (GWP of 0.1). Consumption of HFCs as a cover gas in magnesium production is relatively small, possibly 100s tonnes or less. It is expected that there will continue to be a demand for HFC-134a, especially in locations that are phasing out higher GWP SF_6 and are not yet phasing out HFCs.

Laboratory and analytical uses

Laboratory and analytical uses (LAUs) of controlled substances have included: equipment calibration; extraction solvents, diluents, or carriers for specific chemical analyses, inducing chemical-specific health effects for biochemical research; as a carrier for laboratory chemicals; and for other critical purposes in research and development where substitutes are not readily available or where standards set by national and international agencies require specific use of the controlled substances.

Parties authorised an essential use exemption for LAUs for the first time in decision VI/9, according to conditions set out in Annex II of the report for the 6th Meeting. Annex II authorises essential use production for LAUs only if the controlled substances are manufactured to high purity and supplied in re-closable containers and in small quantities: this became known as the global essential use exemption.

Various decisions have subsequently extended the global LAUs exemption under these specified conditions, excluded additional specific uses from the global exemption, and/or requested the TEAP to report on developments in alternatives to the use of controlled substances. Decision XXXI/5 extended the global LAU exemption indefinitely beyond 2021, without prejudice to the parties deciding to review the exemption at a future meeting.

In 2020, the global production of ODS produced for LAUs was 123.61 tonnes, when CTC and methyl bromide were the only two controlled substances produced for LAUs. CTC remains the predominant ODS during the years, with production of 123.59 tonnes in 2020. In 2020, production of ODS for LAUs was 11 tonnes in non-Article 5 parties and 113 tonnes in Article 5 parties.

Many laboratory uses of controlled substances, e.g., as a common solvent or cleaning agent, have been phased out using alternative chemicals and/or procedures. In 2018, MCTOC reviewed the use of ODS in laboratory and analytical, including CTC used as a solvent in bromination reactions using *N*-bromosuccinimide (NBS). MCTOC identified several procedures where ODS can be replaced by non-ODS solvents and are no longer required for those procedures. Nevertheless, it is challenging to identify alternatives to ODS for some specific laboratory uses within such a wide range of chemical reactions undertaken in laboratories.

International bodies, such as ASTM International and ISO, have been working on the development of new standard methods to replace ODS in laboratory and analytical uses. In this report, MCTOC has updated its review of standards, based on its 2018 Assessment Report. The websites of major global standard organizations were scrutinised, and the results indicated that some bodies seemed to have eliminated the use of some ODS for their standards, e.g., CTC on the European Committee for Standardisation (CEN) database.

Significant progress has been made by the international standard bodies and non-Article 5 parties in the development or revision of standards to replace ODS in analytical use. However, there still exist standards that allow the use of ODS. For some standards, the alternative or alternative procedures may exist, but the ODS method remains as an active standard for these standard bodies, implying some barrier in adopting the alternatives or alternative procedures in standard development or revision. It may be more challenging for Article 5 parties to adopt the alternatives or alternative procedures due to the difficulties and/or complexities in the use of the alternatives.

The reasons that non-ODS methods are not adopted in Article 5 parties are adherence to standard methods that use ODS, and the cost of implementing new methods including training. It takes a lot of time and skilled resources to implement new methods; however, in many cases, non-ODS alternatives are available and may have been adopted by international standards bodies or in non-Article 5 parties.

Therefore, international cooperation between different standards organisations and between parties should be encouraged to facilitate and accelerate the development or revision of standards for the replacement of ODS in analytical uses. Possible actions may include sharing more information on alternatives as well as on the revision of standards that use ODS.

Parties may wish to consider actions to facilitate the adoption of alternatives in Article 5 parties, such as international cooperation between different standards organisations and between parties.

End-of-life management and destruction technologies

This Chapter supplements information on EOL management of ODS/HFC and destruction contained in the 2022 Assessment Reports of the respective Technical Options Committees for Flexible and Rigid Foams, Fire Suppression, Methyl Bromide, and Refrigeration, Air Conditioning and Heat Pumps.

Effective management of accumulated active banks of ODS and HFCs, by maximising recovery, recycling, reclamation, reuse, and ultimately destruction after all other options have been exhausted, can minimise the global impacts associated with the potential release of emissions at EOL. By maximising recovery, recycling, reclamation and reuse, effective banks management can limit the amounts of controlled substances that would otherwise require destruction and minimise associated costs. Furthermore, for the RACHP sector, effective HFC bank management can also minimise the amounts of controlled substances that is newly manufactured, minimising overall HFC emissions, and can also aid parties in managing their HFC phase-down targets.

Based on information available from several sources, a combined 6,000 ktonnes of ODS and HFC are estimated to be contained in the active bank in 2022, equalling 16 $GtCO_2e$.

Annual quantities of between 250 and 400 ktonnes (between 0.5 to 0.8 $GtCO_2e$) of ODS and HFCs are estimated to arise from decommissioning in the refrigeration, air-conditioning, and heat pumps (RACHP) and foams sectors from 2020 to 2050. Combined ODS and HFC annual decommissioning is estimated to start to peak in absolute amounts in the mid-2030s onwards, and peak in amounts by $GtCO_2e$ around 2035.

Active global ODS banks of the 5 most common ODS (CFC-11, CFC-12, HCFC-22, HCFC-141b, HCFC-142b) amount to 3,200 ktonnes substance, equivalent to 9.9 $GtCO_2e$, in 2022. There is a rapid decrease as ODS-containing equipment and products are reaching their end-of-life each year. ODS being decommissioned are estimated at 110 ktonnes (0.27 $GtCO_2e$) in 2022.

Active HFC banks in the RACHP sector, which is the predominant usage of HFCs, are estimated at 2,800 ktonnes (5.5 $GtCO_2e$) in 2022 and 3,900 ktonnes (6.8 $GtCO_2e$) in 2030.

The largest banks overall are currently in non-Article 5 parties and will rapidly reach end-of-life in the next decade. While ODS banks have been more concentrated in non-Article 5 parties, HFC banks are currently more evenly distributed between non-Article and Article 5 parties. Banks in Article 5 parties are growing rapidly and will dominate global banks volumes by the early 2030s, resulting from declining banks in non-Article 5 parties and the rapid uptake of HFC-containing equipment in Article 5 parties.

The shift from HCFCs to HFCs EOL management marks a transition from ozone depletion to climate change issues, with HFC emissions reported under national greenhouse gases and potentially part of nationally determined contributions. Accelerated action on the management of EOL ODS/HFCs might increasingly be considered a priority under national greenhouse gas emissions mitigation objectives.

With quantities potentially available for recovery and management expected to increase in Article 5 parties, timely efforts to establish effective EOL management capacity to prevent HFC emissions would have a significant impact, given the predicted size and growth of these banks in larger industrialised Article 5 parties. With improved economies of scale, through the recovery of increased quantities of ODS/HFCs, the anticipated cost per kg of recovered controlled substances for EOL management could be reduced, or minimised, assuming infrastructure is available and investment in EOL management has been made within a supportive policy framework.

Effective banks management need not be limited to ODS and HFCs. The phase-down of HFCs, and/or the leapfrogging of HFC technologies, will result in increasing banks of other alternative refrigerants and foam blowing agents. HFOs and HCFOs are being used to replace HFCs in some applications, although they are not controlled substances under the Montreal Protocol. Leap-frogging HFC-based equipment into these and other low GWP alternatives contributes to active HFC bank prevention, reducing the quantity of HFCs and the GWP of the bank requiring future EOL management. Nevertheless, resource efficiency and circular economy requirements suggest that effective bank management may also be appropriate for these low GWP alternatives.

For the management of concentrated EOL ODS/HFCs from the RACHP sector, recycling and reclamation are preferable in comparison with destruction because recycling and reclamation reduces the amount of virgin refrigerant required. Where recovered refrigerants are not suitable for reclamation then destruction becomes the only option to avoid emissions. To achieve sufficient quantities for economic destruction, the overall infrastructure needs to be readily adaptable and expandable to collect and securely store EOL ODS/HFCs for refrigerant destruction.

For the management of dilute EOL ODS/HFCs from the foams sector, historically, these waste streams have been mostly part of the general solid waste stream destined for land disposal or open burning. Capture and EOL treatment, largely through thermal destruction, requires several steps starting with separation from the general solid waste stream, either at source or prior to conventional solid waste disposal, resulting in a higher solid waste unit cost relative to land disposal. Given the relatively low proportion of ODS/HFCs as a proportion of the foam product waste volume, low returns are realized in terms of amount captured for EOL ODS/HFCs per volume handled. The net overall cost/kg of ODS/HFC destruction is consequently much higher than for concentrated EOL ODS/HFCs. Several programs to manage EOL ODS/HFCs are implemented through regulatory, circular economy, and extended producer responsibility initiatives.

Several approaches are possible to finance the required infrastructure/capability and to economically incentivise the servicing and waste management sectors that support the management of EOL ODS/HFCs, including regulatory approaches (such as market quotas for new refrigerant, levies), carbon finance mechanisms, extended producer responsibility, early replacement programs for equipment with associated energy savings, MLF support for Article 5 parties, and international cooperation through public and private sector partners.

The ability to smoothly undertake the transboundary movement of EOL ODS/HFCs is necessary to achieve global access to environmentally sound destruction of EOL ODS/HFC. In many countries, EOL ODS/HFCs are considered as hazardous wastes. As such their transboundary movement will be subject to the requirements of the Basel Convention on the Control of Transboundary Movements of Hazardous Waste and their Disposal and related international shipping standards. This requires informed consent by the governments of the exporting, transit, and importing countries, as well as standards for environmentally sound management of environmentally sensitive waste streams.

While effective in restricting illegal trade in waste, the process of informed consent is inevitably bureaucratic and time consuming, resulting in significant transaction costs. This is a significant barrier to EOL ODS/HFC management, including reclamation, and/or destruction, particularly for parties that lack national capability for local reclamation and/or destruction, or the resources to undertake export transactions involving the relatively small quantities low-volume consuming countries might generate.

Parties may wish to consider how the Montreal Protocol, the UNFCCC, and the Basel Convention can work together to facilitate transboundary movement of EOL ODS/HFCs to encourage preferential recovery/recycling and environmentally sound destruction of EOL ODS/HFCs, thereby minimising their emissions.

Environmentally sound destruction of surplus or contaminated ODS and HFCs at end-of-life is encouraged by the Montreal Protocol because it avoids unnecessary emissions and helps protect the stratospheric ozone layer and/or the climate. However, the Montreal Protocol does not mandate the destruction of ODS or Annex F Group I HFCs. The exception is HFC-23 (Annex F, Group II) generated in facilities manufacturing Annex C, Group I or Annex F substances, from which emissions must be destroyed to the extent practicable using technologies approved by parties.

The Protocol's definition of 'production' of controlled substances subtracts the amounts destroyed from the amounts produced. The use of destruction technologies approved by parties applies to the amounts of controlled substances destroyed and accounted for within the Protocol's definition of 'production'. The Protocol's destruction technology approval process sets a benchmark for technologies to achieve a level of efficiency for destruction of controlled substances (destruction and removal efficiency of 99.99% for concentrated sources), which aids in the process of accounting for destroyed amounts.

The Ozone Secretariat provides data reported to the Montreal Protocol under Article 7 on the destruction of controlled substances. Cumulatively, 382,574 tonnes of ODS have been reported as destroyed since 1996; reported CTC destruction accounts for 71% of the total. Global Article 7 reported destruction of ODS other than CTC indicates that annual destruction has been in the range of 4,475 to 6,355 tonnes and may be trending downward. Non-Article 5 parties have accounted for over 99% of the reported destruction of ODS other than CTC since 1996.

There can be purposes for destroying controlled substances other than those within Montreal Protocol requirements. Many countries that destroy controlled substances might not report that destruction under Article 7, which is for the purposes of calculating production under the Montreal Protocol. Moreover, some destruction, like the destruction of dilute sources of waste foams, are rarely reported to the Montreal Protocol. These activities are motivated by other factors, ranging from direct regulatory mandates, integration with broader circular economy policies applied to solid waste streams, and a direct need to conserve scarce landfill capacity by targeting high volume waste streams. Destruction of controlled substances is an activity that can also be undertaken within national waste management, circular economy requirements, or extended producer responsibility.

Despite a few reported effective examples, global recovery and destruction rates of EOL ODS/HFCs from decommissioned equipment and products are likely to fall well below a level where a significant impact is being achieved in mitigating ozone depletion or greenhouse gas emissions.

Parties have taken several decisions to approve destruction technologies that are used for the destruction of controlled substances for the purposes of Montreal Protocol production data reporting requirements under Article 7 and destruction of HFC-23 under Article 2J. Over time, the list of destruction technologies approved by parties has been updated, with the most recent list of approved destruction processes contained in Annex II to the 30th MOP under decision XXX/6. It should be made clear that, in meeting any broader needs for environmentally sound destruction, parties are free to apply technologies, whether on the Montreal Protocol approved list or not, that satisfy national regulatory standards.

Decision XXX/6 on destruction technologies for controlled substances requests TEAP to assess destruction technologies listed (in annex II to the report of the Thirtieth Meeting of the Parties) as not approved or not determined, as well as any other technologies, and to report to parties. A summary of recommendations follow that are elaborated in the chapter.

MCTOC has considered the development of smaller scale variants of currently approved technologies, in particular plasma arc. There is no reason to consider down-sized versions of this technology to be any different on a technical basis, or in terms of performance, to the higher capacity, higher powered torch versions already approved by parties. As a general category these technologies (large and small) are ostensibly the same. As such, MCTOC does not consider there to be a need for parties to approve smaller scale versions as a separate category of technology. Portable Plasma Arc, which employs a small-scale nitrogen plasma arc process, was added to the list as a separate approved technology from Nitrogen Plasma Arc, which is listed as a separate class.

Parties may wish to consider removing the category, Portable Plasma Arc, as a separate approved technology to rationalise and consolidate the list of approved destruction technologies.

Cement kilns are not an approved technology for the destruction of dilute waste, even though it is an approved technology for the destruction of concentrated EOL ODS/HFCs, except for Halons, methyl bromide and HFC-23. In terms of DRE and the technical performance advisory criteria for other pollutants, cement kilns have already demonstrated that they meet DRE for concentrated sources of a range of ODS and Annex F, Group 1, HFCs (99.99% versus 95% for dilute sources), which would qualify them for destruction of dilute sources.

Parties may wish to consider inclusion of cement kilns as an approved destruction technology for dilute sources of ODS and Annex F, Group 1, HFCs, for which there is already approval for concentrated sources.

National and/or local governments require their own performance standards to meet emissions limits, and it is expected that any technology is required to meet local emissions standards on an installation specific basis.

Aerosols

Aerosols are used in a wide range of different applications. The term aerosol product describes a product *pressurised* with a propellant that expels its contents from a canister through a nozzle. Aerosols incorporate propellants and solvents with the appropriate technical properties and characteristics in formulations designed to deliver a product for its intended purpose.

Propellants include compressed gases (nitrogen, nitrous oxide, carbon dioxide) or liquefied gases, which are liquid inside the pressurized container. These liquefied gas propellants include hydrochlorofluorocarbons (HCFCs e.g., HCFC-22), hydrofluorocarbons (HFCs) (e.g., HFC-134a, HFC-152a), hydrofluoroolefins (HFOs, e.g., HFO-1234ze(E)), hydrocarbons (HCs), and dimethyl ether (DME).

Some aerosol products contain solvents, including HCFCs, HFCs, hydrofluoroethers (HFEs), aliphatic and aromatic solvents, chlorinated solvents, water, esters, ethers, alcohols, ketones, and hydrochlorofluoroolefins (HCFO, e.g., HCFO-1233zd(E)).

A significant proportion of aerosol propellants have migrated to hydrocarbons and DME, which dominate in the consumer aerosol market. Hydrocarbons and DME are highly flammable propellants. They are also used in technical aerosols where flammable propellants can be used safely. Hydrocarbons and oxygenated hydrocarbons (such as DME) are volatile organic compounds (VOCs) that contribute to photochemical smog generation. Strict VOC controls can have an impact on the choice of propellant, where hydrocarbons are avoided. The use of compressed gases (nitrogen, nitrous oxide, carbon dioxide) as propellants has increased because of these regulations and the availability of better cans.

A smaller proportion of aerosols migrated to using HFCs. Non-flammable and non-toxic HFCs have been used where flammability, toxicity, safety in use, and/or VOC content are considerations. HFCs, including HFC-152a, are often used where emissions of VOCs are controlled. HFCs and HFO-1234ze(E) are more expensive than hydrocarbons and mostly used when their properties are needed.

While the European Union’s aerosol market is the largest overall globally, its HFC consumption for aerosols has been phased out. This compares with North America, as the second largest regional producer of aerosols with the largest HFC consumption in aerosols.

For 2021, global HFC demand is estimated to be around 44,000 tonnes (~3,000 tonnes HFC-134a; ~41,000 tonnes HFC-152a), corresponding to a warming impact from direct emissions of about 9.4 MMTCO$_2$e. This represents an overall reduction in the global warming impact of HFC-containing aerosols of more than 50% since 2015. These reductions are due to the decrease in global consumption of HFC-134a in aerosols, especially in North America. Meanwhile, there has been an increase in the global consumption of HFC-152a in aerosols since 2015. Overall HFC demand in aerosols continues to be dominated by the North American market, with probable growth in HFC aerosol consumption in the Asia and Asia-Pacific region.

HCFC production and consumption (as defined) in non-Article 5 parties was required to be phased out by 1 January 2020, with allowance for essential use exemptions if authorised by the Montreal Protocol. Between 1 January 2020 and 1 January 2030, for any non-Article 5 party, Article 2F, paragraph 6, allows HCFC consumption and production in any year up to 0.5% of the baseline consumption allowance, for restricted applications including topical medical aerosol applications for the specialised treatment of burns. Otherwise, aerosol use of HCFCs can continue in non-Article 5 parties from recycled or stockpiled sources, for as long as those sources remain. In the Russian Federation, topical medical aerosol applications use HCFC-22 (as a propellant) and HCFC-141b (as a solvent), which are now being sourced from stockpiles. HCFC-22 and HCFC-141b are used in China for aerosols, including for Traditional Chinese Medicines, by several large pharmaceutical companies and some smaller companies.

Technically and economically feasible alternatives to controlled substances are commercially available for all aerosols, although not all alternatives are suitable across all aerosol applications in all locations. Many factors affect the selection of a given propellant or alternative, including regulatory approval of products, industry codes of conduct, VOC controls, supplier, regulatory controls on HCFCs and HFCs, ease of use, and propellant properties, such as flammability or safety for certain uses.

Parties may wish to consider the advantages of reducing the use of HFCs in the aerosol sector, where that is technically and economically feasible. Given that aerosols are totally emissive, any action taken in this area would provide rapid reduction in HFC consumption and emissions. Accounting by a country, including their aerosol production and their import of finished aerosols containing HFCs, might help it determine the implications of any phase-down policies, including financial implications.

Pressurised metered dose inhalers

Asthma and chronic obstructive pulmonary disease (COPD) are the most common chronic diseases of the respiratory tract. Inhalation therapy is the mainstay of treatment for asthma and COPD. Inhalers offer effective symptomatic benefit and control of disease, by delivering drugs directly to the airways, whilst minimising systemic side effects. Oral drugs are also prescribed for asthma and COPD; some of these can have serious side effects.

There are two common types of highly portable inhalation devices for the delivery of respiratory drugs: (pressurised) metered dose inhaler (pMDI) and the dry powder inhaler (DPI) in single- or multi-dose. Other methods of delivering drugs to the lung include soft mist inhalers (SMIs) and nebulisers.

Under the Montreal Protocol, the use of CFCs as propellants for pMDIs was successfully phased out worldwide without significant adverse impact to medical care. Pharmaceutical companies replaced CFCs with HFCs propellants in pMDIs; HFC-134a and to a lesser extent HFC-227ea. With the Kigali Amendment, the production and consumption of HFCs listed in Annex F is scheduled to be phased down. Annex F HFCs include HFC-134a, HFC-227ea and HFC-152a.

For both asthma and COPD, there are two main categories of inhaled treatment, bronchodilators (“relievers”) and anti-inflammatory medications (“preventers”). Inhaled salbutamol (a short-acting reliever) remains by far the most used treatment worldwide, mainly as inexpensive HFC pMDIs. Some estimates put the total global use of salbutamol pMDIs at greater than 60% of total pMDI use.

Following reformulation, the pMDI remains popular, especially because it is relatively affordable for the short-acting bronchodilator salbutamol, which is the predominant short-term relief or “rescue” treatment for acute symptoms in asthma/COPD worldwide. DPIs are suitable for many patients and are widely prescribed for the treatment of asthma and COPD.

Complex considerations are necessary when patients and healthcare professionals make an informed choice about a patient’s inhaled therapy, taking into account therapeutic options, patient history, patient preference, ability (e.g., dexterity, inspiratory flow, vision) and adherence, patient-borne costs, as well as environmental implications, with the overall goal of ensuring patient health. Patient choice may be enhanced with an increase in publicly available information about the environmental impact of different inhaler products. Healthcare professionals and their patients may benefit from this information to take environmental impact into account in their choice of inhaler.

Based on available industry data on the proportion of pMDI, DPI and SMI units sold, while dynamics vary in different markets, pMDIs remain the dominant option sold in most markets for the delivery of all inhaled therapy, except for the European Union and India where DPIs are more dominant. For preventer (or maintenance) therapy only, DPIs are the dominant option sold for the delivery of inhaled maintenance therapy in most markets.

Access to affordable inhaled medicines for chronic respiratory diseases is severely limited in low- and middle-income countries, which causes avoidable morbidity and mortality. Generally, multi-dose DPIs (mDPIs) are less affordable than single-dose DPIs and pMDIs; single-dose DPIs can be more affordable than pMDIs. In Article 5 parties, locally made pMDIs are more affordable than some imported brands. SMIs (are usually more expensive than pMDIs for short-acting reliever medication, but they can be as equally cost-effective as DPIs or pMDIs for some drugs, particularly long-acting bronchodilators. SMIs are generally likely to be unaffordable in Article 5 parties for most patients. In all parties, the cost of some or any treatments can be unaffordable for a portion of patients.

Based on HFC manufacturing industry estimates, approximately 800–825 million HFC MDIs (assuming a global weighted average fill weight: 14.61 g/HFC-134a MDI and 11.38 g/HFC-227ea MDI) are currently manufactured annually worldwide, using approximately 10,700 tonnes HFC-134a and HFC-227ea in 2021. One industry estimate puts the number of DPIs manufactured worldwide at 450 million annually.

All currently available HFC pMDIs have a far greater carbon footprint than DPIs or SMIs. Life cycle assessments consistently demonstrate that the large majority (88–98%) of the carbon footprint of pMDIs is due to propellant release during use or end of life. DPIs and SMIs are propellant-free inhalers and consequently have far smaller carbon footprints. The smallest carbon footprints are seen in reusable SMIs or single-dose DPIs. Re-usable single-dose devices are the most popular devices in some regions due to their affordability.

Two low-GWP (global warming potential) chemicals are under development as potential propellants for pMDIs (HFC-152a and HFO-1234ze(E)) as replacements for HFC-134a and HFC-227ea. Limited carbon footprint information is available for potential new pMDIs in development using lower GWP propellants, though it is clear they will have far smaller carbon footprints.

Three pharmaceutical companies and one major contract development and manufacturing organization (CDMO) have announced plans to reformulate their pMDI products with lower GWP propellants, with their target to begin introducing new pMDIs containing HFC-152a or HFO-1234ze(E) into the market in 2025. Together, these companies account for over 70% of the pMDI market revenues from the United States and Europe. However, to reformulate is a lengthy and costly process, and for many companies it is unclear whether this would be financially justified.

The projected timescale for the introduction of the lower GWP pMDIs from the 4 companies active in the field may be at risk if health authorities require full clinical development programmes to be completed for switches of the propellant when there are no other substantial changes in the formulation. Health authorities have not yet announced specific guidelines; some general guidance on the clinical data requirements is urgently needed, especially given the possibility of accelerated HFC phase-down.

Given the differences in regulatory expectations and the pace of approval in different countries, together with the time it takes to convert both patients and the supply chain, it is currently unlikely that transition in non-Article 5 parties would be completed before 2030, even for the limited number of products announced to date. There is only one company that has publicly announced reformulation of a reliever pMDI, yet salbutamol pMDIs account for well over half of all inhaled doses of medication. Based only on company announcements, a significant proportion of global production of salbutamol pMDI could potentially be in the earlier stages of development of replacements.

For Article 5 parties, the timetable for HFC phase-down is longer than for non-Article 5 parties. Nevertheless, there are multinational inhaler manufacturers based in these countries that have corporate targets to reduce their carbon footprints and that wish to maintain and build global market access. Some are investigating prototype formulations with low-GWP propellants, although none have yet announced plans to launch products. The patent landscape may also play a role in their decision-making because the current suppliers of pharmaceutical grade HFC-152a and HFO-1234ze(E) have several patents pending or granted in this field.

It is likely that the cost of bulk HFC-134a and HFC-227ea propellants will rise substantially over the next few years as other industrial uses decline, and quota mechanisms impact on their availability.

There are a range of issues and potential challenges that could emerge in the transition away from high GWP propellant pMDIs to inhalers with lower GWPs, including pMDIs using lower GWP propellants, DPIs and SMIs, which could create risks and disruptions to inhaler markets and patient health. These include global and national frameworks that establish clear market signals and address transition challenges; continuity in, and stability of, the supply of pharmaceutical-grade HFCs; regulatory approvals; exports of pMDIs; patent protections; manufacturing capacity for pMDIs with the new propellants, DPIs and SMIs; patient and physician information.

The transition of high GWP HFC pMDIs to lower GWP pMDIs within the global HFC phase-down is a complex manufacturing and marketing transition that requires careful forward planning of the supply chain to avoid patient harm. Market authorisation of the new lower GWP pMDIs by health authorities is another critical factor in a successful transition and could benefit from a coordinated approach.

Bulk pharmaceutical-grade HFC-134a manufactured in the United Kingdom is exported around the world, where pMDIs are then manufactured locally. India, and potentially China, also have the capacity to manufacture pharmaceutical-grade HFC-134a; however, certification by pMDI manufacturers of new supply chains for pharmaceutical-grade HFC-134a is difficult to achieve. Several major pharmaceutical companies manufacture pMDIs in Europe from bulk HFC import allocations, for subsequent export of HFC pMDIs around the world.

To guarantee adequate pharmaceutical-grade HFC-134a during transition, adequate amounts of technical-grade HFC-134a from Japan and/or the United States would need to continue to be supplied to the single purifier of bulk pharmaceutical-grade HFC-134a located in the United Kingdom. Technical-grade HFC-134a plants operate at a minimum capacity below which it becomes technically challenging or impractical to continue to manufacture HFC-134a (below 60–70% of normal running rate).

The Kigali Amendment’s 70% reduction of production and consumption from baseline for Annex F HFCs in non-Article 5 parties in 2029 is likely to impact and limit the global supply of pharmaceutical-grade HFCs for pMDIs, at which time it is also possible that an adequate supply of lower GWP pMDIs might not yet be available to meet patient demand.

How different regions manage their HFC phase-down within the global HFC phase-down will be important in ensuring global, regional, and local management of the supply chains during the transition away from high GWP HFC pMDIs. National implementation of HFC phase-down requirements may have implications for the global HFC and pMDI supply chains, including export markets. Flexibility within global and national HFC phase-down frameworks may need to be considered during the transition from high GWP to lower GWP pMDIs.

Regulatory approvals of the new pMDI products may benefit from a coordinated approach, taking into careful consideration the HFC phase-down and the stability in supply of pharmaceutical-grade HFCs, to ensure continued patient access to essential treatments. Timely transition and access to new technology could avoid large price increases with the loss of generic salbutamol HFC-134a pMDIs if or when HFC-134a supplies are shut down for technical and economic reasons.

Parties may wish to consider the range of technical and economic issues associated with the transition from high GWP HFC pMDIs to ensure adequate supplies of pMDIs and other inhalers during HFC phase-down.

Parties may wish to consider the need for global and national coordination in the HFC phase-down and its impact on the transition away from high GWP HFC pMDIs to ensure patient safety.

Parties may wish to consider how to ensure that adequate bulk HFC-134a and/or pMDIs are available in their own markets, and in their export markets, to avoid risks to the continuous supply of pMDIs. This necessity may persist for up to 10 years, until full ranges of affordable low GWP pMDIs are available worldwide.

Parties may wish to consider measures that facilitate efficient, timely development while assuring the safety and effectiveness of the new pMDIs.

Sterilants

Sterilization is an important process in the provision of good quality healthcare services. It is defined as validated processes used to render products free from viable microorganisms. Sterilization requires strict application of the principles of quality management to ensure validation of the selected process and implementation of effective routine control; reliable equipment; and knowledge of materials compatibility and biocompatibility.

Sterilization of materials, including medical devices and pharmaceutical products and packaging, can be performed in facilities ranging from industrial settings with large outputs of similar items (e.g., by manufacturers of sterile medical devices such as single-use syringes, or specialist contractors offering a sterilization service to medical device manufacturers) and dissimilar items (such as procedure packs and kits), to smaller facilities including hospitals and dental clinics with much smaller outputs but great diversity of items. Process requirements for these settings are essentially similar but the types of sterilization processes used, and the challenges presented to assuring sterility, differ.

EO can be used as a sterilant either alone or diluted with other gases to make non-flammable mixtures. A mixture of 12% by weight EO and 88% dichlorodifluoromethane (CFC-12) (12/88) was once widely used for this purpose. CFC-12 use for sterilization has been successfully phased out in non-Article 5 Parties, and in most, if not all, Article 5 Parties, and only then from any remaining stockpile. Although it is difficult to be certain, global total use of CFCs for this application is believed to be zero.

EO/hydrochlorofluorocarbon (HCFC) mixtures (10% by weight EO in a mix of HCFC-124 and HCFC-22) were virtual drop-in replacements for the 12/88 mixture using CFC at that time. Estimated global use of HCFCs in sterilization is now considered to be significantly less than 50 metric tonnes over 10 years ago, which amounts to less than 2 ODP tonnes worldwide. EO/HCFC use has subsequently been significantly reduced or eliminated by converting to 100% ethylene oxide or conversion to other sterilization technologies.

The complete phase-out of HCFCs in sterilization is readily achievable in Article 5 Parties to meet the Montreal Protocol schedule. The useful lifetime of existing EO/HCFC sterilizers is about 20 years when well maintained. Therefore, by 2030, at the latest, any remaining sterilizers in Article 5 parties should be ready for replacement with available alternative technologies that do not use ozone-depleting substances. Industrial and healthcare facility procurement should take into consideration the HCFC phase-out, redundancy of EO/HCFC sterilization equipment, and lack of availability of HCFC-containing blends, in making future investment decisions.

HFC mixtures (10.4% by weight EO in a mix of HFC-125 and HFC-227) used in existing sterilization equipment with modified process controls were initially tested in the United States. Technical problems were identified that would require re-engineering, and potentially new equipment, in addition to validation of the new process. HFC blends have not been broadly adopted or used worldwide, although initially some sterilization service providers in Asia continued to explore the potential application.

There is a range of commercially available sterilization methods including: heat (moist heat or dry heat), ionizing radiation (gamma ray, electron beam, x-ray), alkylating processes (such as ethylene oxide (EO), formaldehyde) and oxidative processes (including hydrogen peroxide gas, gas plasma systems, liquid or gaseous peracetic acid, and ozone). Further sterilization methods based on these and other chemical agents are under continuing investigation for commercialisation.

No single sterilant or sterilization process is compatible with the range of potential products or materials, be they designed for single-use or designed to be processed in healthcare facilities and used multiple times. The nature and complexity of items and loads to be sterilized will vary according to the user requirements. Some items are more robust than others regarding pressure, temperature, moisture, and radiation dose. Therefore, several different processes are available for use, and each will offer specific advantages depending on the need.

Technologies that can be considered to avoid processes using ozone-depleting EO/HCFC blends include use of heat-sterilizable devices, use of single-use devices sterilized by alternative heat, radiation or other chemical technologies, use of 100% EO sterilization processes, and a range of other methods that will sterilize most of the heat sensitive medical devices used in healthcare or industrial settings. Alternative low temperature processes for sterilization that have been commercialised include hydrogen peroxide gas (used with or without the generation of plasma during the process), humidified ozone gas, nitrogen dioxide gas, liquid phase peracetic acid formulation and low temperature steam-formaldehyde processes. Other low temperature methods have routinely reported but have yet to be widely deployed.

Any alternative to the use of any remaining ozone-depleting substances needs to be well proven and tested to avoid putting the health of patients unnecessarily at risk. It is legal requirement in pharmaceutical and medical devices industries that any change in manufacturing processes, including sterilization, must be validated using appropriate guidelines before implementation. Many of these alternative technologies provide significant advances, such as better safety profiles and turn-around times, and reduced cost per cycle.

MCTOC believes that sterilization applications using controlled substances are no longer a relevant risk for the Montreal Protocol. Unless circumstances change, MCTOC proposes not to include sterilization in its technical updates in the next quadrennial assessment. Sterilization technologies and applications continue to move to deploy environmentally safer processes as best practice, in parallel with meeting the essential needs for patient safety.

1 Background to the 2022 MCTOC Assessment Report

1.1 The Technology and Economic Assessment Panel

Four Assessment Panels were defined in the original 1987 Montreal Protocol, namely, the Scientific Assessment Panel (SAP), the Environmental Effects Assessment Panel (EEAP), the Technology, and the Economics Assessment Panels, which were established in 1988–89. The Technology and Economics Assessment Panels were merged after the 1990 Meeting of Parties in London to establish the Technology and Economic Assessment Panel (TEAP). TEAP has five standing Technical Options Committees (TOCs), which are:

a) Flexible and Rigid Foams Technical Options Committee

b) Fire Suppression Technical Options Committee

c) Medical and Chemical Technical Options Committee

d) Methyl Bromide Technical Options Committee

e) Refrigeration, Air Conditioning and Heat Pumps Technical Options Committee

1.2 The Medical and Chemical Technical Options Committee

This report is part of the tenth assessment under Article 6 of the Montreal Protocol. The first assessment reports were prepared in 1989, and subsequently in 1991, 1994, 1998, 2002, 2006, 2010, 2014, and 2018. This 2022 quadrennial report is in response to decision XXXI/2 of the Parties to the Montreal Protocol, which requested an assessment to be undertaken for completion by 31 December 2022 for consideration by parties in 2023.

Article 6 specifically directs parties to assess whether the control measures, as provided for in Article 2 of the Protocol, are sufficient based on a review of the current state of knowledge of technical, scientific, environmental, and economic issues related to stratospheric ozone protection. The assessment reports assist with this review.

Previously, the Aerosols, Sterilants, Miscellaneous Uses and Carbon Tetrachloride Technical Options Committee (ATOC) assessed, *inter alia*, medical aerosols, sterilants, laboratory and analytical uses, and carbon tetrachloride. ATOC was reconstituted in 2005 to form the Medical Technical Options Committee (MTOC) to assess medical applications of ozone-depleting substances (ODS), namely medical aerosols and sterilants.

Previously, the Solvents, Coatings and Adhesives Technical Options Committee (STOC) assessed solvent uses of ozone depleting substances. STOC was reconstituted in 2005 to form the Chemicals Technical Options Committee (CTOC) to assess non-medical aerosol products, carbon tetrachloride, feedstocks, laboratory and analytical uses, process agents, solvent uses, and destruction.

CTOC and MTOC were reconstituted in 2016 to form the Medical and Chemical Technical Options Committee (MCTOC).

MCTOC is made up of experts from industry, government, scientific, research and academic institutions. For the 2022 assessment, MCTOC comprised 3 co-chairs, 39 members, and 2 consulting experts contributing to this assessment from 21 countries – Australia, Austria, Bangladesh, Canada, China, Denmark, Ghana, India, Ireland, Italy, Japan, Kuwait, Mauritius, Pakistan, Russian Federation, Rwanda, Turkey, United Kingdom, the United States and Venezuela.

1.3 The 2022 MCTOC Assessment Report

1.3.1 Content

In this 2022 Assessment Report, MCTOC assesses medical and chemical related applications, namely, chemical production and feedstock uses, including emissions of controlled substances, very short-lived substances that are ozone-depleting substances, process agents, solvent uses, semiconductor and other electronics manufacturing, magnesium production, laboratory and analytical uses, end-of-life management and destruction, aerosols, pressurised metered dose inhalers, and sterilants. This report re-examines the current use of, and alternatives, to ODS and HFCs listed as controlled substances in the Montreal Protocol under this range of sectors.

1.3.2 Relevant decisions for this 2022 Quadrennial Assessment

MCTOC responds to several periodic and thematic decisions of parties that are relevant to MCTOC's sectoral related topics, as outlined below.

Quadrennial Assessment— Decision XXXI/2, paragraph 6, 2022 TEAP Assessment, states:

> *That, in its 2022 report, the [TEAP] should include an assessment and evaluation of the following topics:*
>
> 4. *Technical progress in the production and consumption sectors in the transition to technically and economically feasible and sustainable alternatives and practices that minimize or eliminate the use of controlled substances in all sectors;*
>
> 5. *The status of banks and stocks of controlled substances and the options available for managing them so as to avoid emissions to the atmosphere;*
>
> 6. *Challenges facing all parties to the Montreal Protocol in implementing Montreal Protocol obligations and maintaining the phase-outs already achieved, especially those on substitutes and substitution technologies, including challenges for parties related to feedstock uses and by-production to prevent emissions, and potential technically and economically feasible options to face those challenges;*
>
> 7. *The impact of the phase-out of controlled ozone-depleting substances and the phase-down of HFCs on sustainable development;*
>
> 8. *Technical advancements in developing alternatives to HFCs suitable for usage in countries with high ambient temperatures, particularly with regard to energy efficiency and safety.*

Each sector chapter addresses decision XXXI/2, except for sub-paragraph 6(d) that is addressed in the 2022 TEAP Assessment Report.

Review of alternatives to HFCs— Decision XXVIII/2, paragraph 4, requesting a review relating to the Kigali Amendment phasing down HFCs, states:

> a) *To request the Technology and Economic Assessment Panel to conduct periodic reviews of alternatives, using the criteria set out in paragraph 1 (a) of decision XXVI/9, in 2022 and every five years thereafter, and to provide technological and economic assessments of the latest available and emerging alternatives to hydrofluorocarbons.*

Relevant to decision XXVIII/2(4), paragraph 1(a) of decision XXVI/9 states:

> a) *Update information on alternatives to ODS in various sectors and subsectors and differentiating between parties operating under paragraph 1 of Article 5 and parties not so operating, considering energy efficiency, regional differences and high ambient temperature conditions, in particular, and assessing whether they are:*
>
> - *Commercially available;*
> - *Technically proven;*
> - *Environmentally sound;*
> - *Economically viable and cost effective;*
> - *Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization;*
> - *Easy to service and maintain;*
>
> *and describe the potential limitations of their use and their implications for the different sectors, in terms of, but not limited to, servicing and maintenance requirements, and international design and safety standards.*

End-use sectors, i.e., solvents, semiconductor and other electronics manufacturing, magnesium production, aerosols, and pressurised metered dose inhalers, are relevant to a response to decision XXVIII/2, which can be found in Chapters 4, 5, 6, 9, 10 of this report.

HFCs not listed in Annex F— Decision XXIX/12, Consideration of hydrofluorocarbons not listed as controlled substances in Annex F to the Protocol, states:

> *To request the assessment panels under the Montreal Protocol to provide in their quadrennial reports to be presented to the Thirty-Fifth Meeting of the Parties, in 2023, and every four years thereafter, information on the consumption and production of hydrofluorocarbons not listed in Annex F of the Protocol which have global warming potential no less than the lowest global warming potential of the hydrofluorocarbons listed in Annex F, noting that this is for information purposes only, given that the substances referred to in the present paragraph are not included in Annex F.*

A response to this decision can be found in chapter 2.

HCFC availability— Decision XXX/2, paragraph 4, states:

> *To request the Technology and Economic Assessment Panel to provide in its quadrennial reports to be presented to the Thirty-Fifth Meeting of the Parties in 2023 and to the Thirty-Ninth Meeting of the Parties in 2027 information on the availability of Annex C, Group I substances, including amounts available from recovery, recycling and reclamation, and best available information on country-level and total known stocks, as well as availability of alternative options for the applications described in Article 2F paragraphs 6 (a) and 6 (b).*

Solvents and aerosols end-use sectors are relevant to a response to this decision, which can be found in chapters 4 and 9.

Process agents— Decision XXXI/6, paragraph 3, states:

> *To request the Technology and Economic Assessment Panel to report in its quadrennial reports on any progress made by parties in reducing their use and emissions of controlled substances as process agents and on any new alternatives to such uses, including new production processes and emissions-reduction techniques, on the understanding that should new compelling information become available, that information should be reported in its annual progress report.*

Earlier decisions XVII/6(7) and (8), XXII/8(5), XXIII/7(5), which are relevant to the review expected by parties under decision XXXI/6 above and through decision XXX/15(2) and (3) regarding the periodicity of these reviews, state:

> *To request the TEAP to review the information submitted in accordance with this decision and to report and make recommendations…on process-agent use exemptions; on insignificant emission associated with a use, and process-agent uses that could be added to or deleted from table A of decision X/14.*
>
> *To request Parties with process-agent uses to submit data to the TEAP by 31 December 2007 and 31 December of each subsequent year on opportunities to reduce emissions listed in table B and for the TEAP to review…emissions in table B of decision X/14, taking into account information and data reported by the Parties in accordance with that decision, and to recommend any reductions to the make-up and maximum emission on the basis of that review. On the basis of these recommendations, the Parties shall decide on reductions to the make-up and maximum emissions with respect to table B.*
>
> *To request the TEAP… to review…progress made in reducing process agent uses and to make any additional recommendations to parties on further actions to reduce uses and emissions of process agents.*
>
> *To request the Panel, as further uses cease in the future, to consider corresponding reductions in make-up or consumption and maximum emissions accordingly in future proposals concerning table B.*

Responses to these decisions can be found in chapter 3 on process agents.

Laboratory and Analytical Uses— Decision XXXI/5 paragraphs 1 and 7, state:

> *To extend the global laboratory and analytical-use exemption indefinitely beyond 2021, without prejudice to the parties deciding to review the exemption at a future meeting.*
>
> *To request the Technology and Economic Assessment Panel to report in its quadrennial report on any progress made by parties in reducing their production and consumption of ozone depleting substances for laboratory and analytical uses, on any new alternatives to those uses, and on laboratory standards that can be performed without such substances, on the understanding that, should new compelling information become available, including opportunities for significant reductions in production and consumption, that information should be reported in its annual progress report.*

A response to decision XXXI/5(7) can be found in chapter 7 on laboratory and analytical uses.

n-*Propyl bromide and new substances*— Decision XXX/15, paragraph 6, states:

> *To request the Technology and Economic Assessment Panel to provide information to the parties on n-propyl bromide (nPB) if new compelling information is available, and on possible new substances if any previously unreported substances are identified, that may have a likelihood of substantial production.*

Earlier decisions XIII/7(3) and IX/24(4), which are relevant to the information expected by parties to be provided under decision XXX/15(2) and (6) regarding the periodicity of these reviews, state:

> *To request the TEAP to report…on nPB use and emissions.*

> *To request the Technology and Economic Assessment Panel to report…on any such new substances of which it is aware either as a result of information provided by Parties, or otherwise, and for which the Scientific Assessment Panel has estimated to have a significant ozone-depleting potential. The report shall include an evaluation of the extent of use or potential use of each substance and if necessary the potential alternatives, and shall make recommendations on actions which the Parties should consider taking.*

Information on *n*-propyl bromide is included mostly in chapter 4 on solvents. There are no new substances brought to MCTOC's attention for which the Scientific Assessment Panel has estimated a significant ozone-depleting potential.

Destruction Technologies— Decision XXX/6 paragraphs 2 and 3 state:

> *To request the Technology and Economic Assessment Panel to assess those destruction technologies listed in annex II to the report of the Thirtieth Meeting of the Parties as not approved or not determined, as well as any other technologies, and to report to the Open-ended Working Group prior to the Thirty-Third Meeting of the Parties, with the understanding that if further information is provided by parties in due time, in particular regarding the destruction of Annex F, group II, substances by cement kilns, the Panel should report to an earlier meeting of the Open-Ended Working Group.*
>
> *To invite parties to submit to the Secretariat information relevant to paragraph 2 of the present decision.*

In consultation with the Ozone Secretariat, TEAP and its MCTOC reported in the 2021 TEAP Progress Report that an assessment in response to decision XXX/6 would be included in MCTOC's 2022 Assessment Report based on available information.

MCTOC suggested guidance on the type of relevant information needed for its assessment of destruction technologies in the 2020 and 2021 TEAP Progress Reports. The 2020 and 2021 TEAP Progress Reports invited parties to submit this type of information in response to decision XXX/6 paragraph 3. Information from parties was requested to be submitted no later than January 2022 to allow time for assessment. No information was submitted by parties.

A response to decision XXX/6 can be found in chapter 8 on end-of-life management and destruction of controlled substances.

1.3.3 Development of the report

MCTOC developed the report through a series of online meetings of the committee and sub-groups and through written communication during 2022.

A first order draft report was expanded into a final draft report, which was then circulated electronically to members and consulting experts of MCTOC for online editing review. The final draft was also circulated to TEAP members, SAP co-chairs, EEAP co-chairs and a few relevant members, and RTOC co-chairs and one member.

The final draft report has undergone a limited peer review among experts from industry organisations that assisted MCTOC by providing information during report development. These organisations, and the number of people per organisation, that reviewed relevant sections of the confidential final draft report for the purposes of accuracy, are listed below.

- A-Gas International Ltd. (1 reviewer) (chapter 8).

- Association of Distributors, Fillers, Recoverers and Reclaimers of Refrigerants (1 reviewer) (chapter 8).

- Climalife (1 reviewer) (chapter 8).

- International Pharmaceutical Aerosol Consortium (2 reviewers) and its member companies, AstraZeneca (2 reviewers), Boehringer Ingelheim (2 reviewers), Chiesi Farmaceutici (2 reviewers), GSK (2 reviewers), Kindeva (2 reviewers), Organon (2 reviewers), Cipla (2 reviewers), and Teva (2 reviewers) (chapter 10).

All review comments and edits were considered, and changes to the final draft were made through the consensus of MCTOC membership to achieve a final report.

1.3.4 Glossary and conventions for commonly used terms

CFC	Chlorofluorocarbon
CTC	Carbon tetrachloride
GWP	Global warming potential, according to IPCC 4th Assessment Report, Table 2.14 (errata)[5], unless otherwise specified
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
ODP	Ozone depletion potential
ODS	Ozone-depleting substance
GtCO$_2$e	Gigatonnes (10^9 tonnes) CO$_2$e
MTCO$_2$e	Metric tonnes CO$_2$e
MMTCO$_2$e	Million metric tonnes CO$_2$e
EEAP 2022	Refers to the 2022 Assessment Report of the EEAP
SAP 2022	Refers to the 2022 Assessment Report of the SAP[6]

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[5] IPCC, 2012, *AR4 Climate Change 2007, The Physical Science Basis*, *The Working Group I Contribution to the IPCC Fourth Assessment Report Summary for Policymakers*, Technical Summary and Frequently Asked Questions, Table 2.14 (Errata), 15 June 2012.

[6] World Meteorological Organization (WMO), 2022, *Scientific Assessment of Ozone Depletion: 2022*, GAW Report No. 278; WMO: Geneva, 2022.

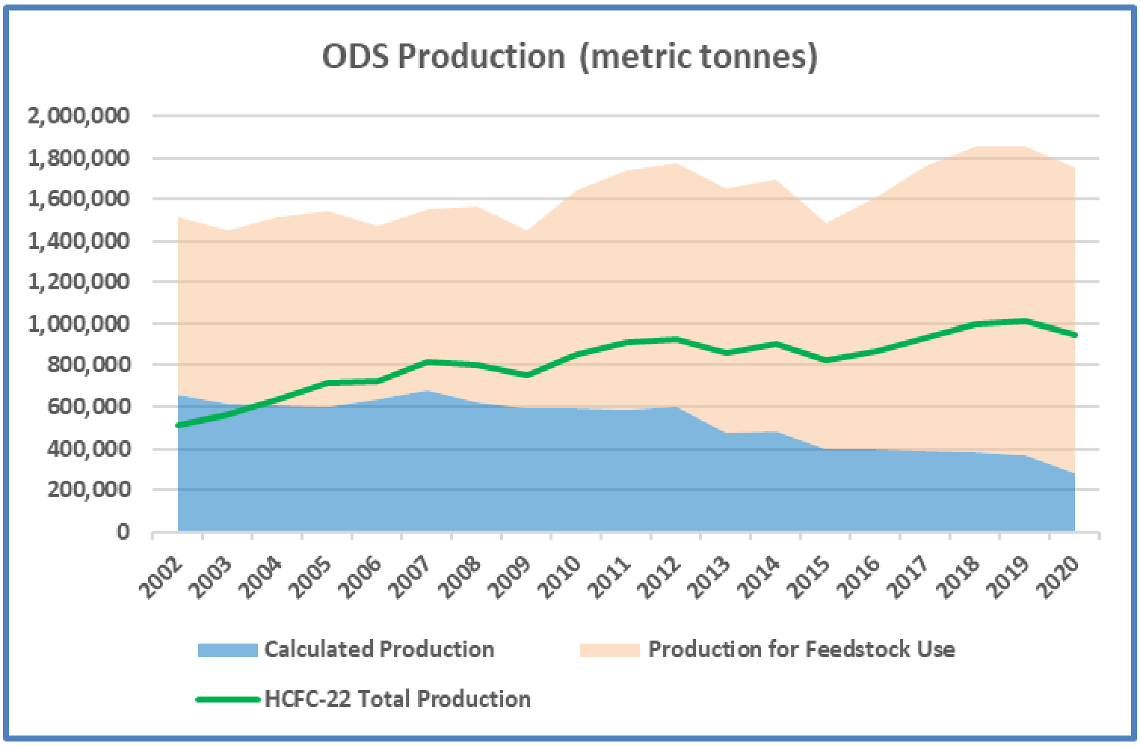
2 Production, including Feedstock

This chapter describes the production of controlled substances, including for feedstock uses, and a wide range of related issues, including by-production, production intermediates, estimated emissions for production, distribution and use of feedstocks, stocks, illegal trade, patents, regulatory issues, precursor substances to per- and polyfluoroalkyl substances (PFAS) and trifluoroacetic acid and its salts (TFA), carbon tetrachloride (CTC), ODS that are not controlled substances such as dichloromethane, chloroform, ethylene dichloride, trichloroethylene, perchloroethylene, and methyl chloride, and HFCs that are not listed in Annex F.

2.1 Production of controlled substances

The total reported production of ODS since 2002 has increased, due to production for feedstock offsetting the decrease in calculated production (which correspond to total production minus feedstock uses minus destruction minus QPS uses for methyl bromide), as shown in Figure 2.1. The figure also shows the total reported HCFC-22 production (calculated and for feedstock use).

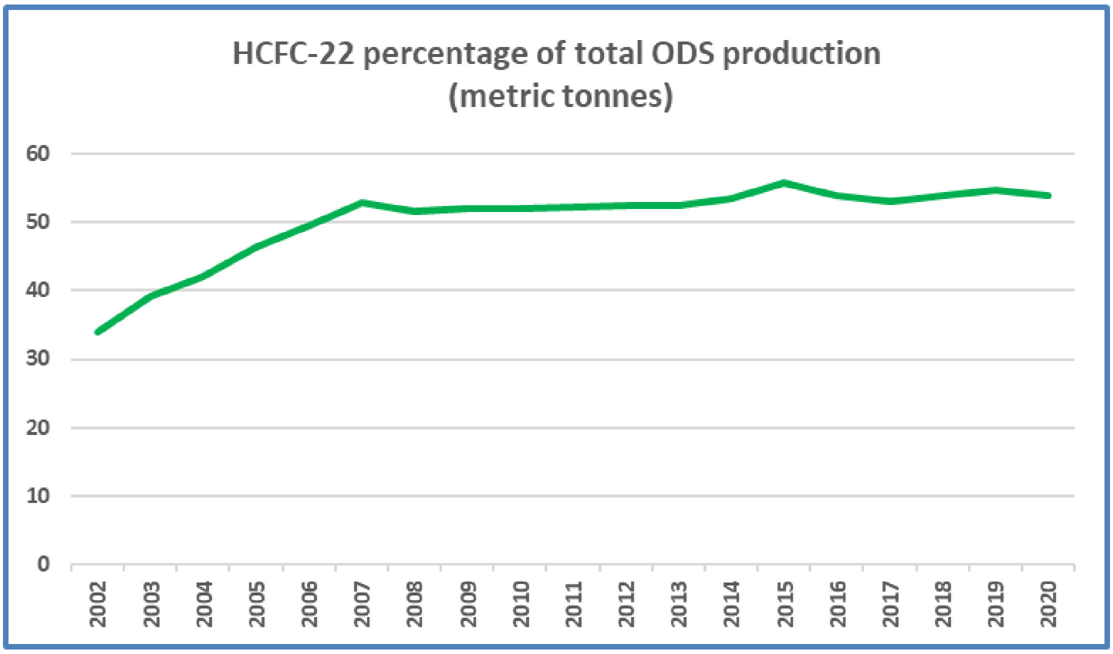
Figure 2.1 Total reported ODS production, 2002–2020



The proportion of HCFC-22 as a percentage of total reported ODS production increased significantly in the period 2002 to 2007, and since then its share is over 50% of total ODS production, due to the increasing use of HCFC-22 as a feedstock, as shown in Figure 2.2. In addition, in 2020 HCFC-22 was nearly 83% of calculated production (excludes feedstock use) for all ODS. Production for feedstock use is discussed in section 2.2.

There is insufficient reported data for HFCs to show any trends.

Figure 2.2 Proportion of HCFC-22 as a percentage of total reported ODS production, by tonnes, 2002–2020



2.2 Production and use of controlled substances for chemical feedstock

Feedstocks are chemical building blocks that allow the cost-effective commercial synthesis of other chemicals. Controlled substances (ODS and HFCs) can be produced and/or imported or exported for use as feedstocks. As raw materials, feedstocks are converted to other products, except for *de minimis* residues and emissions of unconverted raw material. Emissions from the use of feedstock consist of residual levels in the ultimate products, and fugitive leaks in the production, storage and/or transport processes. Significant investments and effort are spent to handle ODS and HFC feedstocks in a responsible, environmentally sensitive manner and, in most countries, are regulated through national pollution control measures. Global emissions from the reported production and use of feedstocks are estimated in the following sections.

The definition of production under the Montreal Protocol excludes the amounts of controlled substances entirely used as feedstock in the manufacture of other chemicals. Notwithstanding, parties are required to report the production of controlled substances for feedstock uses annually.[7] Similarly, the definition of consumption excludes controlled substances entirely used as feedstock, nevertheless, imports and exports of controlled substances to be used entirely as feedstock must be reported by parties.

2.2.1 How Article 7 reporting of production for feedstock uses contributes to understanding atmospheric burdens

Article 7 of the Montreal Protocol prescribes requirements for each party for the annual reporting of statistical data on production, imports, and exports of each of the controlled substances. Reporting is further described in various decisions of the meetings of parties. Some decisions introduce additional data requests that parties may report voluntarily.

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[7] Montreal Protocol, Article 7, paragraph 3.

Article 7, paragraph 3, *Each Party shall provide to the Secretariat statistical data on its annual production (as defined in paragraph 5 of Article 1) of each of the controlled substances listed in Annexes A, B, C, E and F and, separately, for each substance,*

– Amounts used for feedstocks, ...

The Montreal Protocol defines that some quantities of controlled substances are not considered controlled substances under the Protocol owing to the insignificant emissions from their uses. Decision IV/12, clarifies the definition of controlled substances, "*That insignificant quantities of controlled substances originating from inadvertent or coincidental production during a manufacturing process, from unreacted feedstock, or from their use as process agents which are present in chemical substances as trace impurities, or that are emitted during product manufacture or handling, shall be considered not to be covered by the definition of a controlled substance contained in paragraph 4 of Article 1 of the Montreal Protocol*". Decision IV/12 further urges "*…parties to take steps to minimize emissions of such substances, including such steps as avoidance of the creation of such emissions, reduction of emissions using practicable control technologies or process changes, containment or destruction*".

As noted, parties are required to report the production, import and export of controlled substances for feedstock uses annually. Reported feedstock is a valuable data set that can be correlated with related emissions of controlled substances, either from their production, use or with the expected impact of emission abatement measures. However, there are some products that are not reported because they are intermediates not isolated in a chemical manufacturing process.[8] These intermediates may also be emitted in low quantities and detected by atmospheric monitoring.[9]

2.2.2 Reporting of controlled substances for feedstock uses

As revised in decision XXX/10 and Annex III to MOP-30, Article 7 data reporting instructions and guidelines require the reporting of feedstock uses for all controlled substances and, when calculating production, the Montreal Protocol allows countries to deduct amounts of controlled substances used for feedstock and amounts destroyed. When reporting production data, parties are not expected to deduct these figures from their data. The Secretariat makes the necessary deductions. All feedstock produced during a calendar year is reportable for that year, even if it has not been used.

The 1999 Handbook on Data Reporting under the Montreal Protocol provides guidance on data collection for production for use as feedstock.

"*For collecting data on production (including data on production for use as feedstock and process agents, for essential uses, QPS and increased production), you can rely on the sources mentioned in Section 2.4.*

Section 2.4 extract: The relevant data on all categories of production are to be provided by the manufacturers based on voluntary or mandatory reporting. The manufacturers of ODS are usually large chemical companies and are, therefore, in most cases identified relatively easily. Note, however, that halons and carbon tetrachloride may also be manufactured on a smaller scale. For these, you might need to spend some effort to identify relevant companies. To ensure high data quality, the

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[8] UNEP, 2021, *2021 TEAP Report, Volume 1, Progress Report*, September 2021. Section 5.3.5.

[9] Vollmer, M.K., Mühle, J., Henne, S., Young, D., Rigby, M., Mitrevski, B., Park, S., Lunder, C.R., Rhee, T., Harth, C.M., Hill, M., Langenfelds, R.L., Guillevic, M., Schlauri, P.M., Hermansen, O., Arduini, J., Wang, R.H.J., Salameh, P.K., Maione, M., Krummel, P.B., Reimann, S., O'Doherty, S., Simmonds, P.G., Fraser, P.J., Prinn, R.G., Weiss, R.F., and Steele, L.P., Unexpected nascent atmospheric emissions of three ozone-depleting hydrochlorofluorocarbons, *PNAS*, 2021, **118**(5), e2010914118. https://doi.org/10.1073/pnas.2010914118.

information provided by industry can be audited by an independent consultant and verified with the help of on-site inspections and inspection of the company's documentation."

The Montreal Protocol includes the term "used as feedstock", e.g., Article 1, paragraph 5, "*"Production" means the amount of controlled substances produced, minus the amount destroyed by technologies to be approved by the Parties and minus the amount entirely used as feedstock in the manufacture of other chemicals.*"

There is no definition for production for use as feedstock. However, there is the definition of "controlled substances produced" in Article 1, paragraph 5, *"Controlled substances produced" as used in Article 1, paragraph 5 is the calculated level of controlled substances manufactured by a party. This excludes the calculated level of controlled substances entirely used as a feedstock in the manufacture of other chemicals…"* The term "manufactured" is not defined; although a common-sense definition would be "to make or process (a raw material) into a finished product".

In chemical production, a non-isolated intermediate in a chemical process is not considered as a finished product while it remains within the chemical process. As such, a non-isolated intermediate is not commonly reported. For example, the formation of the intermediate HCFC-21 is not commonly reported as a feedstock in the process of manufacturing HCFC-22. However, a substance that is isolated, most likely purified to a specification, and then used in a distinct, separate process, would be considered as a finished product and subject to reporting as production for feedstock use. For example, when HCFC-21 was isolated and then used in the production of HCFC-225, its production was reported as feedstock.

Examples of the use of controlled substances as intermediates and feedstocks and associated reporting, based on the available reported data:

- A controlled substance that is generated and used on the same integrated chemical plant complex, as part of a multistep process, is not a finished product and if regarded as an intermediate would not be reported as feedstock production.

    a. E.g., HCFC-132b and HCFC-133a as non-isolated intermediates for HFC-134a production.

- A controlled substance that is used by the same or a different company on the same or nearby chemical site in a distinct separate chemical process, which may transport the substance by pipeline, rail, or road transfer. The substance is a finished product and has been reported as feedstock production.

    b. HCFC-22 used to produce TFE/HFP

    c. Quantities of HCFC-133a that are isolated and then used in a separate process have been reported as feedstock.

See also section 2.4 on intermediates.

The reporting of production for feedstock use has recently been discussed at the Multilateral Fund Executive Committee (ExCom) meetings and by the Production Sector Sub-group.[10]

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[10] Executive Committee of the Multilateral Fund, Meeting Documents: UNEP/OzL.Pro/ExCom/87/57, 24 June 2021; UNEP/OzL.Pro/ExCom/87/58, 21 September 2021; UNEP/OzL.Pro/ExCom/88/IAP/3, 13 December 2021; UNEP/OzL.Pro/ExCom/88/78, 19 November 2021; UNEP/OzL.Pro/ExCom/90/40, 23 June 2022.

2.2.3 Feedstock applications of controlled substances

Table 2.1 shows some feedstock applications for controlled substances, although the list is not exhaustive. Parties report amounts of controlled substances used as feedstock to the Ozone Secretariat, but they do not report how they are used. Processes are proprietary and there is no official source to define the manufacturing routes followed and their efficacy. The table provides some examples and is the product of the collective experience and knowledge of MCTOC members. Products included are both intermediates as well as final products, including fluoropolymers.

Table 2.1 Feedstock applications of controlled substances (this list is not exhaustive)

Feedstock	Products	Further conversion products	Comments
CFC-113	Chlorotrifluoroethylene	Chlorotrifluoroethylene based polymers	Polymers include poly-chlorotrifluoroethylene (PCTFE), and poly-fluoroethylenevinyl ether (PFEVE).
CFC-113	CFC-113a		CFC-113a may be an intermediate and may be transported off-site for use as a feedstock.
CFC-113a	Trifluoroacetic acid (TFA) and pesticides (including cyhalothrin)		Starting with CFC-113, CFC-113a is as an intermediate for TFA. Alternatively, CFC-113a may be directly produced as the starting feedstock (See line above). TFA is a pesticide and medical intermediate.
CFC-113, CFC-113a, CFC-114a, HCFC-124	HFC-134a		One sequence for production of HFC-134a begins with CFC-113, which is converted to CFC-113a, then to CFC-114a and HCFC-124a as intermediates.
CFC-113a	HFO-1336mzz isomers		Low GWP alternatives for HFC-245fa and HCFC-123.
CTC	CFC-11 and CFC-12		Production and consumption of these CFCs has fallen to zero based on reported data. However, a small quantity of CFC-12 (<100 tonnes) is intermittently reported for feedstock use. It is not known for what the CFC-12 was used.
CTC	With water to make CO_2 and HCl: the HCl is subsequently reacted with methanol to make methyl chloride and water	Methyl chloride in chloromethanes (CMs) plant converted to dichloromethane (DCM) and chloroform (CFM)	A method of recycling CTC into useful products rather than destruction operated in CMs plant complex.
CTC	Perchloroethylene		High volume use as solvent and feedstock
CTC	With hydrogen to make chloroform with methane and HCl as by-products	Chloroform is used to make HCFC-22	A method of recycling CTC into useful products rather than destruction operated in CMs plant complex
CTC	Chlorocarbons including vinyl chloride, chloropropanes chloropropenes and hydrochloroflupropanes (HCFC-241, -242, -243, -244)	Feedstocks for production of HFC-245fa and some HFOs and HCFOs: HFO-1234yf, HCFO-1233zd, and HFO-1234ze.	HFOs and HCFOs are ultra-low GWP fluorocarbons used in refrigeration, air conditioning and insulation and production is increasing.
CTC	With acrylonitrile, intermediates	Pyrethroid pesticides.	CCl_3 groups in molecules of intermediates become $=CCl_2$ groups in pyrethroids.
CTC	With 2-chloropropene - Intermediates	Production of HFC-365mfc	
CTC	With vinylidene chloride - Intermediates	Production of HFC-236fa	

Feedstock	Products	Further conversion products	Comments
CTC	With benzene to make triphenylchloromethane (trityl chloride)	Intermediate for dyes and pharmaceuticals such as antiviral drugs	Trityl chloride is an efficient tritylation agent.
CTC	With 1,3-dichloro-4-fluorobenzene to make 2,4-dichloro-5-fluorobenzoyl chloride (DCFBC)	Intermediate for example in the synthesis of highly active antibacterial agent ciprofloxacin	
CTC	With methyl 3,3-dimethyl-4-pentenoate to produce methyl 4,6,6,6-tetrachloro-3,3-dimethylhexanoate		
1,1,1-trichloroethane	HCFC-141b, -142b, and HFC-143a		Note that an alternative process uses 1,1-dichloroethylene (vinylidene chloride, VDC) as feedstock; VDC is not an ODS.
HCFC-21	HCFC-225 isomers		Reaction of TFE with HCFC-21 to give HCFC-225 isomers. Product used as a solvent or intermediate
HCFC-225ca	HFO-1234yf and HCFO-1224yd		HCFC-225 (produced from TFE and HCFC-21) can be further reacted to produce HFO-1234yf and HCFO-1224yd
HCFC-22	Tetrafluoroethylene (TFE, HFO-1114)	Polymerized to homopolymer (PTFE) and co-polymers. Route to HFC-125	Very high-volume use. Work has been done for decades to find an alternative commercial route to TFE, without success.
HCFC-22	Hexafluoropropylene (HFP, HFO-1216)	Co-produced with TFE and used as monomer or copolymer, e.g., FEP. Route to HFO-1234yf. Route to HFC-227ea.	Fluorinated ethylene-propylene polymers (FEP)
HCFC-22	With 2,2,2-trifluoroethanol, then chlorination to anaesthetic isoflurane $CF_3CHClOCHF_2$	Isoflurane by reaction with HF is converted to anaesthetic desflurane $CF_3CHFOCHF_2$	
HCFC-22	Sulfentrazone		Sulfentrazone (*N*-{2,4-Dichloro-5-[4-(difluoromethyl)-3-methyl-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl] phenyl} methanesulfonamide) is a broad-spectrum herbicide.
HCFC-123	HCFC-124, HFC-125		
HCFC-124	HFC-125		
HCFC-123	Production of TFA		
HCFC-133a	HCFC-123, CFC-113a		HCFC-133a can be transformed to HCFC-123 by chlorination and further to CFC-113a
HCFC-133a	Production of trifluoroethanol		

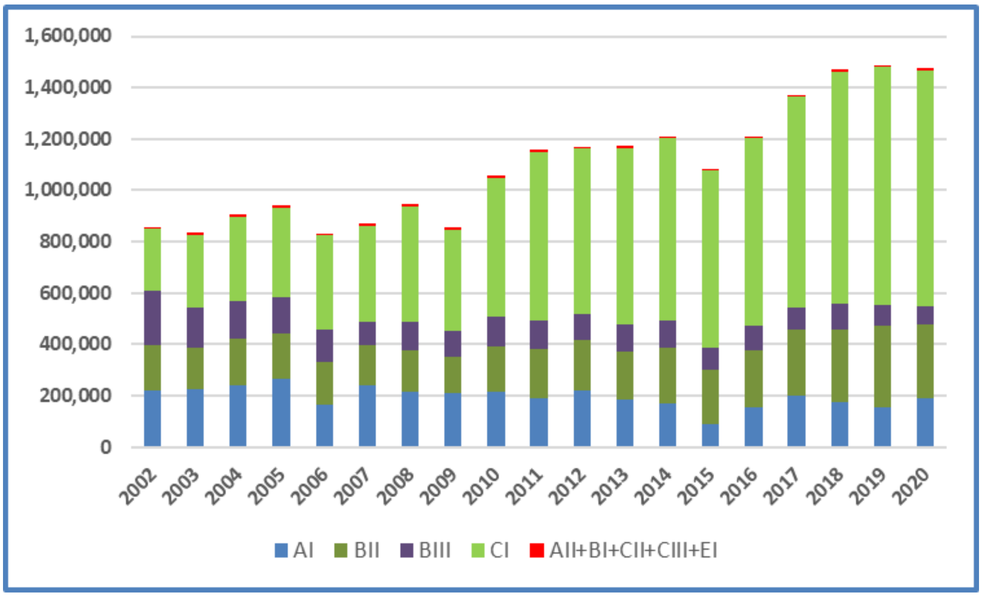
Feedstock	**Products**	**Further conversion products**	**Comments**
Bromotrifluoromethane	Production of the pesticide fipronil and other chemicals		Bromotrifluoromethane may also be an intermediate when HFC-23 is used as a starting material in the production of fipronil and other chemicals. Bromotrifluoromethane is used as feedstock in the preparation of chemicals including fipronil (insecticide), mefloquine (antimalarial), and DPP-IV inhibitor (antidiabetic). CF_3 generated from bromotrifluoromethane can be introduced into a wide range of organic molecules by nucleophilic substitution.
HCFC-141b	HCFC-142b, HFC-143a		
HCFC-142b	Vinylidene fluoride (HFO-1132a)	Polymerised to poly-vinylidene fluoride or co-polymers.	Products are fluorinated elastomers and fluororesins. Vinylidene fluoride is a very low temperature refrigerant
Bromochloromethane	2-(Thiocyanomethyl)-thiobenzothiazole (TCMTB)		TCMTB is a biocide used in the leather industry
HFC-152a	HCFC-142b	Vinylidene fluoride, and subsequent polymerisation products (as above for HCFC-142b).	Photochlorination to obtain HCFC-142b, followed by dehydrochlorination to obtain vinylidene fluoride.
HFC-23	Production of Halon 1301 by bromination for use as a feedstock		HFC-23 is converted to bromotrifluoromethane by bromination. Bromotrifluoromethane is then used as feedstock in the preparation of chemicals including fipronil (insecticide), mefloquine (antimalarial), and DPP-IV inhibitor (antidiabetic). CF_3 generated from bromotrifluoromethane can be introduced into a wide range of organic molecules by nucleophilic substitution.
HFC-23	With chloroform to make HCFC-22 and HCFC-21		Demonstration plant to use HFC-23 as a feedstock with high selectivity and to avoid process inefficiencies in the HCFC-22 production process. Note when integrated with HCFC-22 production process, HFC-23 is an intermediate and not a feedstock
HFC-125	Reaction with iodine to produce C_2F_5I	C_2F_5I is reacted with TFE to produce telomers that can be further reacted	

2.2.4 Recent and historical trends in the production and use of controlled ODS as feedstock

Data reported by parties to the Ozone Secretariat on production and import of controlled ODS used as feedstock for the year 2020 was provided to the MCTOC. These also include quantities used as process agents because parties are required to report such consumption in a manner consistent to that for feedstock. In 2020, a total of 15 parties[11] reported feedstock use of ODS, while 12 of these parties also produced ODS for feedstock uses. In 2019, a total of 16 parties had reported use of ODS as feedstock. Two of these parties had reported imports of less than 0.1 tonne.

In 2020, total ODS production and import reported for feedstock uses was 1,475,007 tonnes, a small decrease compared to 2019 (2019: 1,486,288 tonnes[12]). Figure 2.3 shows that, comparing 2020 with 2019, only small changes have occurred for individual substances resulting in an overall small decrease. The 2020 reported total production and import of ODS for feedstock use in metric tonnes represents 554,116 ODP tonnes.[13] The overall increase in ODS feedstock uses through the last decade has been mostly due to the increase in feedstock uses of Annex C1 HCFCs, particularly HCFC-22, while uptake of HFOs is driving a more recent increase in CTC feedstock use. It is highly likely that the COVID pandemic had an impact on feedstock production and consumption in 2020.

Figure 2.3 Annual reported production of ODS for feedstock and process agent uses, categorised by Montreal Protocol Group, 2002–2020 (metric tonnes)[14]



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[11] This total also includes the European Union as an importer; European Union Member States report their own production for feedstock use.

[12] The 2018 feedstock production was stated as 1,364,998 tonnes in the *2019 TEAP Report, Volume 1, Progress Report*, May 2019. Any data changes result from data revisions that can occur for historical years.

[13] While ODP tonnes are included, it should be noted that presenting production for feedstock use in ODP tonnes does not equate to emissions. From the total amount of ODS produced for feedstock use, only a relatively minor to insignificant quantity will be emitted depending on the abatement technologies and containment measures utilised.

[14] Annex AI CFC-11, -12, -113, -114, -115; Annex BII carbon tetrachloride; Annex BIII 1,1,1 trichloroethane; Annex CI HCFCs. Annex AII Halon-1211, -1301, -2402; Annex BI CFC-13, -111, -112, -211, -212, -213, -214, -215, -216, -217; Annex CII HBFCs; Annex CIII bromochloromethane; and Annex EI methyl bromide.

Table 2.2 Amount of ODS used as feedstock in 2020

Substance	ODP	Metric Tonnes
HCFC-22	0.055	713,536
Carbon Tetrachloride	1.1	288,935
HCFC-142b (reported as HCFC-142 and HCFC-142b)	0.065	166,966
CFC-113 and CFC-113a	0.8	138,443
1,1,1-trichloroethane (methyl chloroform)	0.1	>50,000
CFC-114	1	>20,000
HCFC-124	0.022	>20,000
HCFC-141b	0.11	>10,000
Halon 1301 (bromotrifluoromethane), Bromochloromethane, HCFC-123, Methyl Bromide		1,000 to 5,000
HCFC-133		10 to 1,000
Other substances		<10
Total Metric Tonnes		1,475,007
(Total ODP Tonnes)*		*554,116*

Explanatory notes: For some substances, due to the limited number of parties reporting production for feedstock use or imports for feedstock use, quantities have been approximated. For those substances used in relatively small quantities, a quantity range is indicated. *While the corresponding ODP tonnes are shown, it should be noted that this does not equate to emissions. From the total amount of ODS used as feedstock, a relatively minor to insignificant quantity will be emitted depending on the abatement technologies and containment measures utilised. The ODP tonnes is calculated from the reported data but for some reports it is not certain that the correct isomer is identified.

The proportions of the largest ODS feedstocks in 2020 were very similar to 2019: HCFC-22 (48% of the total mass quantity), CTC (20%), and HCFC-142b (11%). HCFC-22 is by a considerable margin the largest feedstock used, with 713,536 tonnes reported in 2020. HCFC-22 is mainly used to produce tetrafluoroethylene (TFE), which can be both homo- and co-polymerized to make stable, chemically resistant fluoropolymers with many applications, such as polytetrafluoroethylene. TFE may also be used to produce HFC-125, although alternative processes may be lower cost. Polyvinylidene fluoride is made from HCFC-142b. The feedstock use of CTC[15] has increased in recent years, due to growing demand for lower GWP HCFO/HFOs and perchloroethylene (PCE). The trends in the production for feedstock use of the current main ODS feedstocks are shown in Figure 2.4.

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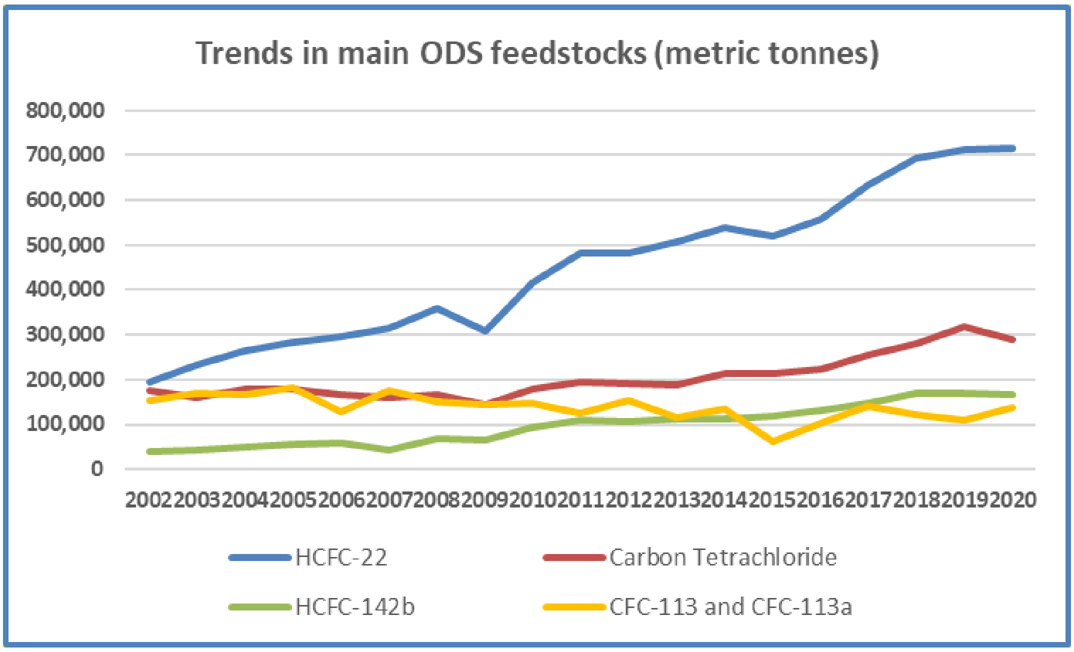
[15] More information on CTC production, and its uses as feedstock, can be found in the *2019 TEAP Report, Volume 1, Decision XXX/3 TEAP Task Force Report on Unexpected Emissions of Trichlorofluoromethane (CFC-11), Final Report*, September 2019, and in section 2.8 of this report.

Figure 2.4 Trends in annual production of the current main ODS feedstocks for the years 2002–2020 (metric tonnes)



2.2.5 Production of HFCs used as feedstock

Following the entry into force of the Kigali Amendment, reporting of HFCs, including production and import for feedstock uses, is required for all parties that have ratified the amendment. In addition to feedstock data reported as part of HFC baseline submissions, obligatory annual HFC data reporting starts with data for 2019 for countries that became party to the Kigali Amendment before the end of 2019, and that 2019 Article 7 data was reported during 2020. Data submissions for 2020 for countries that became parties in 2020 are required before the end of 2021. The feedstock data reported for 2020 and 2021 is incomplete due to the timing of reporting obligations, for example, depending on when some parties ratified. The largest reported feedstock is HFC-152a (thousands of tonnes). In addition to HFC-23 (discussed in detail in section 2.2.6), other HFCs reported in 2020 in quantities between 10 to 1000 tonnes are HFC-32, HFC-41, HFC-125, HFC-134a and HFC-236ea. The total reported quantities of HFC feedstocks are considerably lower than ODS feedstock.

According to a recent paper[16], the dehydrofluorination of 1,1-difluoroethane (HFC-152a) is the most broadly used chemical process to produce vinyl fluoride (used to produce polyvinylfluoride, a polymer used mainly in low flammability coatings). HFC-152a can also be used as a feedstock to produce vinylidene fluoride (CH_2CF_2), via photo-chlorination to obtain HCFC-142b followed by dehydrochlorination.

2.2.6 New feedstock uses for HFC-23

Historically, some of the HFC-23 generated as a by-product during the manufacture of HCFC-22 was recovered and used as a feedstock to produce Halon 1301 (bromotrifluoromethane). When production of Halon 1301 ceased in non-Article 5 parties in 1994, in accordance with the Montreal Protocol, this

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[16] Tang, H., Dang, M., Li, Y., Li, L., Han, W., Liu, Z., Li, Y., Li, X., Rational design of MgF_2 catalysts with long-term stability for the dehydrofluorination of 1,1-difluoroethane (HFC-152a), *RSC Advances*, 2019, **9**, 23744–23751. https://doi.org/10.1039/C9RA04250D.

demand for HFC-23 also largely ceased. However, HFC-23 is still used as a feedstock to produce Halon 1301, which in turn is still used as a feedstock for the manufacture of the pesticide fipronil and other chemicals.[17,18]

Over that last 10 years further uses of HFC-23 as feedstock have been investigated and proposed, but some of these are potentially very low quantities,[19,20] have low selectivity or rapid catalyst deactivation.[21,22] An overview of some feedstock uses of HFC-23 was included in a presentation at the China HFC-23 mitigation workshop.[23] According to available information, these are chemical manufacturing processes that use HFC-23 as a feedstock and are not destruction processes. One particularly attractive process is the Cl/F exchange reaction for HFC-23 with chloroform,[24] producing HCFC-22 and HCFC-21, using HFC-23 as a valuable feedstock, reducing waste, and improving the efficiency of the overall HCFC-22 manufacturing process.

$$\begin{array}{ccccccc} CHF_3 & + & CHCl_3 & \rightarrow & CHClF_2 & + & CHCl_2F \\ \text{HFC-23} & & \text{chloroform} & & \text{HCFC-22} & & \text{HCFC-21} \end{array}$$

2.2.7 HFO-1234yf produced using HCFC-22 as feedstock

There are multiple production pathways possible for the manufacture of HFO-1234yf. One of the process routes that is being used has associated emissions of HFC-23 because it uses HCFC-22 and HFP as feedstocks. In this pathway to manufacture HFO-1234yf, the manufacture of HCFC-22 generates HFC-23 emissions, and the manufacture of TFE/HFP from HCFC-22 used as feedstock also generates HFC-23 and PFC-c-318 emissions (discussed in section 2.3.2). The reaction pathways from HCFC-22 to HFO-1234yf are shown below by arrows.

HCFC-22 → TFE/HFP

HFP → HFO-1225ye (1,2,3,3,3-pentafluoropropene) via hydrogenation then dehydrofluorination

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[17] UNEP, 2019, *2019 TEAP Report, Volume 1, Decision XXX/3 TEAP Task Force Report on Unexpected Emissions of Trichlorofluoromethane (CFC-11), Final Report*, September 2019, page 69.

[18] CF_3 generated from Halon 1301 can be introduced into a wide range of organic molecules by nucleophilic substitution to produce chemicals, including fipronil (insecticide), mefloquine (antimalarial), and DPP-IV inhibitor (antidiabetic).

[19] See, for example, Grushin, V.V., Fluoroform as a feedstock for high-value fluorochemicals; Novel trends and recent developments, *Chim. Oggi – Chem. Today*, 2014, **32**(3), 81–90.

[20] See, for example, Köckinger, M., Ciaglia, T., Bersier, M., Hanselmann, P., Gutmann, B., Kappe, C.O., Utilization of fluoroform for difluoromethylation in continuous flow: a concise synthesis of α-difluoromethyl-amino acids, *Green Chem.*, 2018, **20**, 108–112. https://doi.org/10.1039/C7GC02913F.

[21] Wang, J., Han, W., Wang, S., Tang, H., Liu, W., Li, Y., Lu, C., Zhang, J., Kennedy E.M., Li, X., Synergistic catalysis of carbon-partitioned LaF_3–BaF_2 composites for the coupling of CH_4 with CHF_3 to VDF, *Catal. Sci. Technol.*, 2019, **9**, 1338. https://doi.org/10.1039/C8CY02376J.

[22] Cheng, Y., Wang, J., Han, W., Song, Y., Liu, W., Yang, L., Wang, S., Wu, Z., Tang, H., Zhang, J., Stockenhuber, M. and Kennedy, E.M., Catalytic coupling of CH_4 with CHF_3 for the synthesis of VDF over LaOF catalyst, *Greenhouse Gas. Sci. Technol.*, 2018, **8**, 587–602. https://doi.org/10.1002/ghg.1769.

[23] Zhang, J., 2021, *Research progress on the conversion of HFC-23*, Foreign Environmental Cooperation Office, Ministry of Ecology and Environment (FECO/MEE) and Energy Foundation China, HFC-23 Mitigation Workshop, Beijing, 19th November 2021. Accessed via personal communication with Jianjun Zhang, 2022.

[24] Hana, W., Wang, J., Chen, L., Yang, L., Wang, S., Xi, M., Tang, H., Liu, W., Song, W., Zhang, J., Li, Y., Liu, H., Reverting fluoroform back to chlorodifluoromethane and dichlorofluoromethane: Intermolecular Cl/F exchange with chloroform at moderate temperatures, *Chemical Engineering Journal*, 2019, **355**, 594–601. https://doi.org/10.1016/j.cej.2018.08.135

HFO-1225ye → HFO-1234yf via hydrogenation then dehydrofluorination

According to one report[25] the unit ratio of HFP to HFO-1234yf is close to 1.4–1.5 units per unit of HFO-1234yf.

The report comments that an alternative process, which is now fully operational, uses an existing modified plant. TFE is reacted by pyrolysis with HCFC-21 (dichlorofluoromethane), which is an intermediate that can be extracted from HCFC-22 production. The resultant product is a commercial chemical HCFC-225 (a mixture of 50:50 3,3-dichloro-1,1,1,2,2-pentafluoropropane, or HCFC-225ca, and 1,3-dichloro-1,1,2,2,3-pentafluoropropane or HCFC-225cb). The HCFC-225ca isomer is hydrogenated to HFC-245cb (2,2,3,3,3-pentafluoropropane) and then dehydrofluorinated to create HFO-1234yf. HCFO-1224yd is also produced using this process.

The HCFC-22 production routes to HFO-1234yf may require access to or integration into TFE/HFP production as TFE is not transportable and must be available on-site or from adjacent sites. Producers of HFO-1234yf who are not integrated into TFE/HFP would need to purchase HFP, which is much more transportable, although local availability would be preferred.

Before 2017, HFO-1234yf was only produced by the HFP route. Since 2017, potentially about 15,000 to 20,000 tonnes HFO-1234yf is produced using the HFP-based production route. For these processes, the HFC-23 emissions from the production of HCFC-22 are required to be destroyed to the extent practicable. HFP produced as a co-product with TFE, is not an Annex C, Group I, or Annex F substance, and any HFC-23 emissions are not required to be destroyed according to Article 2J, even if the TFE production plant is located on the same production site as the HCFC-22 production because they are separate independent processes with the HCFC-22 being a manufactured feedstock. The quantities HCFC-22 or HCFC-21 used as feedstock are required to be reported and should already be included in annual reporting as required by Article 7.

2.2.8 HFCs produced using HCFC-22 as a feedstock

Some HFCs are produced using process routes that may have associated emissions of HFC-23, as they use HCFC-22, TFE or HFP as feedstocks, and which may be followed by further reactions to give the final product. HFP is a co-product of TFE production from HCFC-22. Routes that use TFE or HFP may also have associated emissions of high GWP PFC-c-318. Relevant HFCs include:

- HFC-227ea, from hexafluoropropene HFP (C_3F_6) by reaction with HF.
- HFC-125, from TFE by reaction with HF
- HFC-32 from HCFC-22 by hydrodechlorination.

2.3 By-production of controlled substances

There are several *mechanisms* that account for the by-production of controlled substances in other production processes including,

- Over or under reaction enroute to the intended product e.g., HFC-23 is an over fluorination of HCFC-22.

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[25] David Sherry and Maria Nolan (Nolan Sherry & Associates, NSA), Stephen Seidel (Center for Climate and Energy Solutions – C2ES) and Stephen O. Andersen (Institute for Governance & Sustainable Development, IGSD), 2017, *HFO-1234yf: An Examination of Projected Long-Term Costs of Production*, April 2017.

- Presence of impurities in the feedstocks being reacted to an intended by product e.g., the presence of CTC in chloroform used to produce HCFC-22 will result in the formation of CFC-12.

- Unintended side reactions where the feedstock follows a different reaction path than the one that is desired to make the product. For example, when perchloroethylene is used to produce HFC-125, there are several side reactions that can result in the formation of a CFC, most likely CFC-115 but other less fluorinated CFCs, such as CFC-113 or CFC-114, may be formed.

The design intent of most plants is to minimise the by-production of these controlled substances as they tend to have a detrimental economic effect, because they:

- Consume feedstocks that cannot be sold as the final product.

- May require additional process steps to remove them from the final product and/or mitigate the release of the by-product e.g., through thermal oxidation.

- In some cases, risk making the final product unsaleable.

The following sections outline some of the by-production of controlled substances considered by the MCTOC.

2.3.1 HFC-23 by-production from HCFC-22 production

The reaction of chloroform ($CHCl_3$) and anhydrous hydrogen fluoride (aHF) to use HCFC-22 ($CHClF_2$) is employed in many plants around the world.

$$CHCl_3 + 2HF \rightarrow CHClF_2 + 2HCl$$

Ideally the HCFC-22 is removed from the reactor as soon as it is formed however in all cases some HCFC-22 is further fluorinated to HFC-23 before it can be removed from the reactor.

$$CHClF_2 + HF \rightarrow CHF_3 + HCl$$

The fraction of HFC-23 produced on HCFC-22 plants has, due to both economic and regulatory pressure, reduced over time (from as high as 4% to nearer 2% by weight or less), through better control of the reactor conditions and changes to plant designs. Many plant now employ destruction facilities as a means of preventing emissions of the by-produced HFC-23, typically this involves high temperature conversion to CO_2, water, and HF.

According to a recent paper[26], global HFC-23 emissions derived from atmospheric measurements were historically at their highest level in 2018, in contrast to expected emissions of HFC-23 by-product, primarily from reported HCFC-22 production, that were much lower. The paper concludes that the discrepancy between expected emissions and observation-inferred emissions makes it possible that planned reductions in HFC-23 emissions may not have been fully realised or there may be substantial unreported production of HCFC-22, both or either of which would result in unaccounted for HFC-23 by-product emissions.

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[26] Stanley, K.M., Say, D., Mühle, J. *et al.*, Increase in global emissions of HFC-23 despite near-total expected reductions, *Nature Communications*, 2020, **11**, 397. https://doi.org/10.1038/s41467-019-13899-4.

2.3.2 Emissions of HFC-23 and PFC-c-318 from the manufacturing process used to produce tetrafluoroethylene and hexafluoropropene from HCFC-22

HCFC-22 is by a considerable margin the largest feedstock used, with 713,536 tonnes reported in 2020. About 97% of this is used to produce tetrafluoroethylene (TFE) and hexafluoropropene (HFP), both used primarily to manufacture fluoropolymers. Article 2J of the MP, sets out destruction requirements for HFC-23 from HCFC-22 production; however, there are also significant high GWP by-products associated with TFE/HFP production from HCFC-22, that if emitted contribute to global warming.

ExCom meetings[27] have discussed what residual emissions of HFC-23 by-product would satisfy the requirement that HFC-23 by-product is destroyed to the extent practicable. ExCom decided at its 89th meeting, part II (June 2022)[28] to confirm:

- That HFC-23 by-product was destroyed to the extent practicable in the context of Multilateral Fund-supported projects when up to a maximum of 0.1 kg of HFC-23 by-product was emitted per 100 kg of the relevant Annex C, Group I or Annex F substance produced.

- That HFC-23 by-product controls would be eligible independent of whether the relevant production that generated the HFC-23 was for controlled or for feedstock uses.

- That the term "production" in the context of HFC-23 by-product emission control projects supported by the Multilateral Fund meant the total amount of relevant Annex C, Group I or Annex F substance produced for all uses, including controlled and feedstock uses, irrespective of any subsequent destruction, recycling, and reuse.

Some HCFC-22 production units achieve significantly lower HFC-23 emissions than 0.1 kg/100 kg HCFC-22 by adopting a range of emission abatement measures. The production of TFE/HFP from HCFC-22 also generates high GWP by-product emissions (HFC-23 and PFC-c-318). If unabated, these emissions as CO_2e are higher than the estimated emissions of HFC-23 from HCFC-22 production when applying the Executive Committee indicated maximum emission rate for HFC-23 from HCFC-22 production. Parties may wish to consider the significance of these potential emissions.

Emissions of octafluorocyclobutane (PFC-c-318, $c\text{-}C_4F_8$), inferred from atmospheric measurements have been increasing sharply since the early 2000s. Emissions rose from near zero in the 1960s then declined to in the mid-1990s to early 2000s, followed by a rise since the early 2000s. PFC-c-318 is a by-product from TFE and HFP production and its emissions have been correlated[29] with the production and use of HCFC-22 as feedstock[30] as almost all HCFC-22 (97%) is used to produce TFE/HFP. Process controls or abatement to reduce the PFC-c-318 by-product were probably not in place in the early decades, explaining the increase in emissions in the 1960s and 1970s. With the advent of by-product reporting requirements to the United Nations Framework Convention on Climate Change (UNFCCC) in the 1990s, concern about climate change and product stewardship,

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[27] Executive Committee of the Multilateral Fund, Meeting Documents: UNEP/OzL.Pro/ExCom/88/76, 9 December 2021; UNEP/OzL.Pro/ExCom/89/13, 11 February 2022.

[28] Executive Committee of the Multilateral Fund, Meeting Document: UNEP/OzL.Pro/ExCom/89/16, 18 June 2022.

[29] A correlation is a derived mathematical association between emissions of octafluorocyclobutane (PFC-318), the high-GWP by-product in the manufacture of TFE and HFP, and HCFC-22 production, used as the feedstock in TFE and HFP production. TFE and HFP are used in fluoropolymer production. Almost all HCFC-22 that is produced and used as feedstock is pyrolysed to produce TFE and HFP, a process in which PFC-318 is a known by-product. This process, using HCFC-22 as feedstock, results in a significant proportion of the global PFC-318 emissions.

[30] Mühle, J., *et al*., Global emissions of perfluorocyclobutane (PFC-318, c-C4F8) resulting from the use of hydrochlorofluorocarbon-22 (HCFC-22) feedstock to produce polytetrafluoroethylene (PTFE) and related fluorochemicals, *Atmos. Chem. Phys*., 2022, **22**, 3371–3378. https://doi.org/10.5194/acp-22-3371-2022.

abatement, and perhaps the collection of PFC-c-318 by-product for use in the semiconductor industry where it can be easily abated, it is conceivable that emissions in developed countries were stabilised and then reduced, explaining the observed emission reduction in the 1980s and 1990s.[31] In 2020, emissions of PFC-c-318, inferred from atmospheric measurements, were 2,320 tonnes (24 million metric tonnes CO_2e or $MMTCO_2e$). The global emission factor is estimated to be about 0.3 kg PFC-c-318 per 100 kg of HCFC-22 feedstock used (to produce TFE and HFP).

The GWP of PFC-c-318 is very high (10,300 AR4), similar to HFC-23 (14,800) but it has an extremely long atmospheric lifetime (3200 years compared to 228 years for HFC-23, AR6 values). However, as noted some TFE/HFP production plants, particularly in non-Article 5 parties have emission abatement technology, such as a thermal oxidiser. PFC-c-318 may also be recovered or recycled or captured for others uses[32] and according to published information it can be pyrolyzed to TFE[33,34], although it is not known if this process is used. Therefore, the PFC-c-318 by-product generation rate is expected to be higher than the inferred global emission factor. According to the Mühle 2022 paper, process control and optimization to reduce the formation of PFC-c-318 and other by-products are complex, and under unsuitable conditions PFC-c-318 by-production could be as high as 14%. On the other hand, co-feeding several percent of PFC-c-318 to the HCFC-22 feed could reduce additional PFC-c-318 formation to less than 0.5% of the combined TFE and HFP yield, thus increasing combined TFE and HFP yield to more than 96 %. However, perfect process control may be impractical.

The TFE/HFP production process generates several other by-products, including HFC-23. The HFC-23 generation rate will depend on the reaction conditions and a wide range of HFC-23 yields relative to TFE production have been reported in process patents and papers (see Table 2. 3). Converting these to HFC-23 generation rates relative to HCFC-22 feedstock consumption is imprecise, as complete mass balance data is not included in the published information, in particular the yields of HFP and by-products. HFP yields depend on reaction conditions.[35] However, indicative generation rates can be estimated and are shown in Table 2.3 and a widely different HFC-23 generation rates have been reported.

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[31] Mühle, J., *et al.*, Perfluorocyclobutane (PFC-318, c-C4F8) in the global atmosphere, *Atmos. Chem. Phys.*, 2019, **19**, 10335–10359. https://doi.org/10.5194/acp-19-10335-2019.

[32] Recent industry marketing information indicates PFC-c-318 offered for sale "*to make mixed refrigerant to replace CFCs refrigerant, electronic industrial cleaner, aerosol, spray, solvent, super-large scale integrated circuit etchant, electrolyte when mixed with sulphur hexafluoride, and medium of fluorinated compound*".

[33] Butler J.N., The Thermal Decomposition of Octafluorocyclobutane, *J. Am. Chem. Soc.*, 1962, **84**, 8, 1393–1398, https://doi.org/10.1021/ja00867a012.

[34] Bjornson, G., *et al.*, Pyrolysis of octafluorocyclobutane, United States Patent US-3652691-A, Mar 28, 1972.

[35] Broyer, E., Bekker, A.Y., Ritter, A.B., Kinetics of the pyrolysis of chlorodifluoromethane, *Ind. Eng. Chem. Res.*, 1988, **27**, 208–211. https://doi.org/10.1021/ie00073a039.

Table 2.3 HFC-23 generation rates relative to TFE/HFP and HCFC-22

Data Source	HFC-23 generation rates kg/100 kg		Comments
	relative to TFE/HFP	relative to HCFC-22	
European Patent EP 1 260 494 B1, 2008, Method for producing tetrafluoroethylene	0.08 – 0.09	0.04 – 0.05	HFP yield is not reported, assumed that HFP is 10% of TFE, and unconverted HCFC-22 is recycled, other by-products assumed to be minor
United States Patent No. 4898645, 1990, Process for the production of pure tetrafluoroethylene	0.26	0.15	HFP yield is not reported, assumed that HFP is 90% of a group of by-products and HCFC-22 use takes these into account, and unconverted HCFC-22 is recycled
Catalytic Pyrolysis of Difluorochloromethane to Produce Tetrafluoroethylene, D. Sung, D. Moon, Yong Jun Lee, Suk-In Hong 2004, International Journal of Chemical Reactor Engineering, https://doi.org/10.2202/1542-6580.1065	0.93	0.52	The paper reports a range of selectivities for TFE, HFC-23 and HFP. Data reported here is for the non-catalytic process. The catalysed processes mainly produce similar selectivities for HFC-23

Although some TFE/HFP plants have emission abatement technology, HFC-23 emissions might be expected to be associated with PFC-c-318 emissions[36] for those plants that do not have emission abatement technologies. The table compares HFC-23 and PFC-c-318 by-product factors from TFE/HFP production with the emission factor of HFC-23 from HCFC-22 that ExCom considers meets the requirement of destroyed to the extent practicable. In this table, only the low (0.04) and medium (0.15) HFC-23 generation rates are used to calculate potential emissions, in the absence of abatement technologies.

Table 2. 4 By-product emission or generation factors for HFC-23 and PFC-c-318 from the overall manufacturing process to produce TFE and HFP from HCFC-22

	Emission or generation factor kg/100 kg HCFC-22	GWP (AR4)	Emissions	
			Metric tonnes	MMTCO$_2$e
Maximum allowable HFC-23 by-product emission from HCFC-22 FS (meeting requirements *destroyed to the extent practicable* in the context of Multilateral Fund-supported projects)	0.1 emission factor	14,800	710	11
HFC-23 by-product generation from TFE/HFP production based on HCFC-22 FS use	indicative generation factors MEDIUM 0.15 LOW 0.04	14,800	generation 1,040 280	generation 15 4
PFC-c-318 by-product emission from TFE/HFP production based on HCFC-22 FS use	0.3 emission factor	10,300	2,080	21

Notes: HFC-23 by-product is from HCFC-22 feedstock only, i.e., excludes non-feedstock use to allow comparison with TFE/HFP related emissions. Reported 2020 HCFC-22 feedstock data is used, with 97% of this used for TFE/HFP production. As expected, calculated emissions of PFC-c-318 are slightly different to those inferred from atmospheric measurements. The global emission factor for HFC-23 from TFE/HFP will depend on the relative use of abatement technologies.

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[36] Note that for any distillation process for TFE purification, HFC-23 is a 'light' with a very low boiling point -82.1°C, similar to TFE (-76.3°C), whereas PFC-c-318 is a high boiler with a boiling point -6°C. HFC-23 and PFC-c-318 may be separated or emitted at different points in the purification process.

2.3.3 Emissions of HFC-23 from production of HFC-32 by hydrofluorination of dichloromethane

It is known that HFC-23 can be formed as a by-product during the production of HFC-32 from dichloromethane by reaction with hydrogen fluoride.

HFC-23 emissions are reported from one HFC-32 producer in the United States (Envirofacts[37]). Assuming all HFC-23 emissions are from the production of HFC-32 at the facility, which is likely based on knowledge of the fluorochemicals produced by the facility, the emission rate of HFC-23 from this plant is estimated at 0.1% or less in 2020, based on the reported emissions (Envirofacts) and publicly stated production capacity. The reported emissions of the site have decreased over the period 2012–2020 by 86%. This facility has reported abating HFC-23 emissions (EPA 2021 Facilities with HFC-23 emissions[38]).

Information provided from China also suggests up to about 0.1% HFC-23 may be generated from an HFC-32 production process.

Some information about HFC-23 generation is available in patent literature. While the patent literature most likely does not reflect what is achieved in a well-designed production unit, it does indicate that HFC-23 may be generated in some liquid phase and vapour phase processes.

According to one published process patent[39], in a vapour phase fluorination process, HFC-23 is formed with a selectivity of 1.3% in one reaction example. In this reaction example, the by-products are chiefly trichloromethane, HCFC-21 (fluorodichloromethane), HCFC-22 (chlorodifluoromethane) and HFC-23 (trifluoromethane), with average selectivity of 0.5%, 0.1%, 0.1% and 1.3% respectively. Another reaction example found the same by-products, but no yields were reported. The vapour phase process uses a gaseous feed of hydrogen fluoride, chlorine, and dichloromethane. The reaction is carried out in the presence of chlorine to lengthen the lifetime of the catalyst.

One patent application[40] covers the liquid phase fluorination by hydrogen fluoride of dichloromethane to give HFC-32 in the presence of chlorine and of a catalyst, which has antimony pentachloride as one component of the catalyst. The application states that other fluorocarbons are capable of being produced during the catalytic reaction, in particular HCFC-22 and HFC-23. Recycle to the catalytic reaction chamber results in the eventual conversion of HCFC-22 to HFC-23. The patent application states that the HFC-23 by-product production represents an amount of less than 2%, preferably of less than 0.5%, and typically of less than 0.1%. Examples also show the absence of HFC-23. The application claims that a previously patented process[41] to produce HFC-32 from dichloromethane in the liquid phase, using antimony pentachloride catalyst, without the addition of chlorine, leads to the formation of HCFC-22 and HFC-23.

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[37] U.S. EPA, 2021, *Greenhouse Gas Reporting Program (GHGRP), 2020 Envirofacts, Subpart HH: Municipal Solid Waste Landfills and Subpart L: Fluorinated Gas Production*. https://www.epa.gov/enviro/greenhouse-gas-customized-search

[38] U.S. EPA, 2021, Stratospheric Protection Division, Office of Air and Radiation (OAR), *Facilities with HFC-23 emissions*, April 2021. https://www.regulations.gov/document/EPA-HQ-OAR-2021-0044-0046.

[39] Requieme, B., *et al.*, 2001, Process for the manufacture of difluoromethane, United States Patent US-6242659-B1, Jun. 5, 2001. Example 4 gives by-product yields, including HFC-23. See also example 1.

[40] Pigamo, A., *et al.*, Method for producing difluoromethane, United States Patent Application Publication US 20150210617-A1, Jul. 30, 2015.

[41] Cerri, G., *et al.*, Process for the preparation of difluoromethane, World Patent WO/1999/025670, May 27, 1999.

Patents[42,43] for processes to purify crude HFC-32 from dichloromethane reaction with hydrogen fluoride, in the liquid or vapour phase, discuss the separation of HFC-32 from hydrogen fluoride and by-products including HFC-23.

There are at least four possible routes that could lead to the formation of HFC-23 as by-product during the production of HFC-32 by fluorination of dichloromethane.

a) Chloroform impurity in the dichloromethane feedstock, which could be fluorinated to HFC-23. This is the same process that produces HFC-23 by-product during HCFC-22 production. However typically only very small quantities of HFC-23 would be produced, around 10–20 ppm.

b) For swing plants there is the risk of ineffective cleaning of the plant when swinging from HCFC-22 to HFC-32 leaving traces of chloroform, HCFC-21 or HCFC-22 that may react further to give HFC-23, but this should be transient and minor.

c) For liquid phase fluorination, chlorine may be added to the reactor to maintain the antimony catalyst in its pentavalent state. The addition of chlorine to the reactor to maintain the catalyst in its pentavalent state could also cause some production of HFC-23, via chlorination of dichloromethane to chloroform, or HCFC-31 to HCFC-22.[44] Fluorination would then eventually lead to HFC-23. Increased generation of CFC-12 on HCFC-22 plants occurs in the same way if the chlorine addition is excessive. Similar reactions may occur for vapour phase fluorination in the presence of chlorine.

d) If HFC-23 is produced then this may also result from the composition and condition of the catalyst, the possible presence of other oxidising substances and disproportionation/ dismutation reactions. However, the mechanism to produce these by-products is uncertain.

Further information is required to better characterise the range of HFC-23 by-product generation from the production of HFC-32 by hydrofluorination of dichloromethane process.

2.3.4 Electronic fluorination of alkanes and by-production of HFC-23

Electrochemical fluorination is used to produce a variety of organofluorine compounds including fluorinated intermediates and fully fluorinated fluids. The process passes electric current through a mixture of an organic compound and anhydrous hydrogen fluoride to replace C-H bonds with C-F bonds. In most cases, the intent is to create a perfluorinated analogue of the starting organic compound.

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

During electrochemical fluorination, some carbon-carbon bonds can be cleaved and various partially fluorinated by-products, including HFC-23, may be produced depending upon the process conditions. The largest commercial-scale operations of electrochemical fluorination use emission control technologies such as thermal oxidizers to abate emissions. Destruction efficiency of the thermal oxidation processes have been measured at > 99.9%.

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[42] Galland, J-M., *et al.*, Process for the separation of hydrogen fluoride and of difluoromethane, United States Patent US-5707497-A, Jan. 13, 1998.

[43] Tsuda, T., *et al.*, Process for producing difluoromethane, United States Patent US-6375808-B1, Apr. 23, 2002.

[44] Antimony pentachloride can be used as a chlorination (oxidation) catalyst, methane can be chlorinated by $SbCl_5$ using different reaction conditions to give to methyl chloride, methylene chloride and chloroform. See Krause, E., Process for the chlorination of methane, United States Patent US-1677831-A, Jul. 17, 1928.

2.3.5 *Other possible pathways to the by-production of HFC-23 during the production of controlled substances*

In a similar manner to the way that low or trace levels of HFC-23 can be generated in and emitted from HFC-32 production plants, other fluorocarbon production processes, such as for HFC-134a, HFC-125, HFC-143a, and possibly from some steps of HFO production processes, can result in by-production of HFC-23[45], amongst a range of other fluorochemicals, although preliminary data indicates at much lower generation rates.

The likely routes for by-production of HFC-23 include:

- Chloroform being an impurity in the chlorinated feedstock, which is hydro fluorinated to HFC-23
- Dichloromethane being an impurity in the chlorinated feedstock, which is subsequentially converted to chloroform in the presence of chlorine and then hydro-fluorinated to HFC-23
- Breaking of the C-C bond in chemicals species of that contain 2 or more carbon molecules with a near fully or fully halogenated terminal group. This terminal group is then split off and hydro fluorinated to form HFC-23.

The generation rate of HFC-23 in any given process can vary as its formation will depend on several factors including the availability of chlorine, the catalyst and its composition, temperature, pressure, the presence of free radicals, amongst others. For example, if the periodic regeneration of the catalyst causes a transient higher level of high oxidation states of the chromium component, then the HFC-23 generation rate from breaking of the C–C bond may increase until the catalyst composition stabilises.

Preliminary data from a small selection of HFC-134a and HFC-125 production processes indicate that HFC-23 generation rates average less than ~0.01% by weight HFC-23/tonne of HFC-134a/HFC-125, which is considerably lower than the HFC-23 by-production generation rates in HCFC-22 and HFC-32 production.

The quantity of HFC-23 emitted will also vary depending on the design of the plant. Plants with an integral destruction facility to treat fluorocarbon containing vents will only emit a fraction of their total HFC-23 generation rate.

2.3.6 *CFC-113, CFC-114, CFC-115 by-production on HFC-125 plants*

Perchloroethylene (PCE) can be used to make either CFC-113/-114/-115 or HCFC-123/HCFC-124/HFC-125 using anhydrous hydrogen fluoride (aHF).

The CFC-113/-114/-115 process initially reacts the PCE with chlorine to produce hexachloroethane which is then successively reacted with aHF to substitute the chlorine atoms for fluorine ones.

$$C_2Cl_4 + Cl_2 \rightarrow \underset{\text{hexachloroethane}}{C_2Cl_6}$$

$$C_2Cl_6 + HF \rightarrow C_2Cl_5F + HCl$$

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[45] It is noted that HFC-23 is only likely to be identified if it is specifically analysed for, so some fluorocarbon plants could be forming and emitting small quantities of HFC-23 without being aware that they are.

CFC-111

$C_2Cl_5F + HF \rightarrow C_2Cl_4F_2 + HCl$

CFC-112

$C_2Cl_4F_2 + HF \rightarrow C_2Cl_3F_3 + HCl$

CFC-113

$C_2Cl_3F_3 + HF \rightarrow C_2Cl_2F_4 + HCl$

CFC-114

$C_2Cl_2F_4 + HF \rightarrow C_2ClF_5 + HCl$

CFC-115

The HFC-125 process initially reacts the PCE with aHF to produce HCFC-121 which is then successively reacted with aHF to substitute the chlorine atoms for fluorine ones.

$C_2Cl_4 + HF \rightarrow C_2HCl_4F$

HCFC-121

$C_2HCl_4F + HF \rightarrow C_2HCl_3F_2 + HCl$

HCFC-122

$C_2HCl_3F_2 + HF \rightarrow C_2HCl_2F_3 + HCl$

HCFC-123

$C_2HCl_2F_3 + HF \rightarrow C_2HClF_4 + HCl$

HCFC-124

$C_2HClF_4 + HF \rightarrow C_2HF_5 + HCl$

HFC-125

The omission of chlorine from the HFC-125 production process should prevent the formation of CFC-113/-114/-115, however analyses of the streams within HFC-125 plants indicate that low levels (less than a few thousand ppm) of CFC-113/-114/-115 is present. The source of this CFC-113/-114/-115 is believed to be due to a combination of factors including impurities in the PCE feed stock being precursors to CFC-113/-114/-115, the composition and status of the catalyst, the possible presence of other oxidising substances and dismutation/disproportionation reactions with some of the later intermediates such as HCFC-123 being more likely to produce CFC-113/-114/-115 than others. CFC-115 is difficult to separate from HFC-125 with additional separate steps being required. As the CFC-115 has no commercial value it is likely to be emitted unless abatement technology is installed.

The HFC-125 production process can also form small quantities of HFC-23 as a by-product with emissions being reported with indicative emission factors of less than 0.01% by weight per tonne of product (see section 2.3.5).

2.4 Production of intermediates that are substances listed in Annexes A to F

Intermediates are the chemical building blocks that raw materials go through when being chemically transformed into products. As mentioned above for feedstocks there is also no definition for intermediates. However, there is the definition of "controlled substances produced" in Article 1, paragraph 5, *"Controlled substances produced" as used in Article 1, paragraph 5 is the calculated level of controlled substances manufactured by a party. This excludes the calculated level of controlled substances entirely used as a feedstock in the manufacture of other chemicals…"* The term "manufactured" is not defined; although a common-sense definition is "to make or process (a raw material) into a finished product". In addition, Decision IV/12, clarifies the definition of controlled substances "*That insignificant quantities of controlled substances originating from inadvertent or coincidental production during a manufacturing process, ……, shall be considered not to be covered by the definition of a controlled substance contained in paragraph 4 of Article 1 of the Montreal Protocol*".

In this section, intermediates are substances that are formed and subsequently consumed within the same process during the production of a final product.

In chemical production, intermediates are either isolated or not isolated within the same process prior to consumption to make the final product.

A non-isolated intermediate formed in a chemical process is not considered as a finished product while it remains within the chemical process. As such, a non-isolated intermediate is not commonly reported under Article 7 (see section 2.2.2).

For the purposes of this section, controlled substances that are produced, isolated, and stored prior to being transferred to a different process plant (even if within the same establishment) are not considered intermediates because they follow a more traditional feedstock definition used by industry.

The production, handling, and subsequent consumption of intermediates can vary significantly:

- Some intermediates are extremely transitional being consumed practically as soon as they are formed within the same reactor vessel, with only low concentrations within the reactor and little or no presence outside of the reactor.

- Other intermediates, such as HCFC-21 in the HCFC-22 production process, are formed and consumed in the same reactor vessel but have a low, but measurable, concentration in the reactor vessel and within other downstream parts of the processes. Hence a feedback route to the reactor vessel is usually employed for these intermediates to maximise conversion.

- Other intermediates, such as HCFC-133a in some HFC-134a processes, can be formed in one reaction loop, separated, and then consumed in a subsequent reaction loop within the same process.

With these different possible intermediate formation and consumption routes it follows that there will be a wide range of emission factors for intermediates from these processes. Logically, those intermediates that are formed and consumed almost immediately within a single vessel will have a much lower intrinsic, tending to insignificant, potential for emission, with an emission factor of near zero. Whereas, an intermediate formed, processed, and potentially held between different reaction loops within the same process will have a higher intrinsic potential for emission, although the emission factor could still be expected to be considerably lower, by one or more orders of magnitude, than those of the final product, which goes through a more extensive range of purification process and hence has a higher number of possible emission points (see section 2.5.5 on emission factors due to production).

Examples of high-volume chemical products that may be produced via non-isolated intermediates that are controlled substances are presented in Table 2.5.

Table 2.5 High-volume chemical products that may be produced by non-isolated intermediates listed in Annexes A to F (non-exhaustive list)

Product	Feedstock	Non-isolated intermediates listed in Annexes A to F
CFC-11	CTC	
CFC-12	CTC	CFC-11
CFC-113	Perchloroethylene	CFC-112
CFC-114	Perchloroethylene	CFC-112, CFC-113
CFC-115	Perchloroethylene	CFC-112, CFC-113, CFC-114
HCFC-22	Chloroform	HCFC-21
HFC-32	Dichloromethane (CH_2Cl_2)	HCFC-31
HFC-125	Perchloroethylene	HCFC-121, HCFC-122, HCFC-123, HCFC-124
HFC-134a	Trichloroethylene; or CFC-113	HCFC-132b, HCFC-133a, HCFC-131a; or CFC-113a, CFC-114a, HCFC-124a
HFC 143a	1,1-dichloroethylene or 1,1,1-trichloroethane	HCFC-141b, HCFC-142b
HFC-152a	Vinyl Chloride	HCFC-151a
HFC-245fa	HCC-240fa	HCFC-243fa, HCFC-244fa
HFO-1234yf	Hexafluoropropene	HFC-236ea, HFC-245eb
HFO-1234yf	HCC-1230xa or HCC-240db	HCFC-244bb
Trifluoropropylene	Tetrachloropropane	HCFC-253ea

Explanatory note: CFC-11, CFC-12 and CFC-115 are not, or not typically, used as feedstock. Small quantities of CFC-12 may be reported in some years. Previously they were high volume chemicals. As the production of CFC-113 for emissive uses in no longer permitted, the conversion of CFC-113 to CFC-113a is assumed to be a feedstock use (as noted in UNEP/OzL.Pro/ExCom, 88/78 Annex and in the 2021 TEAP Progress Report). Where some chemicals are formed, their isomeric forms might also be formed in side-reactions. For example, where CFC-112 is formed, CFC-112a might also be formed in low concentrations. HCC-240fa is 1,1,1,3,3-pentachloropropane; HCC-1230xa is 1,1,2,3-tetrachloro-1-propene; HCC-240db is 1,1,1,2,3-pentachloropropane.

2.5 Production emissions and their mitigation

An emission is usually considered to be the release of a substance into the environment; although often used to describe gas releases to the atmosphere, they can also include substances released in solids or liquids that later transition to the atmosphere. For example, the HFC-23 emission from an HCFC-22 process may include both direct emissions of HFC-23 from a vent and HFC-23 degassed to atmosphere during subsequent treatment of the aqueous effluent.

In some processes, substances can be dissolved or entrained in some of the co-products and can then be released to the environment in the location where these co-products are subsequently stored and used, which is often remote from the plant that produced them. For example, HFC-23 can be dissolved or entrained in the co-produced hydrochloric acid on an HCFC-22 process. The dissolved or entrained HFC-23 is then degassed to atmosphere from locations where the hydrochloric acid is subsequently stored and used. This can result in a wide dispersal of the eventual HFC-23 transitions to atmosphere and an apparent proliferation of secondary HFC-23 emission sources. It should be noted that this is not additional by-production of HFC-23 from either the HCFC-22 process or at the point of emission. The quantity of HFC-23 released in these dispersed emissions can vary widely as the quantity involved is dependent on several factors involved in the design and operation of the producing plant. These dispersed emissions are expected to account for <1% by weight of the total HFC-23 by-production of the HCFC-22 process. These dispersed emissions are typically unmitigated at point of release.

Emissions can be of products, co-products[46], intermediates, feedstock, or by-products; which of these are being emitted will have an important bearing on how the operation mitigates those emissions.

2.5.1 Emission of products, co-products, intermediates, and feedstocks

Emissions of products, co-products, intermediates, and feedstocks from processes are economically undesirable and the operators of the process will seek to minimise them. To achieve this the process will usually be designed, operated, monitored, and controlled to optimise feedstock to product ratios, and hence minimise product, co-product, intermediate and feedstock emissions within the limits of the plant design capability.

Most processes will employ a range of elements of good practice for minimising emissions of feedstocks, intermediates, and products, such as:

- Operating instructions documenting how to consistently achieve the desired optimum operation
- Training
- Instrumentation to allow suitable monitoring and control of the process
- Routine sampling and analysis of raw material, product and solid and liquid effluent and vent streams
- Routinely recording, trending, and reviewing relative feedstock consumption and product production ratios

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[46] Associated products that have a commercial value but are not the main product of the process, e.g., in the case of controlled substances, hydrochloric acid (HCl aq.) is a common co-product with a low sales value relative to the cost of chlorine.

- Periodic plant mass balancing
- Plant tours
- Maintenance procedures including routine leak checking
- Consideration of inherent emissions when selecting equipment, e.g., sealless pumps
- Consideration of the materials of construction.

The operator may even, in some cases, alter the physical design of the process to reduce these emissions if there is a suitable case to do so.

2.5.2 Emissions of unwanted by-products

Emissions of unwanted by-products, and to a lesser extent low value co-products, is a different consideration. For financial reasons, a process will typically seek to minimise the formation of unwanted by-products because by doing so it will typically maximise its desired product to feedstock conversion ratios. Nevertheless, in some cases an increase in the rate of production of the desired product at the expense of a higher by-product production rate may be economically attractive. There would usually be a need to include additional equipment (such as destruction or separation and chemical transformation technologies), with further operating and maintenance costs to the process to mitigate these unwanted by-product emissions. However, the lack of a clear environmental, safety or economic drivers has often meant that, once produced, these unwanted by-products are emitted unabated.

If there are no financial incentives, regulatory controls may be needed to ensure that the emissions of unwanted by-products produced by the process are minimised. Various techniques are possible to treat unwanted by-products to minimise their emission. These techniques are typically end-of-pipe processes that destroy or convert the unwanted by-products to environmentally acceptable substances; e.g., conversion of the HCl and HF to hydrochloric and hydrofluoric acids or salts such as NaF and NaCl using aqueous scrubbing systems; or the thermal oxidation of HCFCs to water, CO_2, HCl and HF and the subsequent conversion of the HCl and HF to salts such as CaF_2 and $CaCl_2$ or in some cases the absorption of certain organic species on an absorbent (e.g., activated carbon) prior to appropriate disposal or regeneration of the absorbent.

2.5.3 Emissions monitoring

The determination of emission rates by process operators can be complex often requiring the monitoring of the flow and composition of numerous process streams. The physical and chemical characterises of these streams may also present significant challenges to achieve a sufficiently reliable and accurate set of data. In additional it is difficult to obtain a complete coverage of all emission as, for example, fugitive (unintended) emission points (e.g., leaks from pipework, flanges or fittings) are not suitable for continuous measurement and usually must be estimated/determined by mass balancing the flows into and out of the process.

The ability of processes to monitor, and the accuracy of the determination of, their substance emissions rates will vary. Some modern suitably designed, operated and highly instrumented processes may have continuous flow and frequent composition monitoring of all relevant flows into and out of the plant and be able to consistently balance the inputs and outputs, including emissions, from the plant to a reasonably high degree of accuracy, less well instrumented and monitored plants, maybe only covering the major raw material, product and vent steams, are still likely to mass balance their process but will only be able to do so to a lower accuracy and will be less able to determine the chemical species and route of any emissions.

Factors that affect the amount of instrumentation and the accuracy of the determination of emissions are numerous and include, for example:

- the age and design of the plant
- the presence (where in the process, for how long, with which other substances and in what physical state) of the chemical species being emitted
- the suitability of the measurement technique for the parameter to be measured
- the degree of accuracy and frequency of measurements of the flows and compositions of the various feedstocks, products, and emission points
- the number of possible (normal, emergency and fugitive) emission points to be monitored
- the percentage of the emission points monitored
- the regulatory requirements to measure and document emissions,
- the perceived economic value and hence resources expended by the operator to estimate, control, minimise, and mitigate emissions.

In general, the more resource and importance an operator places on determining emissions and the higher the completeness, reliability and accuracy of the data obtained from the plant, the more accurate the mass balance and hence the more accurate the determination of the emissions.

2.5.4 Emission reporting

Many national regulations require the operators of chemical processes to report the level of emissions from the production of a range of substances including many controlled substances. Many of these reports are publicly available although it is often difficult to derive an accurate emission factor as a percentage of the product produced as typically only incomplete data on production rates is publicly available.

There is also a requirement to report a basket of HFCs to the UNFCCC[47]; these emissions cover a different scope and often a different calculation methodology to the paragraph above as they include an estimation of emissions whilst in use and at end of life.

2.5.5 Emission factors for production and distribution and use as feedstock for controlled substances

Previously, MCTOC used an emission factor of 0.5%, based on HFC production default emission factor, 2006 IPCC Guidelines on National Greenhouse Gas Inventories, to estimate emissions from production of ODS for feedstock use.[48] In 2020, MCTOC[49] updated its emission factors for production and use of feedstock, taking into account the IPCC 2019 Refinement to the 2006 IPCC Guidelines (Tier 1) emission factor applicable to HFCs, which has a default emission factor of 4%, with a range between 0.1% to 20%. The unexpected emissions of CFC-11 prompted a further review of the emissions factors that could apply to a range of production plant vintages, design and operation

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[47] For example, UNFCCC, National Inventory Submissions 2021 | UNFCCC

[48] UNEP, 2018, *2018 Report of the Medical and Chemical Technical Options Committee, 2018 Assessment Report*, December 2018.

[49] UNEP, 2020, *Report of the Technology and Economic Assessment Panel, Volume 1, Progress Report*, May 2020.

and maintenance policies. The 2019 TEAP Task Force on Unexpected Emissions of CFC-11 estimated a range of emission rates scenarios for CFC-11 production and distribution:

- 4% by weight for low emissions
- 7% by weight for medium emissions
- 10% by weight for high emissions.

These were based on assumptions around combinations of modern, well-designed, operated and maintained facilities with low emission rates together with older facilities and some small micro-scale plants with considerably higher emission rates, and consider the long range of years of production for which the modelling extended (1930s to 2010s).

More recently, MCTOC has reviewed and revised emission factors set out in the following Tables (2.6, 2.7, 2.8) for production, distribution, and feedstock use. These points are important for the applicability of the emission factors:

- Controlled substances have a wide range of boiling points which affects the requirements for storage distribution handling and use. For example, HFC-32 boiling point -52°C, and 1,1,1-trichloroethane boiling point 74.1°C.
- Modern well designed, maintained, and operated production units can have a range of emissions, including depending on abatement technologies used.
- Distribution emissions will depend on the transport and handling requirements, from pipeline, bulk transport, e.g., for feedstock use or equipment manufacturing such as car air-conditioning, and bulk transport followed by repackaging into smaller containers for on-site Refrigeration and air-conditioning equipment charging and servicing. Emissions from storage and distribution of bulk quantities are likely to be significantly lower than during production. However, the contribution of emissions from distribution depends on where the distribution boundary is set. If it includes delivery to end user for refrigerants, large-scale use of disposable containers could lead to significantly increased emissions.
- Bulk feedstocks are typically consumed early in the subsequent chemical process, likely resulting in minimal rates of emissions. Emissions during feedstock production are likely to dominate related overall total emissions for feedstock production and use. For example, the reported emission rate for feedstock use in the European Union was 0.03% in 2018.[50] Feedstock transported by pipeline between production plant and feedstock use plant will eliminate most distribution emissions. Distribution EF can be weighted for onsite/offsite feedstock use, e.g., in 2019, CTC was estimated as 50% onsite and 50% offsite feedstock use.
- By-product emissions, e.g., HFC-23 from HFC-22 production, are not included in this section.

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[50] UNEP, 2020, *Report of the Technology and Economic Assessment Panel, Volume 1, Progress Report*, May 2020.

Table 2.6 **Emission factors for modern-day, regulated manufacturing from production and supply chain (by weight of production)**

Production and supply chain emissions – Current Day in Heavily Regulated Sophisticated Plants	**Low**	**Most Likely**	**High**
Production			
Losses from normal chemical plant production including maintenance [a]	0.1%	**0.5–2% [b]**	4%
Losses when filling drums, tanks, cylinders and containers using quick-connects or hoses under vacuum return systems or other abatement	*de minimis* 0.1%	**0.4–2%**	3%
Production emission factor (most likely) **Emission factors from use as feedstock are different and additive**		**0.9–4%** **Mean ~ 2.5%**	
Distribution			
Losses from drums, isotanks, cylinders, and containers through shipping and storage in supply chain	*de minimis* 0.1%	**0.1–1%**	2% [c]
Non-returnable cylinder heels Relevant only if non-returnable cylinders are used to a significant extent for distribution. See explanation below for emission factors.	3%	4%	6% [d]
Returnable cylinder, tank and other heels that are collected at end-of-life and likely recycled or destroyed includes maintenance and de-NAG and testing tanks and cylinders	*de minimis* 0.1%	**0.2%**	0.5%
Distribution emission factors to be used depend on knowledge of applicable supply chain but could *most likely* add 0.3 – 1.2% (excluding disposable cylinders). EF this range will depend on distribution method. Pipeline transport to a feedstock plant would essentially eliminate these emissions.			
[a] Irregular leaks (hole in plant equipment or piping) are included in overall plant losses above (as determined by mass balance) [b] Varies by chemical, boiling point, mitigation, and local regulations, ambient temperature etc. [c] Includes an element for low frequency fugitive emissions due to container or fitting damage or relief stream activation resulting in an unintended leak [d] Values above 6% on individual cylinders or certain container substance combinations would be possible but would indicate that the container had not been fully emptied before the emission occurred either because it was deliberately vented or discarded prior to being fully emptied or the contents leaked in use or storage			

Table 2.7 Emission factors for modern-day, regulated production for feedstock use (by weight of production)

Feedstock emissions from feedstock conversion plants – Current Day in Heavily Regulated Sophisticated Plants	Low	Most Likely	High
Production: feedstock processing			
Losses from feedstock process including maintenance [a]	0.1%	**0.3%–0.9% [b]** **Mean 0.6%**	3%
Distribution: supply to feedstock processing production unit			
Most deliveries in isotanks or pipeline so losses lower, accounting for supply chain losses under feedstock production (not counted here).			
[a] These losses are additive to production losses [b] Liquids at ambient temperatures e.g., CTC & 1,1,1-trichloroethane would be at the upper end if stored in atmospheric tanks (not-pressurised). Liquified gases e.g., HCFCs and HFCs would be at the lower end as stored in an enclosed system			

Table 2.8 Emission factors for 1960–1980s vintage, regulated manufacturing annual emissions from production (by weight of production)

Production emissions: 1960–1980s, regulated manufacturing plants	**Low**	**Most Likely**	**High**
Production			
Losses from normal chemical plant production including maintenance [a]	0.5–1%	**2–3% [b]**	4–5%
Losses when filling drums, tanks, cylinders and containers hoses typically without other abatement	0.5–1%	1–2%	3%
Production emission factor (most likely) [c]		**3–5% Mean 4%**	
Distribution			
Losses from drums, isotanks, cylinders, and containers through shipping and storage in supply chain	*de minimis* 0.1%	0.5–1% [d]	2.0%
Non-returnable cylinder heels Relevant only if non-returnable cylinders are used to a significant extent for distribution. See explanation below for emission factors.	3%	4%	6% [e]
Returnable cylinder, tank and other heels that are collected at end-of-life and likely recycled includes maintenance and de-NAG and testing tanks and cylinders	*de minimis* 0.1%	0.2%	0.5%

[a] Irregular leaks (hole in plant equipment or piping) are included in overall plant losses above (as determined by mass balance)
[b] Varies by chemical, boiling point, mitigation, and local regulations, ambient temperature etc.
[c] Higher emission factors were determined to be applicable for some small micro-scale plants with considerably higher emission rates (CFC-11 unexpected emissions)
[d] includes an element due to some packages (typically disposibles) arriving at end destination empty due to leaks or relief stream activation e.g., due to high ambient temperatures *en route*
[e] Values above 6% on individual cylinders or certain container substance combinations would be possible but would indicate that the container had not been fully emptied before the emission occurred either because it was deliberately vented or discarded prior to being fully emptied or the contents leaked in use or storage

In summary, based on the assumptions used, the mean values for the *most likely* emission factors for modern day regulated manufacturing are:

i. Production 2.5% (0.9–4%)

ii. Feedstock process 0.6% (0.3–0.9%)

iii. Distribution by bulk supply (not pipeline) for large volume users (feedstock and equipment manufacturers) is expected to be towards the lower end of the most likely range (0.3–1.2%), as it excludes transfers to smaller packages.

iv. Supply using repackaged smaller containers, and in particular disposable containers, will contribute to additional emissions depending on their relative use for each controlled substance.

2.5.6 Estimated emissions of controlled substances from production, distribution, and feedstock use

Emissions of controlled substances during their production, distribution and feedstock use contribute to overall global emissions. The global emissions are estimated using the most *likely emission* factors, not considering regional variations in emission rates. Distribution emissions depend on specific supply chains and containers used, such as disposable cylinders. Most feedstock uses bulk supply or pipeline delivery and, for this emission estimate, emission factor of 0.5% is used for distribution emissions (towards the lower end of the *most likely* range). For non-feedstock use, an emission factor of 0.8% is used for distribution emissions, which excludes any additional emissions due to the use of disposable cylinders.

Some controlled substances only have feedstock uses (1,1,1-trichloroethane and CTC). Total emissions of CTC are discussed in detail in Section 2.8.4. Emissions for total ODS are estimated for feedstock and non-feedstock uses as tonnes and ODP tonnes. Detailed analyses for individual substances might use different emission factors based on specific information.

The HFC data reported for 2020 and 2021 is incomplete due to the timing of reporting obligations, for example, depending on when some parties ratified the Kigali Amendment. Data confidentiality requirements mean that HFC production and estimated emissions are given as total metric tonnes and CO_2e. HFC used as feedstock is included in total HFC production, due to the dominance of one reported feedstock (HFC-152a). An indicative estimate of the yet to be reported HFCs is added as a note.

Table 2.9 Estimated emissions of controlled substances

Reported Production 2020	Production Tonnes	Emission Factor (EF)				Emissions		
		Production	Distribution	Feedstock use	Total EF	Metric Tonnes	ODP Tonnes	MMT CO_2e
ODS feedstock use	1,475,007	2.50%	0.50%	0.60%	3.60%	53,100	19,948	
ODS non-feedstock	284,942	2.50%	0.80%		3.30%	9,403	672	
HFCs total production incl. feedstock use	779,644	2.50%	0.80%		3.30%	25,728		42.8

Notes: *ODS non-feedstock production is the calculated production [calcProd = Production - Feedstock uses - Destruction - QPS uses for MeBr], negative reports were excluded. HFC reported production in 2020 probably accounts for about 80% of total HFC production (due to the timing of reporting obligations). Excludes emissions due to the use of disposable cylinders.*

2.6 Stocks of controlled substances

Stocks of controlled substances are held throughout the whole value chain of the production, distribution, equipment manufacturers, installation, and equipment maintenance industry. Stocks can also be in transit. The source of a company's supply of controlled substances, delivery times as well as the turnover of products needed to maintain a production facility for equipment containing controlled substances will determine the quantities of stocks (and the types of specific products) required to be kept.

The holding of stocks is a cost to the businesses and, in most cases, is carefully managed and minimised to reduce costs. For the producers of controlled substances, stocks can also be held to enable the efficient use of production facilities, to manage shutdowns of manufacturing facilities as well as for feedstock processes and for blending blends of products for the market (such as HFC blends). Producers are required to report their stocks to regulatory authorities on an annual basis.

The wide variety of types of stocks, the diverse numbers and types of companies that hold stocks, the commercial nature of this information, and changing stock quantities based on commercial factors, make it not possible for MCTOC to assess the quantity of stocks globally. Individual parties are likely to know stock quantities based on annual regulatory reporting.

Stocks will be held in a variety of containers that can range from stock tanks with a capacity of several hundred tonnes, either on major chemical facilities or offsite. They can also be held in iso-containers of approximately 20 metric tonnes or in tanks/drums from 1 tonne to a few kilogrammes. Emissions from the larger containers of controlled substances are already considered in the data considered by MCTOC. Most of the smaller containers will not leak and will retain the controlled substances until they are used by the end-user.

2.7 Some issues related to the chemicals industry sector

2.7.1 Illegal trade

The control of consumption and production of controlled substances and their import and export has led to illegal activities, primarily the illegal import into a wide variety of countries through smuggling or other methods.

Under the guidance of the Parties, UNEP OzonAction and the Ozone network have taken a wide variety of actions to assist Parties to detect and prevent illegal trade. These have included the provision of a detailed handbook as well as a series of Network meetings on the topic. The implementation of the Kigali Amendment has resulted in the control of Hydrofluorocarbons (HFCs). The European Union has already identified instances of illegal trade in HFCs and has both taken, and has in preparation, several measures to tackle the issue. The United States has, and is, taking action to combat illegal trade in HFCs. China has introduced a detailed reporting and monitoring system of imports and exports of HFCs to enable the control of HFCs.

Parties were invited in accordance with decision XIV/7, para.7 to report to the Ozone Secretariat fully proved cases of illegal trade in ozone-depleting substances to facilitate an exchange of information. The decision also requested the Secretariat to collect any information on illegal trade received from the parties and to disseminate it to all parties.

Decision XXXI/3 para. 5 (d) further encouraged parties to take action to identify and prevent illegal production, import, export and consumption of controlled substances and to report to the Ozone Secretariat on the cause of significant cases and actions taken to address them, to facilitate an exchange of information. The reports submitted by parties in relation to this decision are listed in the link, https://ozone.unep.org/countries/additional-reported-information/illegal-trade.

Parties were reminded in Decision XIX/12, "*Preventing illegal trade in ozone-depleting substances*" of their obligation under Article 4B of the Protocol to establish an import and export licensing system for all controlled ozone-depleting substances and urged to fully and effectively implement and actively enforce their systems for licensing the import and export of controlled ozone-depleting substances as well as recommendations contained in existing decisions of the Parties, notably decisions IX/8, XIV/7, XVII/12, XVII/16 and XVIII/18.

Several voluntary measures were proposed for Parties wishing to improve implementation and enforcement of their licensing systems to combat illegal trade:

i. Sharing information with other Parties, such as by participating in an informal prior informed consent procedure or similar system.

ii. Establishing quantitative restrictions, for example import and/or export quotas.

iii. Establishing permits for each shipment and obliging importers and exporters to report domestically on the use of such permits.

iv. Monitoring transit movements (trans-shipments) of ozone-depleting substances, including those passing through duty-free zones, for instance by identifying each shipment with a unique consignment reference number.

v. Banning or controlling the use of non-refillable containers.

vi. Establishing appropriate minimum requirements for labelling and documentation to assist in the monitoring of trade of ozone-depleting substances.

vii. Cross-checking trade information, including through private-public partnerships.

viii. Including any other relevant recommendations from the ozone-depleting substances tracking study.

2.7.2 Patents

Patents are complex and challenging to understand for both policy makers and civil society experts. With the global implementation of Kigali amendment, the production and application of HFCs alternatives become crucial for successful phase-down of HFCs, and patents are increasingly becoming a cause for concern for both the chemical manufactures and equipment manufacturers related to those HFCs alternatives. There are as many as several thousand patents that have been filed around the world to date, which cover production process, blends of these components and applications, including the specific means of production and the type of synthesis, and the applications of a single fluid or its blends. Most of the patents are highly concentrated in a few large transnational corporations and usually filed in major global markets in the form of patent families, known as a patent thicket. Furthermore, the core patents of some alternatives are controlled by a few companies and may have different patent protection scope and patent validity status in different countries. The restriction of free access to these patents has raised great concerns about the technology ability, as well as the availability of the alternatives, especially by Article 5 parties. Challenges against some of these patents have been filed in some countries, where the cost of challenging a patent may amount to more than $500,000 in each country.

Parties may wish to consider mechanisms to facilitate technology transfer to enable the most rapid global fulfilment of the Kigali Amendment.

2.7.3 Production and chemical supply issues in the transition to low-GWP HCFOs and HFOs

There have been reported challenges relating to production and chemical supply in the transition to low-GWP HCFO and HFO foam blowing agents, namely HCFO-1233zd, HFO-1234ze, and HFO-1336mzz. Similar challenges have not been reported for the production of alternatives for other sectors. The challenges relating to foam blowing agents are related to several factors.

Firstly, there are currently production constraints for these HCFO/HFOs worldwide, partly resulting from the global economic environment, making it difficult to meet demand. Global development and manufacturing of HCFO/HFO blowing agents is also limited due to the restriction of patents, especially application patents; at present, only a few companies have established production capacity. New production capacity for HCFO/HFOs foam blowing agents is being built in China and the United States, which is expected to become available in 2023.

Secondly, the high price of HCFO/HFOs has had a major impact on global use. For instance, the price of HCFOs/HFOs is currently much higher than HCFC-141b and even higher than HFC-245fa and HFC-365mfc. This is another reason why markets are continuing to use HCFC-141b, HFC-245fa and HFC-365mfc. HCFO/HFOs production is still in the early stages of commercialisation and high prices are to be expected, just as they were for HFCs in their early commercialisation. The complexity of manufacturing processes for some HCFO/HFOs may also be contributing to their higher price because the production processes are relatively more complicated than for HFCs.

Another challenge is regional shortages of CTC for feedstock use in HCFO/HFO production.[51] CTC is the main starting raw material in the process to manufacture HFC-245fa, HFC-365mfc, HFO-1234ze, HFO-1234yf, and HCFO-1233zd. While it is likely there is adequate global production capacity of chloromethanes-CTC and perchloroethylene (PCE)/CTC to meet global CTC demand, CTC production, supply, use, and export are subject to factors that could inadvertently impact global supply and availability. These factors include national licensing controls; rights to place on market; and regional imbalances in supply and demand. With the increasing demand for CTC as a raw material for a range of chemicals, regional shortages of CTC for feedstock use have become a challenge for both producers and users.

2.7.4 PFAS and TFA precursor substances

2.7.4.1 PFAS Definitions

There is an increasing focus on the emissions, environmental and health effects of PFAS (per- and polyfluoroalkyl substances). The Organisation for Economic Co-operation and Development (OECD) recent guidance "Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance"[52] (OECD, 2021) provides a very broad revised definition for PFAS. The rationale behind the revision is to

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[51] HFO-1336mzz production does not use CTC.

[52] OECD, 2021, *Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance*, Series on Risk Management No.61, OECD Publishing, Paris, 9 July 2021, p.45.

have a general PFAS definition that is coherent and consistent across compounds from the chemical structure point of view and is easily implementable for distinguishing between PFAS and non-PFAS, also by non-experts.

PFAS are defined, by the OECD, as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($–CF_3$) or a perfluorinated methylene group ($–CF_2–$) is a PFAS.

This definition excludes several fluorinated gases such as HFC-32, HFC-23, CF_3I, HFC-152a, HCFC-22, but does include trifluoroacetic acid and its salts (TFA) and other commercially used HFCs and HFOs.

The OECD guideline notes that "*As PFASs are a chemical class with diverse molecular structures and physical, chemical and biological properties, it is highly recommended that such diversity be properly recognized and communicated in a clear, specific and descriptive manner. The term "PFASs" is a broad, general, non-specific term, which does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene carbon moiety*." According to the OECD guidelines, individual users may define their own PFAS working scope for a specific activity according to their specific needs by combining this general definition of PFASs with additional considerations (e.g., specific properties, use areas).

The U.S. EPA "National PFAS Testing Strategy: Identification of Candidate Per- and Polyfluoroalkyl substances (PFAS) for Testing"[53] uses the prior U.S. EPA TSCA definition for PFAS: "*a structure that contains the unit* $R–CF_2-CF(R')(R'')$*, where R, R', and R'' do not equal "H" and the carbon-carbon bond is saturated (note: branching, heteroatoms, and cyclic structures are included)*." According to the U.S. EPA, "*this working definition provides focus on PFAS of concern based on their persistence and potential for presence in the environment and human exposure. For example, chemicals with* ($-CF_2-$) *that are not* ($-CF_3$) *are expected to degrade in the environment and most substances with only one terminal carbon* ($-CF_3$) *are expected to degrade to trifluoroacetic acid (TFA), which is a well-studied non-PFAS*.", (according to the EPA working definition, although TFA is a PFAS according to the OECD definition).

In the European Union, a REACH restriction[54] for PFAS has been proposed, to be based on the assessment of the information collected. The PFAS Restriction Intention is available on the ECHA website[55] and the PFAS scope definition is broadly aligned with the OECD definition, which excludes several fluorinated gases such as HFC-32, HFC-23, CF_3I, HFC-152a, HCFC-22. *"This definition is similar to the OECD definition, derived in 2021, which reads as: "PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group* ($–CF_3$) *or a perfluorinated methylene group* ($–CF_2–$) *is a PFAS." [OECD. Series on Risk Management No. 61, 2021]. Substances meeting the chemical scope definition for this restriction proposal will therefore also meet the OECD PFAS definition."* The outcome of the

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[53] U.S. EPA, 2021, *National PFAS Testing Strategy: Identification of Candidate Per- and Poly-fluoroalkyl Substances (PFAS) for Testing*, October 2021. National PFAS Testing Strategy (epa.gov).

[54] REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Restrictions are an instrument to protect human health and the environment from unacceptable risks posed by chemicals. Restrictions are normally used to limit or ban the manufacture, placing on the market (including imports) or use of a substance, but can impose any relevant condition, such as requiring technical measures or specific labels.

[55] ECHA, Registry of restriction intentions until outcome - ECHA (europa.eu).

restriction proposal and its potential impact, if any, on the use of some HFCs and HFOs, is unknown at present, as the REACH restriction dossier is scheduled for submission to ECHA in January 2023.

2.7.4.2 TFA precursors

The atmospheric breakdown of some HCFCs, HFCs and HFOs/HCFOs results in the formation of different yields of TFA. HFOs and HCFOs are being used to replace HFCs in some applications but are not controlled substances under the Montreal Protocol. In addition, other substances not controlled by the Montreal Protocol, such as some gaseous anaesthetics, yield TFA on degradation in the atmosphere.

In its 2022 Assessment Report, the Environmental Effects Assessment Panel presents information on the contribution of chemicals relevant to the Montreal Protocol to the global load of trifluoroacetic acid. Estimated yields of TFA (%) for various ODS replacements, and reported global emissions of those replacement chemicals, are provided in Figure 12, section 3.3, of that report and reproduced below.[56]

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[56] With acknowledgment to Mads Peter Sulbaek Andersen, Environmental Effects Assessment Panel, via personal communications.

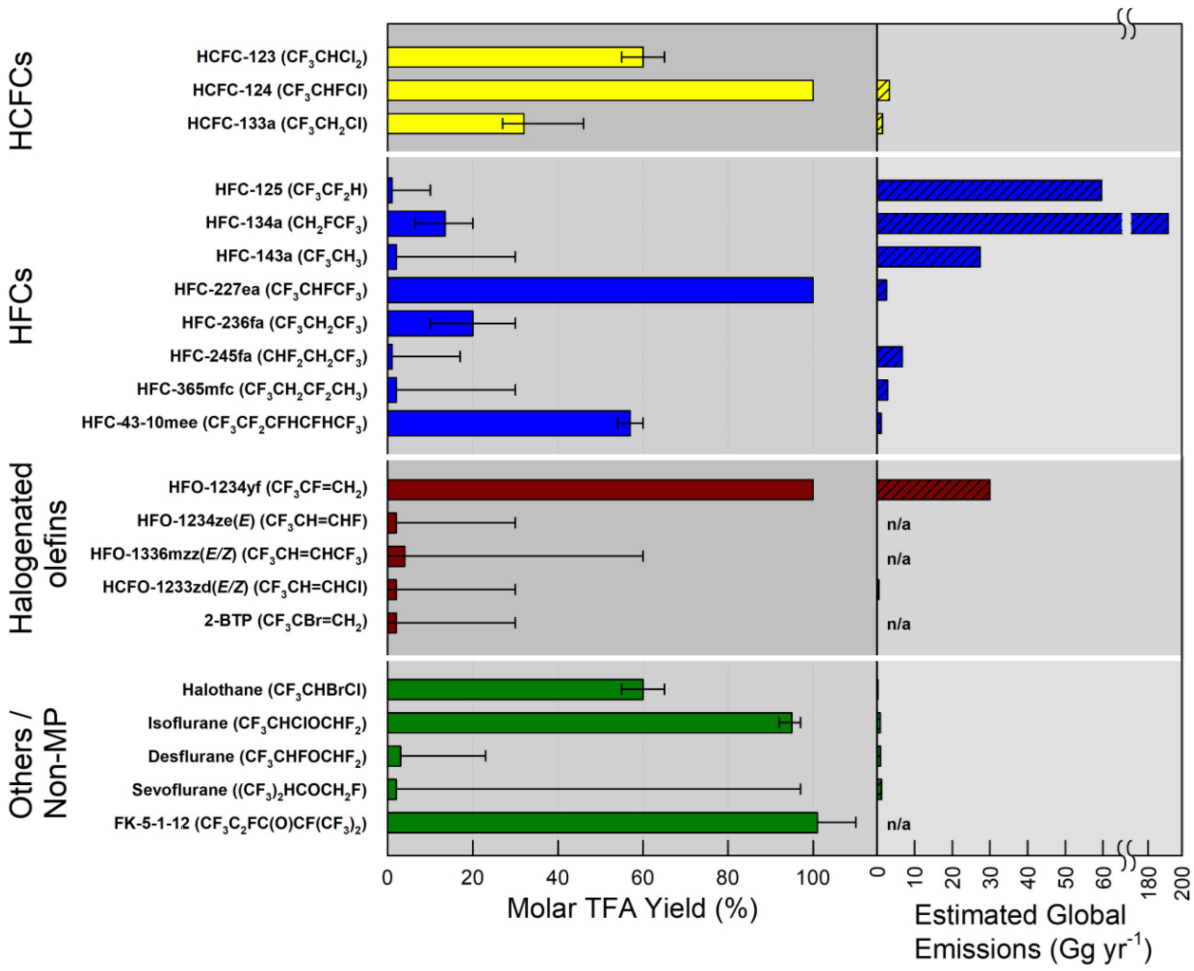

Fig. 12. Yields of TFA from selected individual CFC replacement compounds, as well as the estimated global emissions of these compounds. The figure also includes selected compounds not under the purview of the Montreal Protocol and Amendments. Error bars represent both experimental uncertainties and upper and lower yield ranges due to competing reaction channels that depends on environmental conditions. The yields of TFA from individual compounds are estimated based on evaluations of the available literature as described in SI Section 4. Note split scale for the emission for HFC-134a which are much higher than those of other compounds.

2.8 Carbon tetrachloride

2.8.1 Summary

- Production of carbon tetrachloride (CTC) has grown steadily to a recent peak of 318 ktonnes in 2019, due mainly to CTC use as feedstock to HFCs and HFOs/HCFOs and to perchloroethylene.

- Growing CTC demand is because of the displacement of higher GWP HCFCs and HFCs by HFOs and is likely to continue. New HFO/HCFO plants/expanded capacities have been announced in India, the United States, and China.

- Regional shortages (Japan, the United States) have led to an increased export trade in CTC, mainly from Europe. Just under 50% of CTC consumption requires road, rail, or overseas transport.

- Based on Article 7 reported CTC production of 289 ktonnes for 2020, MCTOC has estimated 17.8 ktonnes (7.1–28.1) CTC emissions globally in 2020. Of this, 12.8 ktonnes (4.6–20.6) arise directly from CTC production, handling, supply chain, and use. A further 5 ktonnes (2.5–7.5) CTC emissions are estimated from anthropogenic non-CM production.

- A new potential source of unreported emissions of CTC is identified from the production process of the vinyl chain (production of ethylene dichloride (1,2-dichloroethane, EDC) to vinyl chloride monomer (VCM) to polyvinyl chloride (PVC)), which occurs on chlorine producing sites (see Figure 2.6). This is dissociated from chloromethanes production.

2.8.2 Introduction

The 2018 MCTOC Assessment Report noted that "*Regarding the reported discrepancy between emissions of CTC calculated from atmospheric observations and those estimated from industrial activity, experts under the auspices of Stratosphere-troposphere Processes And their Role in Climate (SPARC) concluded that some of the discrepancy could be explained by unreported emission sources, including from contaminated soils and industrial waste, and from chloromethanes production, and by revised estimates of partial CTC lifetimes (stratosphere, ocean, or soil). With the new total lifetime, the global top-down emissions calculation decreases to 40 (25–55) ktonnes per year. The new industrial bottom-up emissions estimate (including unreported emissions from chloromethanes plants, feedstock fugitive emissions, legacy emissions and unreported inadvertent emissions, for example from use of chlorine as disinfectant) could be up to 25 ktonnes per year.*"

Subsequently, there was emerging scientific evidence of new and unreported CFC-11 emissions from East China[57], followed by indications of increased CTC – the feedstock to CFC-11 – emissions also related to East China[58].

2.8.3 CTC production routes

The most recent CFC-11 TEAP Task Force Reports[59] have already given detailed information on the production of CTC. It is an inevitable co-product of chloromethanes production which can be minimised, by careful production management, to 5% or less of the total output of the chloromethanes family, which includes methylene chloride or dichloromethane (DCM) and trichloromethane or chloroform (CFM). Global capacity for chloromethanes is estimated to have been more than 4.3 million tonnes in 2020, and actual production, for all uses, is estimated at 3.4–3.6 million tonnes, indicating a minimum of 150–160 ktonnes CTC at a

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[57] Montzka, S. *et al.*, An unexpected and persistent increase in global emissions of ozone-depleting CFC-11, *Nature*, 2018, **557**, 413–417. https://doi.org/10.1038/s41586-018-0106-2.

[58] Lunt, M.F., Park, S., Li, S., Henne, S., Manning, A.J., Ganesan, A.L., *et al.*, Continued emissions of the ozone-depleting substance carbon tetrachloride from eastern Asia, *Geophysical Research Letters*, 2018, **45**, 11,423–11,430. https://doi.org/10.1029/2018GL079500.

[59] UNEP, 2019, *Report of the Technology and Economic Assessment Panel, Volume 1, Decision XXX/3 Task Force Report on Unexpected Emissions of Trichlorofluoromethane (CFC-11), Final Report,* September 2019.

UNEP, 2021, *Report of the Technology and Economic Assessment Panel, Volume 3: Decision XXXI/3 Task Force Report on Unexpected Emissions of Trichlorofluoromethane (CFC-11),* May 2021.

default of 5% CTC in the higher chloromethanes. Much of the chloromethanes production capacity is concentrated in China at over 3 million tonnes, whilst Indian companies have started a course of expansion which will take capacity from around 300 ktonnes/year in 2020 to over 500 ktonnes/year by 2025.

The output of CTC can also, globally, be increased from its 5% minimum in the production of chloromethanes. It is estimated that this capacity could be as much of 15% of chloromethanes output, meaning that in China a theoretical 450 ktonnes CTC production would be possible: obviously with a downwards impact on DCM and CFM output. To some extent this is already happening: some CM plants in the United States, India, Japan and the European Union are operating at ±10% CTC production.

A downwards trend in CFM production due to the regulated phase-down of emissive HCFC-22 production is expected, whereby CFM demand to HCFC-22 is under 1.5 units (i.e., 148 ktonnes of CFM are required to produce 100 ktonnes of HCFC-22). However, growth in HCFC-22 use as feedstock to fluoropolymers and other fluorinated specialities is expected to compensate for this loss within 5 years, barring any unexpected changes in the production or use patterns of fluoropolymers.

CTC is also potentially available from PCE/CTC plants, which were initially designed to convert chlorinated by-product streams into raw materials for the CFC-producing industry. With the decline of CFCs through the 1990s, many of these plants were closed and the remainder invested in plant modifications such that 100% perchloroethylene could be produced if required. Of the non-Article 5 parties, only the United States (2 plants) and the European Union (3 plants) have operating PCE/CTC facilities, with a total PCE/CTC production capacity estimated at less than 350 ktonnes/year. U.S.A, with total capacity around 135 ktonnes/year of mixed PCE and CTC, was already close to capacity in 2017, and subsequently has needed to import CTC. Spare capacity to produce PCE or CTC from the current plants is estimated to be between 50 and 100 ktonnes/year, existing mainly in the European Union. The United States is structurally short of CTC and currently (in 2021) imports over 20 ktonnes/year, all for HFC, HFO, and HCFO production. Japan is also structurally short of CTC for HFC and HFO production and has imported 2–3 ktonnes/year in recent years. Exporting CTC from any producing region would be subject to considerable regulatory compliance, including the legal requirements of importing countries.

Since 2008, chloromethanes producers in China have been obliged to ensure that their CTC output was either fully consumed as feedstock to non-ODS chemicals or permitted process solvent and LAU demand, or failing this, to incinerate it. The consequence of this led to the progressive construction of plants that were designed to convert CTC, in the presence of chlorine and methane, to perchloroethylene (PCE), which usefully was required as feedstock in increasing volumes for the growth of HFC-125. During the 2010s it was realised that other chlorinated streams such as mixed chloromethanes (including CTC) could be used in PCE production, helping CM plants to operate closer to capacity and offsetting some of the high cost of using methane as feedstock. Effectively these plants become PCE/CTC plants, with the permitting only allowing PCE production, but with the intrinsic potential to produce refined CTC. This is carefully monitored by Chinese authorities. It is estimated that 8–9 such plants exist on the sites of chloromethanes producers (and perhaps 2 elsewhere, using different feedstocks such as 1,2-dichloropropane), and the total PCE capacity is estimated at 250–300 ktonnes/year. Of the 16 chloromethane producer sites, only three are permitted to put CTC on the market: in other words, to supply CTC to the producers of HFCs and HFOs, producers of DVAC etc., that do not have their own back-integrated chloromethanes production. Most of the rest have installed PCE/CTC plants with 100% PCE output.

The PCE produced from CTC is used as feedstock to HFC-125 with plants in U.S., India, and China. PCE is also used as feedstock to CFC-113 for chlorotrifluoroethene (CTFE, a fluorochemical monomer) production, and otherwise to use as feedstock to CFC-113a, in turn used as feedstock to trifluoroacetic acid (TFA), to HFO-1336mzz), and to CFC-114a as feedstock to HFC-134a.

2.8.4 CTC production and emissions

Since the 2018 MCTOC Assessment Report, CTC production for use as feedstock, process agent, and LAU has steadily increased from some 220 ktonnes in 2017 to a recent peak of 318 ktonnes in 2019[60] before dipping to below 300 ktonnes in 2020, partly because of reduced demand due to the global COVID pandemic and in some part because of restrictions on placing CTC on the market.

Figure 2.5 below presents MCTOC's 2020 estimation of global CTC production, usage, and emissions, noting that the estimates are based on reported production only. A figure for the 2019 estimation of global CTC production, usage, and emissions can be found in Appendix 1. A similar graphic for the year 2019 appears in SAP 2022.[61] Production of CTC dropped slightly in 2020, while the quantity of CTC used for feedstock in the production of HFOs and HCFOs increased by 25% compared with 2019, and the quantity used for feedstock in the production of PCE declined.

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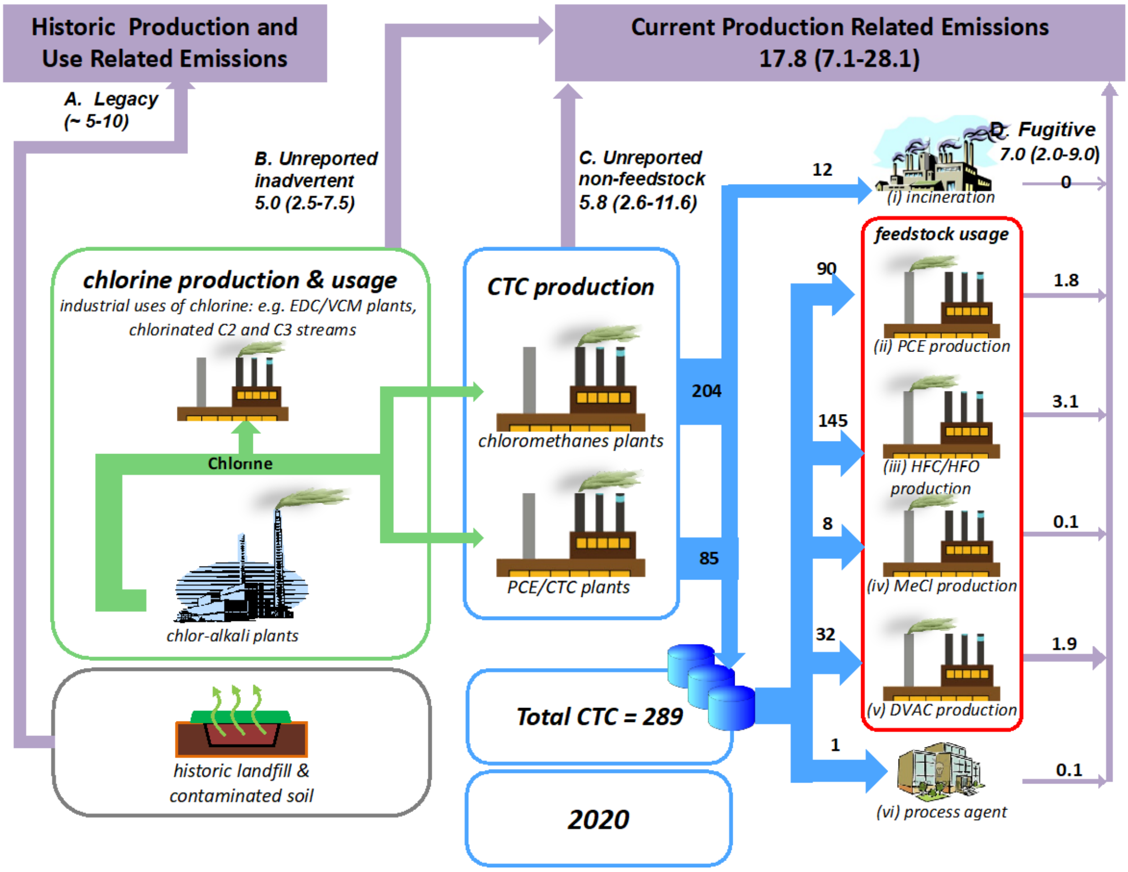
[60] Reported Article 7 data.

[61] World Meteorological Organization (WMO), 2022, *Scientific Assessment of Ozone Depletion: 2022*, GAW Report No. 278; WMO: Geneva, 2022.

Figure 2.5 Estimated global CTC production, usage, and emissions, 2020 (ktonnes)



Notes to this Figure:

A) Legacy emissions arise from historic landfill disposal of contaminated waste, site contaminated soils, or from historic production or user sites of CTC, especially from older military sites where CTC was extensively used as both solvent and fire extinguisher.

B) Unreported inadvertent emissions may arise from other chlorination processes including EDC, VCM, and other chlorinated ethanes. Notably, the production of EDC and the cracking to VCM all produce waste streams that to a lesser or greater extent contain CTC. This is discussed in Chapter 2.8.7

C) Unreported non-feedstock CTC emissions from chloromethanes plants are fugitive from pipework, compressors, valves and other junction points, and may arise from crude CTC production off CM production plants up to charging of finished CTC (via distillation or PCE/CTC unit) into intermediate storage, following by loading into transport mode-road or rail bulk shipment, or drums. The range of these emissions according to TEAP Emissions Calculation is 0.9–4.0% of the total CTC output. The calculated production emissions shown in the graphic is 2%, reflecting the modernity of most of the production units in China, which have a close to 70% stake in global CM-CTC production capacity. The higher percentage includes an uncertainty about the disposal of the distillate after crude CTC finishing

D) Emissions from transport from the producer site to the user, possibly via intermediate storage, and user-site emissions, are assessed to be most likely to fall in the range 0.9–3.1% according to the use and the proximity to the source of CTC although may reach as high as 5% or more. Emissions from the individual uses are based on factors such as pipeline transfer versus road transport, the potential for supplies of drummed material, and other multiple handing situations. The CTC volume estimate for each user industry may have ±10% error.

Based on Article 7 reported data of 289 ktonnes of CTC production for 2020, MCTOC has estimated 17.8 ktonnes (7.1–28.1) CTC emissions globally. Of this, 12.8 ktonnes (4.6–20.6) arise directly from CTC production, handling, supply chain, and use. A further 5 ktonnes (2.5–7.5) CTC emissions are estimated from anthropogenic non-CM production.

2.8.4.1 Incineration

"Incineration" is used here as a proxy for all destruction of unwanted CTC (i.e., there is no available feedstock or process agent market for it) as well as CTC bottoms collected post distillation. Incineration is sometimes seen as the last resort for any chemical, but in at least one plant, in Europe, the HCl recovered from CTC and other chlorinated waste products is vital to the continuity of the plant, which is HCl short. This process may be called "HCl recovery, or revalorisation" as opposed to incineration, where by-product acids are often neutralised. In Japan, chloromethanes CTC was commonly incinerated post CFC production, but in the meantime production of HFC-245fa and HFCO-1233zd has grown to the extent that Japan has become a CTC importer, mainly from Europe. Other chemical site incinerators are permitted to receive CTC for destruction, with HCl recovery. The output of crude CTC from the chloromethanes plant needs to be distilled if refined CTC is to be used as fluorocarbon feedstock. The distillation residues, which are a viscous, highly chlorinated CTC cocktail, should be destroyed. The figure of 12 ktonnes incineration is a best estimate.

2.8.4.2 Feedstock to perchloroethylene

The process to make PCE from chlorinated by-product streams, and notably from CTC in China, has been covered in depth in the 2021 CFC-11 Task Force Report. Reduction in HFC-125 production in China[62] in 2020 led to a parallel drop in PCE demand and hence reduced requirement of CTC to the PCE plants; and equally chloromethane feedstock costs increased dramatically and several the CM units in China had prolonged periods of slow running or plant shutdowns. This partly explains the 2020 reduction in demand of CTC to feed PCE/CTC plants versus 2019.

2.8.4.4 Feedstock to HFCs and HFOs

The increase of over 30 ktonnes CTC in feedstock use to HFCs and HFOs can be in large part explained by the consumption of two large new HFO-1234yf plants in U.S.A. This chlorocarbon process, using CTC as a chlorinated chain extender to convert ethenes into chloropropanes, consumes approximately 2 units of CTC per unit of HFO-1234yf. The product has enabled full compliance in Europe with the F-gas Regulation, which since 2017 has required all automobiles to use a mobile air-conditioning (MAC) circuit where the fluid must have a GWP of less than 150, thereby eliminating the use of HFC-134a in new cars. In the United States, many automobile producers have for some years been using HFO-1234yf instead of HFC-134a. This HFO-1234yf was initially based on product from China and Japan, using the HCFC-22 to HFP process as initiator.

Early, pre-marketing production of HFO-1234yf for MAC use was made by a complex set of reactions starting with the manufacturing route of HCFC-22 to produce TFE and then to produce HFP followed by many subsequent fluorinations and hydrogenations. By-product production of HFC-23 is inherent in this process up to the HFP stage, and mitigation is a necessary process step. Routes to produce HFO-1234yf and most notably its application in MAC have been patent protected, resulting in production licences to produce by this route (but not to put on market) in China and India and preventing other suppliers from entering the

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[62] Data from chinaiol.com, accessed August 2022.

market. A similar production technique is used in Japan, replacing CTC by HCFC-21, a co-product in HCFC-22 manufacture which normally is recycled back to the HCFC-22 process. Placing this HFO-1234yf on the market is rigidly managed by the application patent holder, which is a demonstration of the validity of the application patent for the mobile air conditioning market for HFO-1234yf, regardless of the production route.

These complex, multi-stage HCFC-22 based routes to HFO-1234yf have, in the United States, been replaced by higher capacity and lower cost chloro-chemical routes which involve the reaction of ethylene with CTC as a starting point to manufacture HCC-250fb (1,3,3,3-tetrachloropropane) which then, by different process steps, can be processed to HFO-1234yf.

The HFCs, HCFOs, and HFOs that require CTC feedstock as part of the process include HFC-236fa, HFC-245fa, HCFO-1224yd, HCFO-1233zd, HFO-1234yf and HFO-1234ze. As noted above, HCFC-22 can be used as a feedstock for HFO-1234yf. HFC-227ea and HFO-1336mzz do not use CTC.

The reason for the use of CTC is that it enables both chain extension to an olefin and that it enables exact placement of the chlorine molecules in the 1,3,3,3- position, which can be subsequently hydrogenated, re-isomerised, and fluorinated. Alternative chlorocarbon routes, not using CTC, to minimal GWP fluorocarbons have been patented, notably to HCFO-1233zd, and may come into use as production capacity is expanded to meet consumer demand.

Growth in HFO and HCFO demand has been rapid in response to the Kigali Amendment and its regional implementations, which is curbing demand for high-GWP HFCs. Already in mid-2022 new capacity for HCFO-1233zd has been announced in the United States and India, for HFO-1234ze in China, and for expansion of current capacity for HFO-1234yf by one of the two U.S. producers. In addition, a new HFO-1336mzz plant is under construction in the United States, although this does not use CTC. Using 2019 as a more realistic base than Covid-influenced 2020, HFO/HCFO demand is expected to rise at some 8–10% per annum through and beyond 2025 as Kigali measures begin to influence Group 1 Article 5 Parties, with most of this requiring additional production of CTC. As MAC application patents begin to expire in 2023, we expect additional production of HFO-1234yf from new entrants to the market, notably from existing factories in China and using the HCFC-22/HFP route. One driver may be that using spare HCFC-22 capacity to produce HFO-1234yf would enable higher capacity utilisation of both HCFC-22 and TFE/HFP production units.

2.8.4.5 Feedstock to methyl chloride and chloroform

The production of methyl chloride from CTC involves the latter's reaction with water to produce CO_2 and HCl. The HCl is recovered, purified, and then used to produce methyl chloride by reaction with methanol. This methyl chloride can then be re-used by the CM plant or can also be used as a starting point to organic silicone chemistry. It is believed that two CM plants in China use this technology.

The process of removing chlorine from the CTC molecule can also be applied to produce chloroform. CTC is hydrogenated to remove one Cl molecule from CTC to restore it to trichloromethane, or CFM. The yields are not high and there is potential for over-hydrogenation to DCM. At least one producer in China who used this approach to convert CTC has now switched to a PCE/CTC process.

2.8.4.6 Feedstock to divinyl acid chloride

Similar to HFOs, the production of divinyl acid chloride (or cypermethric acid chloride, DVAC) involves the first stage reaction of CTC with the olefin acrylonitrile (C_3) into tetrachlorobutyronitrile (C_4). This demonstrates the functionality of CTC in adding to the carbon chain length and adding four chlorine molecules where they are necessary for the next production stages. The end-product is a synthetic pyrethroid pesticide. Production of DVAC was largely in India until about 2010, when production started in China. No DVAC producer is back integrated into CTC on-site, so in consequence CTC is delivered by road tanker. It is estimated that 33 ktonnes of CTC were used in this process in 2020, with the majority being produced in India. Continued growth is foreseen, but this is based more on seasonal conditions rather than GDP based. Imports of CTC to India should abate as new chloromethanes capacity comes on-line between now (mid-2022) and end 2025. Consumption of CTC seems to vary by producer and is a calculated range of 1.1–1.3 units of CTC per unit of DVAC. The high-end emission rate used of 6% is because of the road transportation that is required for virtually all the CTC that is delivered to DVAC manufacturers, involving multiple handling transfers; the possibility of some drum handling; and the possibility that there may be some excess consumption of CTC being used as a reactive process agent through the reaction.

2.8.4.7 Process agents and laboratory and analytical uses

In 2020, reported make-up/consumption of ODS used in process agent uses was reported as 477.275 tonnes (excludes the United States) (see Chapter 3, Table 3.3). While the United States does not report make-up/consumption[63], it is estimated that global make up/consumption of ODS is about 1,200 tonnes. It has been assumed that CTC consumption is about 90% of the total ODS consumption quantity, indicating about 1,000 tonnes. Reported emissions from process agent use for all ODS were 146.51 ODP tonnes, of which the United States is 25.7 ODP tonnes (109.4 metric tonnes, excluding the United States that only reports in ODP tonnes) (see Chapter 3, Table 3.5). Total CTC emissions are estimated to be about 120 tonnes, representing 12% emissions from CTC consumption (see Figure 2.5, where numbers are rounded).

In 2020, the global production of ODS produced for laboratory and analytical uses (LAUs) was 123.61 tonnes. Within this reported consumption of CTC was 123.59 tonnes (0.04% of total CTC consumption in 2020), meaning that CTC remains the prominent ODS used in LAU. Figures 7.1 and 7.2 visualise the progress in eliminating CTC as an LAU over time.

2.8.5 Transport of CTC

Regarding the production of 289 ktonnes CTC in 2020, MCTOC estimates that just under 50% is not used on the plant where it is produced and requires it to be transported. In 2020, nearly 20 ktonnes were shipped overseas, likely in iso-tankers, mostly from Europe to the United States, India, and Japan. There are cross-border movements of CTC within the European Union. As mentioned previously, the United States is structurally short of CTC due to the expansion of the production of HFO-1234yf, although it may be anticipated that regulatory reduction of demand for PCE-consuming fluorocarbons including HFC-125 and HFC-134a may allow for increased CTC production from PCE/CTC plants. Japan also seems to be producing more HFC-245fa and HCFO-1233zd than local CM-CTC production can supply, and imports of CTC are expected to continue in the medium term, when new HCFC-1233zd capacity will come on stream in India and the United States.

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[63] Maximum make-up/consumption associated with process agents for the United States as defined in Table B is 2,300 metric tonnes.

2.8.6 *Outlook for CTC as feedstock*

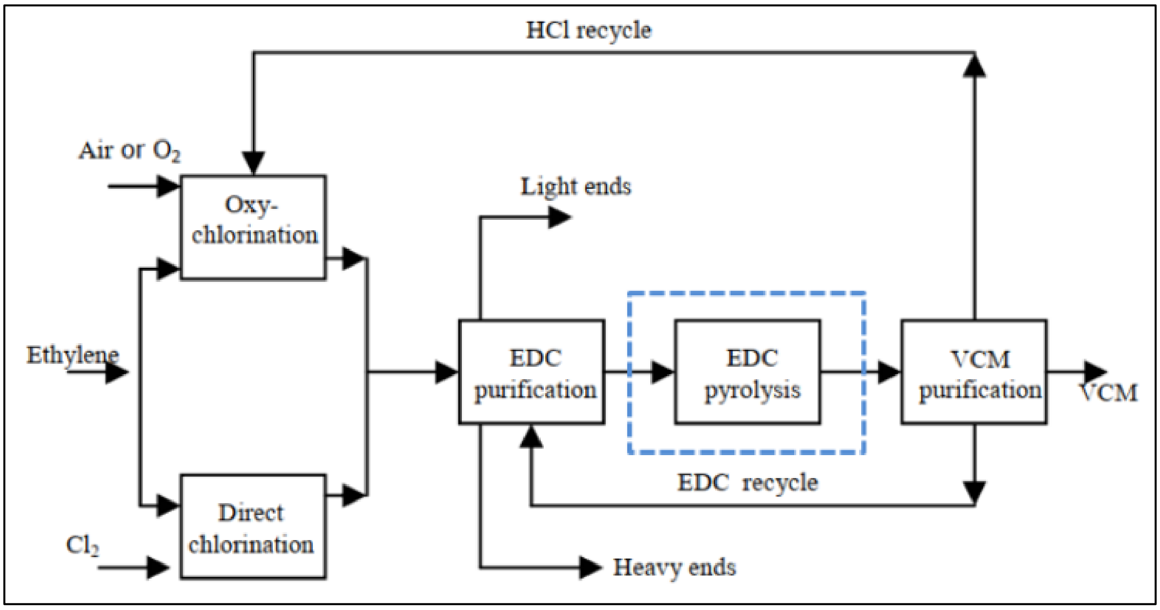
Based on the growth potential for all HFO derivatives in partial replacement for the existing uses of HCFCs and HFCs, it is very likely that CTC consumption in these applications will continue to grow. Production and consumption of HFC-245fa and HFC-365mfc as foaming agents, and to a smaller extent as solvent, will start to be controlled as of 2025 in Group 1 Article 5 parties. Non-Article 5 parties are already well on the way to displacing HCFCs and high GWP refrigerants by low/no GWP products, as well as by hydrocarbons or carbon dioxide in many applications. However, the use of higher GWP HFC products and blends, such as HFC-134a, HFC-245fa, R-404A (blend of HFC-125, HFC-134a, HFC-143a), and R-410A (blend of HFC-32, HFC-125), is not yet being phased down in Article 5 parties. HFO-1234yf is well established already as a replacement for HFC-134a in MAC applications and is already being supplied as a top-up MAC fluid in the service sector.

Equally, DVAC synthetic pyrethroid pesticide has continued growth in recent years, and additional production capacity has been installed in China.

2.8.7 *Other sources of CTC: the vinyl chain*

Based on current knowledge, it seems unlikely that the use of chlorine as disinfectant, as reported in the 2018 Ozone Assessment, would be an important unreported source of emissions of CTC. However, there is some evidence that the ethylene-based vinyl chain may be very relevant to unexplained emissions of CTC. The vinyl chain is a term used to describe the set of reactions that form vinyl chloride monomer (VCM), which is then polymerised to produce polyvinyl chloride. Figure 2.6 shows the sequence process of VCM production. Attention is drawn to the removal of heavy and light ends from EDC purification and from the VCM reactor.

Figure 2.6 Flow chart of the vinyl chain: EDC, oxy-EDC, and VCM[64]



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[64] See section 2.10. The vinyl chain is a term used to describe the set of reactions that form vinyl chloride monomer (VCM), which is then polymerised to produce polyvinyl chloride. Ethylene dichloride is produced through the reaction of ethylene and chlorine ($H_2C=CH_2 + Cl_2 \rightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}Cl$). This is called direct chlorination, or EDC-DC. In subsequent reactions, notably to vinyl chloride (chloroethene), hydrogen chloride is

Analysis of EDC *light ends* streams from different sources identify a proportion of 12–25% of CTC in the waste stream. The total waste stream of mixed chemicals, according to technology, may be 0.3–0.8% of EDC production. Regulatory standards require the chemical conversion (often to on-site PCE/CTC or PCE/TCE plants) or destruction of these waste streams, but the risk of emissions via water, air or soil cannot be discounted. Other common by-products in the light ends include chloroform, trichloroethylene and chlorobutadienes (see Appendix 1, section A1.2).

It is estimated that production of EDC was over 62 million tonnes in 2020. Whilst Figure 2.6 shows a balanced system, in which all the HCl is returned to the oxy-chlorination reactor, many chlorine plants enable the supply of chlorine to other consuming industries, such as isocyanates and chloromethanes, and the HCl produced as a co-product from these processes can be returned by pipeline to the oxy-EDC reactor. Effectively, this is using chlorine twice. Therefore, it seems likely that some 55–60% of EDC production is via oxy-chlorination, which is considered to have a higher by-product stream than direct chlorination EDC, due in part to the presence of water in the waste stream from oxy-EDC.

Chloromethanes plants are very often situated on a chlorine/vinyl chain complex: however, in many parts of the world, such as Middle East and South America, there are stand-alone large chlorine and vinyl chain complexes with no local chloromethane plants, and nominally no CTC should be traceable. Chloromethanes are not made in Africa, the Middle East, and Latin/South America. It also worth noting that the vinyl chain in China is some 80% acetylene-based, with the direct conversion of acetylene to VCM by the addition of HCl, and no EDC is involved in this process. The balance is ethylene based, for which China imports some of its EDC requirement.

It is estimated that some 35–40 million tonnes of VCM are produced by the ethylene route (i.e., using EDC), with concentrations of production in Europe, the United States Gulf, Brazil, the Arabian Gulf, India, and Southeast and East Asia, especially Japan, Republic of Korea, and China East Coast.

Emissions from EDC/VCM plant complexes may be traceable outside plant boundary limits and placing low level tracers close to the perimeters of large EDC/VCM complexes could detect any possible chlorinated contaminants, including CTC. If such testing is initiated, it might to useful to choose EDC/VCM plants that do not have chloromethanes production on-site or nearby, to capture CTC emissions solely related to the vinyl chain.

2.9 Update on CFC-11 production

In response to reported scientific findings of an unexpected increase in global emissions of CFC-11 between 2013 and 2018, and since the 2018 MCTOC Assessment Report, the TEAP Task Force on Unexpected Emissions of CFC-11 has reported in 2019 and 2021. The 2021 Task Force analysis using global and regional inventory-based modelling of CFC-11 showed a difference between the inventory-based model's estimation of expected CFC-11 emissions and CFC-11 emissions derived from atmospheric observations. This difference is indicative of unreported CFC-11 production and use; emissions from CFC-11 banks alone cannot explain the unexpected increase in CFC-11 emissions between 2013 and 2018. Unreported CFC-11 production would also seem to have been occurring in the period from 2007 to 2012. This unreported production is necessary to explain the difference between inventory-based expected emissions and derived CFC-11 emissions during this earlier period. A resumption of

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formed and re-used to produce more EDC in reaction with ethylene and oxygen. ($H_2C{=}CH_2 + 2\ HCl + \frac{1}{2}\ O_2 \rightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}Cl + H_2O$). This is called oxy-chlorination, or oxy-EDC.

newly produced CFC-11 usage in closed-cell foams was considered the most likely explanation of the unexpected increase in CFC-11 emissions.

Based on estimations of the additional CFC-11 production necessary for the inventory-based expected emissions to align with the derived emissions, unreported CFC-11 production was estimated to be:

- 10 to 40 kilotonnes per year between 2007–2012
- 40 to 70 kilotonnes per year between 2013–2018
- 15 to 40 kilotonnes of new production, or use from recent inventory, for 2019

The estimated cumulative total of unreported CFC-11 production was 320–700 kilotonnes during the period 2007–2019.

The most likely CFC-11 production routes were:

- CTC to CFC-11/-12 on a large-scale ($\geqslant$ 50,000 tonnes/year) in an existing liquid phase plant (HCFC-22 and/or HFC-32 plant).
- CTC to CFC-11 on micro-scale (100 to 2,000 tonnes/year) plants using minimal equipment (to make low grade CFC-11 for foam blowing use).

Any additional unexpected emissions of CFC-12 were likely to be as a co-product associated with the production of CFC-11, rather than from any specific production initiated to supply CFC-12 in its own applications.

Between 45 to 120 kilotonnes of CTC would have been required to supply between 40 to 70 kilotonnes of CFC-11 production annually in the period 2013 to 2018, depending on the proportion of co-produced CFC-12 and expected to be at the lower end of the range. In the period 2007–2019, the cumulative CTC quantity required to produce 320–700 kilotonnes of CFC-11 was at least 360 kilotonnes. More information can be found in the CFC-11 TEAP Task Force reports.[65]

2.10 Very short-lived substances

Many ozone-depleting substances not controlled under the Montreal Protocol that are being evaluated by atmospheric scientists are chlorinated hydrocarbons with a very low, but non-zero, ODP. Collectively they are known as very short-lived substances (VSLS) because of their short atmospheric lifetimes. These chemicals include dichloromethane (methylene chloride, DCM), trichloromethane (chloroform, CFM), ethylene dichloride (1,2-dichloroethane, EDC), trichloroethylene (TCE), and perchloroethylene (PCE), which are all very high-volume products.

Each of these chemicals are used as feedstocks, and some also have considerable emissive solvent use. Methyl chloride is only produced as feedstock to produce other chemicals, mainly for organic silicones and chloromethanes. Feedstock usage of both EDC and CFM is

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[65] UNEP, 2019, *Report of the Technology and Economic Assessment Panel, Volume 1, Decision XXX/3 Task Force Report on Unexpected Emissions of Trichlorofluoromethane (CFC-11), Final Report,* September 2019.

UNEP, 2021, *Report of the Technology and Economic Assessment Panel, Volume 3: Decision XXXI/3 Task Force Report on Unexpected Emissions of Trichlorofluoromethane (CFC-11),* May 2021.

more than 90%, with some solvent use for each. EDC can be used as a feedstock for both TCE and PCE manufacture and some minor solvent use.

This section focuses on DCM, CFM, EDC, TCE, PCE, and methyl chloride (MeCl).

2.10.1 Summary

- *Dichloromethane (DCM)* production in 2020 is estimated at over 1,800 ktonnes. Feedstock use for HFC-32 manufacture exceeded 400 ktonnes in 2020. Solvent use and emissions in non-Article 5 parties peaked in the early 2000s and have now stabilised at around 200 ktonnes/year; solvent growth in Article 5 parties has led to calculated global emissions of greater than 1,400 ktonnes in 2020. New regulations in China will ban the use of DCM in foam blowing agent and public paint stripping applications by 2025, resulting in a possible usage reduction of about 300 ktonnes/year.

- *Chloroform (CFM)* production exceeded 1,500 ktonnes in 2020, mostly used as feedstock for HCFC-22. HCFC-22 production for emissive uses is expected to decline sharply in 2025. However, growth of CFM as a feedstock for TFE/HFP production will likely result in maintenance of a similar level of global CFM production. Solvent uses are expected to account for some of the unexpectedly high emissions of chloroform.

- *Ethylene dichloride (EDC)* production in 2020 was more than 62,000 ktonnes, with a great deal of global trade. EDC is used to make vinyl chloride monomer (VCM), which is then polymerised to make PVC. Emissions from production and feedstock use are expected to be at the very low end of the TEAP range, at the low end of 0.1–0.175% (60–105 ktonnes). Consumption for solvent use is not tracked because there are no reporting requirements; nevertheless, solvent use could amount to an additional 3–20 ktonnes of emissions globally.

- *Trichloroethylene (TCE)* production and use in non-Article 5 parties are in decline (two trichloroethylene plants have recently closed); however, TCE production for feedstock is expected to continue at close to current global levels before the Kigali Amendment starts to freeze and phase down production of HFC-134a. The use of TCE as feedstock to HFC-134a has continued to grow and was an estimated 360–380 ktonnes in 2020. TCE consumption as an emissive solvent has dropped by 40% globally since 2000 and is now around 110 ktonnes/year (2020). TCE emissions are widespread from its main solvents markets in South and East Asia.

- *Perchloroethylene (PCE)*— The largest use of PCE, currently close to 400 ktonnes/year, is as feedstock to several fluorocarbons. PCE is used as a feedstock for CFC-113, which is then used to produce the fluoromonomer chlorotrifluoroethene (CTFE). PCE is also used to produce CFC-113a, used as feedstock for HFC-134a and to HFO-1336mzz. The HFC-134a portion of this PCE usage is expected to decline under the Kigali Amendment. PCE is also a feedstock for HFC-125 production, which is expected to stabilise and decline after 2025. Solvent use, for dry-cleaning and metal cleaning, has declined from a level above 200 ktonnes/year in the 2000s to around 175 ktonnes/year in recent years. Absent regulations, it is expected that perchloroethylene consumption as solvent will remain close to present levels. Solvent emissions of 160–170 ktonnes/year dwarf emissions from feedstock production and use, which are expected to be in the range of 8–16 ktonnes.

- *Methyl chloride (MeCl)* is produced and used almost exclusively as feedstock for two main families of products: chloromethanes and organic silicone compounds. There are smaller feedstock demands in the production of methyl cellulose thickeners, cationic starches and polymers for water treatment and paper processing, cationic surfactants, and in the production of butyl rubber. From the limited available data, methyl chloride production is estimated to be in the range 4,500–5,000 ktonnes/year. Emissions from production and feedstock uses are estimated to be at the low end of TEAP emission factors, in the range 5–8 ktonnes. Global MeCl emissions originate largely from natural sources.

2.10.2 Background to very short-lived substances (VSLS)

Chlorinated VSLS have a relatively small, but growing, contribution to total tropospheric chlorine, assessed at 4% in 2020.[66] However, their relevance for stratospheric ozone depletion has increased over time.[67,68,69,70] Since the 2018 Scientific Assessment of Ozone Depletion, new studies have reported substantial increases in chlorinated VSLS emissions from Asia and new information on the ODPs of chlorinated VSLS has become available.[71]

Claxton (2020) notes that the ODP of the chlorinated VSLS under discussion here show both seasonal and geographic sensitivity. "*The seasonal dependence of the ODPs is small, but ODPs vary by a factor of 2–3 depending on the continent of emission. Asian emissions produce the largest ODPs owing to proximity to the tropics and efficient troposphere-to-stratosphere transport of air originating from industrialized East Asia.*". The study notes that the top-range effect of emissions of VSLS are comparable to the mean ODP range of methyl chloride (0.2). The ODPs of the studied VSLS are tabulated below. Trichloroethylene was not considered by Claxton *et al.*

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[66] World Meteorological Organization (WMO), 2022, *Scientific Assessment of Ozone Depletion: 2022*, GAW Report No. 278; WMO: Geneva, 2022. "*Total tropospheric chlorine from VSL source gases and their stratospheric entrainment increased by about 10 ppt between 2016 and 2020. The input of chlorine VSLSs to the stratosphere now amounts to 130 ± 30 ppt, corresponding to contribution of 4.0% relative to the total chlorine input*". Laube, J. and Tegtmeier, S., (Lead Authors), Fernandez, R.P., Harrison, J., Hu, L., Krummel, P., Mahieu, E., Park, S., Western, L., Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1.

[67] Hossaini R., Chipperfield M.P., Montzka S.A., Leeson A.A., Dhomse S.S., Pyle J.A., The increasing threat to stratospheric ozone from dichloromethane, *Nat Commun.*, 2017, **8**, 15962. https://doi.org/10.1038/ncomms15962.

[68] Fang, X., Park, S., Saito, T. *et al.*, Rapid increase in ozone-depleting chloroform emissions from China, *Nature Geosci.*, 2019, **12**, 89–93. https://doi.org/10.1038/s41561-018-0278-2.

[69] Hossaini, R., Atlas, E., Dhomse, S.S., Chipperfield, M.P., Bernath, P.F., Fernando, A.M., Mühle, J., Leeson, A.A., Montzka, S.A., Feng, W., Harrison, J.J., Krummel, P., Vollmer, M.K., Reimann, S., O'Doherty, S., Young, D., Maione, M., Arduini, J., and Lunder, C.R., Recent trends in stratospheric chlorine from very short-lived substances, *J. Geophys. Res. Atmos.*, 2019, **124**, 2318–2335. https://doi.org/10.1029/2018JD029400.

[70] Bednarz, E.M., Hossaini, R., Chipperfield, M.P., Abraham, N.L., and Braesicke, P., Atmospheric impacts of chlorinated very short-lived substances over the recent past – Part 1: Stratospheric chlorine budget and the role of transport, *Atmos. Chem. Phys.*, 2022, **22**, 10657–10676. https://doi.org/10.5194/acp-22-10657-2022.

[71] Claxton, T., Hossaini, R., Wilson, C., Montzka, S.A., Chipperfield, M.P., Wild, O., *et al.*, A synthesis inversion to constrain global emissions of two very short lived chlorocarbons: dichloromethane, and perchloroethylene, *Journal of Geophysical Research: Atmospheres*, 2020, **125**, e2019JD031818. https://doi.org/10.1029/2019JD031818.

Table 2.10 Calculated ODP range of some VSLS showing seasonal/geographic sensitivity

Substance	ODP range
Dichloromethane	0.0097–0.0208
Chloroform	0.0143–0.0264
Perchloroethylene	0.0057–0.0198
Dichloroethane	0.0029–0.0119

***Note**: TCE breaks down rapidly in the troposphere and an ODP value has not been allocated.*

Dichloromethane (DCM, also known as methylene chloride) is posited in the ODP range of 0.0097–0.0208.[72] DCM was specifically mentioned in the SAP 2018[73] , which concluded that elimination of future DCM emissions would have a substantial positive impact on total column ozone.

In the 2018 MCTOC Assessment report, it was noted that the then level of DCM emissions, inferred from atmospheric measurements, was about 1,300 ktonnes/year. This was consistent with historical capacity in the developed world of about 700 ktonnes/year and the reported growth of emissions from China.[74] These emissions were assessed as contributing less than 1% to the current total stratospheric chlorine loading, which is small and within the uncertainty of the total chlorine loading estimate. It was noted that, given the reductions in HCFC-22 production and subsequent reduction in chloroform production, resulting from the Montreal Protocol phase-out of HCFCs, and other trends in DCM usage, global DCM production was considered unlikely to increase significantly.

Subsequently, the contribution of DCM to stratospheric chlorine loading has been updated given continued growth[75,76] and new aircraft measurements that indicate larger localised

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[72] Claxton, T., Hossaini, R., Wild, O., Chipperfield, M.P., & Wilson, C., On the regional and seasonal ozone depletion potential of chlorinated very short-lived substances, *Geophysical Research Letters*, 2019, **46**, 5489–5498. https://doi.org/10.1029/2018GL081455.

[73] World Meteorological Organization (WMO), 2018, *Executive Summary: Scientific Assessment of Ozone Depletion: 2018*, World Meteorological Organization, Global Ozone Research and Monitoring Project – Report No. 58, 67 pp., Geneva, Switzerland, 2018. Appendix, Chapter 5.

[74] Feng, Y., Bie, P., Wang, Z., Wang L., and Zhang, J., Bottom-up anthropogenic dichloromethane emission estimates from China for the period 2005–2016 and predictions of future emissions, *Atmos. Environ.*, 2018, **186**, 241–247.

[75] Hossaini, R., Atlas, E., Dhomse, S.S., Chipperfield, M.P., Bernath, P.F., Fernando, A.M., Mühle, J., Leeson, A.A., Montzka, S.A., Feng, W., Harrison, J.J., Krummel, P., Vollmer, M.K., Reimann, S., O'Doherty, S., Young, D., Maione, M., Arduini, J., and Lunder, C.R., Recent trends in stratospheric chlorine from very short-lived substances, *J. Geophys. Res. Atmos.*, 2019, **124**, 2318–2335, https://doi.org/10.1029/2018JD029400.

[76] Bednarz, E.M., Hossaini, R., Chipperfield, M.P., Abraham, N.L., and Braesicke, P., Atmospheric impacts of chlorinated very short-lived substances over the recent past – Part 1: Stratospheric chlorine budget and the role of transport, *Atmos. Chem. Phys.*, 2022, **22**, 10657–10676. https://doi.org/10.5194/acp-22-10657-2022.

injections of DCM to the stratosphere over Asia during certain meteorological conditions.[77,78] Retrospectively, the emissions of DCM estimated in 2018 were slightly overstated; however, with constant growth, notably in South and East Asia, DCM emissions are now estimated to have surpassed 1,300 ktonnes/year, including an estimated 10 ktonnes/year DCM emissions from its use as feedstock for HFC-32 production.

2.10.3 Production and use of dichloromethane (DCM) and chloroform (CFM)

The production of chloromethanes is virtually all by the reaction of chlorine with methyl chloride, although a small part continues to use the older method of methane chlorination. Methyl chloride is produced by the reaction of hydrochloric acid (HCl) with methanol, with the HCl feed returning from the production of DCM, CFM, and CTC. "Higher chloromethanes" is a collective term for these products. DCM and chloroform (and CTC) are co-produced on a chloromethanes plant, so they are also considered together here.

It is not possible to make just DCM or CFM alone: typically, the ratio of DCM to chloroform is flexible enough to move between 40–60%. The products are separated by distillation. A few plants have been constructed to a chloroform balance of 70% (often linked to an HCFC-22 plant) and others have a 70% DCM ratio (often older plants), built at a time when the only use for chloroform was as industrial or pharmaceutical solvent/anaesthetic; but it could be processed further to CTC, which, once refined, was the feedstock for CFC-11/-12 production. This seems to be partly a factor for continued use of chloroform as a solvent, because once established in a pharmaceutical process, it is very difficult to change. DCM and CFM are not usually interchangeable as solvents, as the boiling point of DCM is 40°C, while that of CFM is 61ºC. Some pharmaceutical companies use both chloromethanes in large quantities, although DCM is usually larger volume. CTC is described in section 2.8, but it is worth noting here that the proportion of CTC in the higher chloromethane mix can be managed to <5% of the total, but can be, and is, extended to up to 10–15% without significant plant modification.

Production of DCM globally has been estimated at more than 1,800 ktonnes (2020)[79], while chloroform production is estimated at over 1,500 ktonnes. Around 1,450 ktonnes of DCM are ascribed to emissive use, whilst almost 1,500 ktonnes of CFM were produced as feedstock for HCFC-22, used as refrigerant fluid and foam blowing agent and with an increasing majority used as feedstock to produce TFE/HFP, which are vital precursors to fluoropolymer production and other speciality fluoro-derivatives. Background natural sources of DCM are believed to be small, in the range of 70 ktonnes, arising from phytoplankton in seawater and the burning of biomass.

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[77] Oram, D.E., Ashfold, M.J., Laube, J.C., Gooch, L.J., Humphrey, S., Sturges, W.T., Leedham-Elvidge, E., Forster, G.L., Harris, N.R.P., Mead, M.I., Samah, A.A., Phang, S.M., Ou-Yang, C.-F., Lin, N.-H., Wang, J.-L., Baker, A.K., Brenninkmeijer, C.A.M., and Sherry, D., A growing threat to the ozone layer from short-lived anthropogenic chlorocarbons, *Atmos. Chem. Phys.*, 2017, **17**, 11929–11941, https://doi.org/10.5194/acp-17-11929-2017.

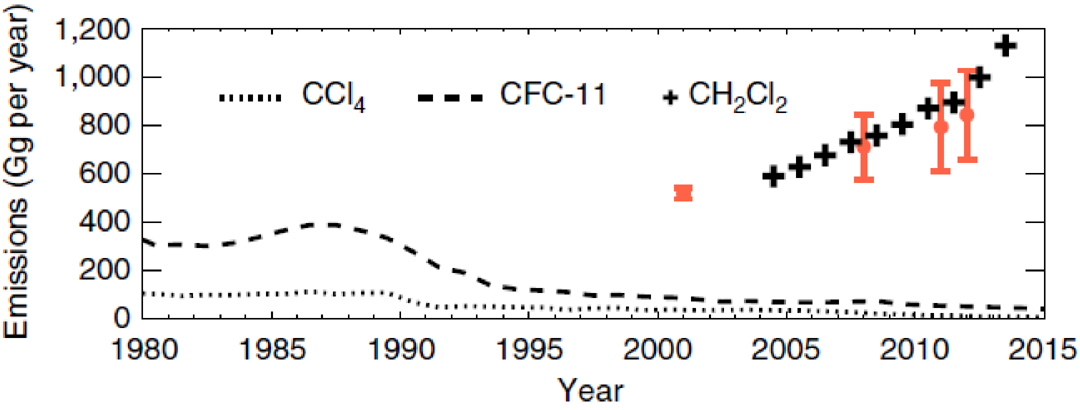
[78] Adcock, K.E., Fraser, P.J., Hall, B.D., Langenfelds, R.L., Lee, G., Montzka, S.A., Oram, D.E., Röckmann, T., Stroh, F., Sturges, W.T., Vogel, B., and Laube, J.C., Aircraft-Based Observations of Ozone-Depleting Substances in the Upper Troposphere and Lower Stratosphere in and Above the Asian Summer Monsoon, *J. Geophys. Res. Atmos.*, 2021, **126**, e2020JD033137, https://doi.org/10.1029/2020jd033137.

[79] Information compiled by NSA Ltd, provided via David Sherry, MCTOC member, personal communications. Many of the numerical market data here are supplied by NSA Ltd., with the approval of the contractors.

2.10.4 Dichloromethane

While controls on DCM emissions in the European Union, the United States, and Japan have led to long-term reductions in demand, there has been substantial growth in DCM solvent use, notably in South and East Asia. The following Figure 2.7 (taken from Hossaini *et al.*, 2017)[80] demonstrates the growth in global emissions and emissive use.

Figure 2.7 Global Atmospheric DCM emissions, Gg per year, 2005–2014



A recent study[81] notes that global DCM emissions are likely to be above 1,000 ktonnes. The study noted: "*…we report an increase in emissions from China of the industrially produced chlorocarbon, dichloromethane (CH_2Cl_2). The emissions grew from 231 (213–245) Gg yr^{-1} in 2011 to 628 (599–658) Gg yr^{-1} in 2019, with an average annual increase of 13% (12–15%), primarily from eastern China. The overall increase in CH_2Cl_2 emissions from China has the same magnitude as the global emission rise of 354 (281−427) Gg yr^{-1} over the same period.*" The study also noted that "*Dichloromethane (CH_2Cl_2), the most abundant chlorine-containing VSLS with a lifetime of ~6 months, accounts for ~70% of the total stratospheric source gas injection from chlorine-containing VSLS*".

This study used chloromethanes data provided by the China Chlor-Alkali Industry Association (CCAIA), which also indicated the consumption of the DCM feedstock to the manufacture of HFC-32. The supplementary information provided in this study indicates, for the most recent year 2019, the production (1,300 ktonnes) and use of DCM for its various applications in HFC-32 (feedstock, 319 ktonnes at a unit ratio (UR) of DCM to HFC-32 of 1.67–1.71%), pharmaceutical (312 ktonnes) and general solvent use (emissive, 487 ktonnes). The difference between production and consumption should be the exported amount (187 ktonnes), which is consistent with the Comtrade[82] export data reported below. The study also made use of the Chinese Household Airconditioning and Refrigeration Industry (chinaIOL.com) data on annual fluorocarbon production to confirm the HFC-32 output, and

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[80] Hossaini R., Chipperfield M.P., Montzka S.A., *et al.*, The increasing threat to stratospheric ozone from dichloromethane, *Nat Commun.*, 2017, **8**, 15962. https://doi.org/10.1038/ncomms15962.

[81] An, M., Western, L.M., Say, D. *et al.*, Rapid increase in dichloromethane emissions from China inferred through atmospheric observations, *Nat Commun.*, 2021, **12**, 7279. https://doi.org/10.1038/s41467-021-27592-y.

[82] UN Comtrade Database, https://comtrade.un.org/data. Accessed August 2022. Imports of DCM to any country without HFC-32 manufacture are presumed to be emissive.

although this does not necessarily include the total output of China it is useful for trend analysis.

Table 2.11[83] shows the build-up of exports of DCM from China since 2016. This indicates that the present market for DCM in China is saturated, with the slight decline of exports in 2020 versus 2019 possibly indicating increased domestic use of DCM to HFC-32 production. By comparison, for China, in 2008 DCM imports equalled exports at 14 ktonnes, and by 2012 China was exporting nett 26 ktonnes.

Table 2.11 Exports of DCM, China, 2016–2020

Period	Trade Flow	Reporter	Partner	Commodity Code	Net weight (kg)
2016	Export	China	World	290312	86,730,576
2017	Export	China	World	290312	145,231,856
2018	Export	China	World	290312	148,743,991
2019	Export	China	World	290312	186,339,442
2020	Export	China	World	290312	155,622,287

Table 2.12 presents an evaluation of global DCM emissions from 2002 to 2020.[84] Emissions include all known emissive uses of DCM. Emissions are assumed to be made in the same year of supply, understanding that stocks held, and December shipments, may distort accuracy; however, the inaccuracy balances over time. Emissions from the DCM bank retained in flexible foams has not been considered; however, over time, these are not expected to distort the trend in emissions.

Table 2.12 Estimated global emissions of DCM, 2002–2020 (ktonnes)

Year	2002	2005	2010	2015	2020
DCM emissions from emissive uses	655	790	970	1120	>1400

Within this global analysis, in 2020 the regions of East Asia (China, Japan and Korea) and South Asia (India, Pakistan, Bangladesh) contributed 56% and 22%, respectively, of global emissions from all uses. There would appear to be no specific reason to distinguish between pharmaceutical uses and other solvent uses because solvent purchased is necessarily replacing solvent that is lost or destroyed. Many non-Article 5 parties have recognised the toxicological profile of DCM and imposed regulatory restraints on its use. The combined consumption of DCM as a solvent in Europe, the United States, and Japan is estimated at ±180 ktonnes (13% of global total), which is a 50% reduction in quantities consumed in 2005. However, the production in all three regions is higher due to export markets.

Since the late 2000s, the production of HFC-32 has grown very rapidly, for which DCM is the feedstock (1.67–1.71 units per unit of HFC-32) estimated as 400 (370–430) ktonnes in 2020.

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[83] UN Comtrade Database, https://comtrade.un.org/data. Accessed August 2022.

[84] Information compiled by NSA Ltd, provided via David Sherry, MCTOC member, personal communications.

It is believed that more than 80% of global HFC-32 capacity is placed in China, with remaining production in India, Japan, and the United States. Continued expansion of HFC-32 production is expected in the near future, with flattening towards the end of the decade.

DCM consumption as a solvent dominates demand, with around 75% of the global production, which is used in pharmaceutical processing, paint-stripping, foam blowing, adhesives carrier, electronics surface cleaner, and as a general low-boiling solvent. It has been used for the solvent-decaffeination of coffee. Some of the solvent uses, such as domestic paint stripping or degreasing of parts, are totally emissive. Domestic solvent use of DCM is banned in Europe and the United States, and industrial paint-stripping plants must ensure strong evacuation of the solvent, following which it can be partly recovered for reuse (this depends on the solvent mix used in the process). ECHA in Europe and OSHA/TCSA in the United States regard DCM as a possible human carcinogen with a potential to damage eyes, skin, liver, and heart, reflecting the IARC view that it “is suspected of causing cancer”.

The pharmaceutical use as process solvent is by far the largest single global outlet, enabling a solvent-based medium in which complex pharmaceutical intermediate reactions can be performed, with the DCM being readily evaporated and recovered. Tablet coating may also be applied using DCM as the carrier medium. The possible means of emissions are by direct evacuation to the atmosphere, evacuation to a distillation tower allowing for recycling and reuse of the DCM, and continued recycling until the product becomes too spoiled for continued use, at which point it may still be sold via distributors as a paint stripper or general solvent.

Under air pollution controls in China, several regulations have been issued to restrict the use of DCM since DCM is a volatile organic pollutant. It is already prohibited for public use. Considering the health hazards of DCM, in October 2021, the Ministry of Ecology and Environment included DCM in the Action Plan for New Pollutant Control (Draft) and clarified 9 management measures, such as: (1) according to the “Industrial Structure Adjustment Guidance Catalog”, prohibiting DCM used for paint strippers; (2) by the end of 2025, phase-out DCM use for flexible polyurethane foaming agents.

Figure 2.8 illustrates the DCM market in China in 2017[85], with growth forecasts out to 2030, although the recent environmental legislation will curb some of this growth. For example, by comparison with the United States and Europe where domestic use of paint strippers using DCM has already been banned, the loss of this market segment in China could amount to a reduction of about 90 ktonnes/year after 2025. In addition, it might be noted that foam blowing using DCM accounted for close to 150 ktonnes in 2017, which may have subsequently increased. Reduction of DCM emissions from these two use sectors may amount to some 250–300 ktonnes/year by 2026 when regulations to restrict the use of DCM are implemented.

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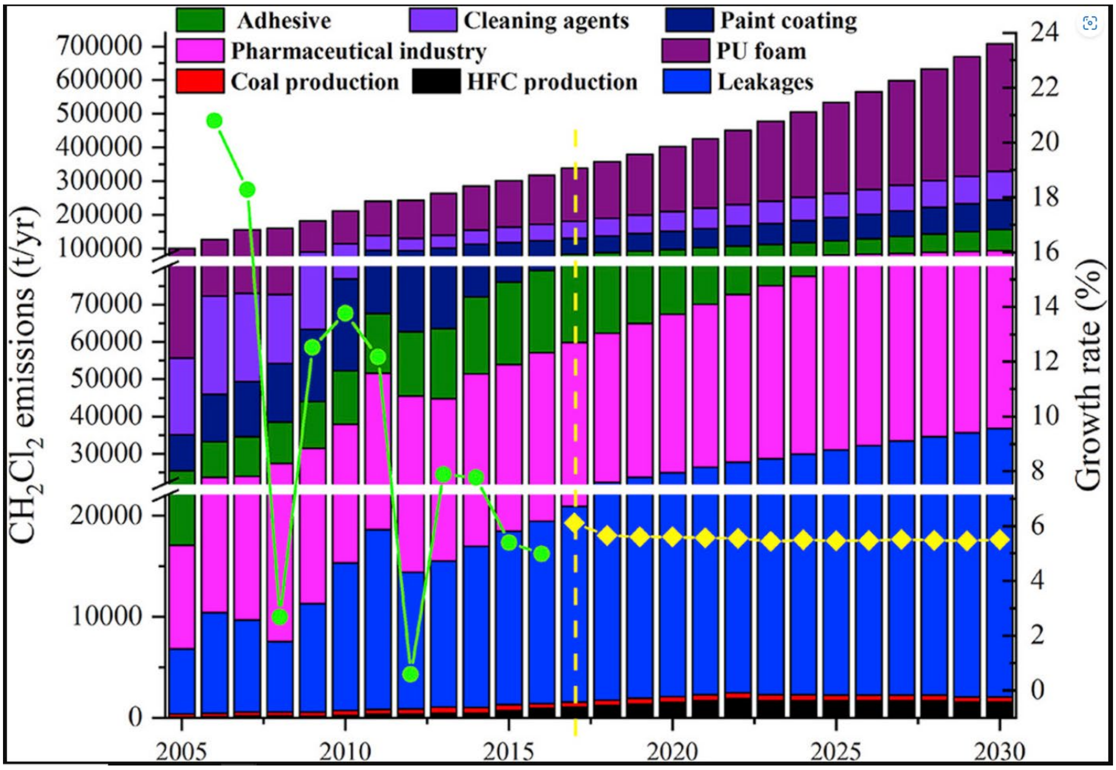
[85] Feng, Y., Bie, P., Wang, Z., Wang L., Zhang, J., Bottom-up anthropogenic dichloromethane emission estimates from China for the period 2005–2016 and predictions of future emissions, *Atmos. Environ.*, 2018, **186**, 241–247.

Figure 2.8 DCM emissions per year, by source, China, 2005–2030, business-as-usual case (tonnes)



The market trajectory for DCM's immediate future is hard to predict. Concerns about toxicity and carcinogenicity, as well as possible suffocation by inhalation of vapours in enclosed spaces, have led Europe, Japan, and the United States to confine its use, with consumption about a third of what it was in the 1980s. IARC classifies DCM as class 2B "possibly carcinogen to humans".

India is a globally leading drug manufacturer, and its demand for DCM has caused new CM capacity to be built or planned. 2020 Indian CM capacity is estimated to be 320–340 ktonnes, and planned increases will provide >500 ktonnes capacity by 2025. Despite new manufacturing capacity India still imports tens of kilotons of DCM, likely to be due to continuing growth in the pharmaceutical business, and the start of production of HFC-32.

China, with >3 million tonnes of chloromethanes capacity, is in a similar situation, although China must export around 150–180 ktonnes DCM as local demand is currently saturated. As noted, China is taking measures to decrease public exposure to DCM from two common applications. The probable scenario for emissive DCM is that its growth rate will flatten and then decline as increased regulatory supervision is put in place globally, and public sales are disallowed. This would be dependent upon the rate at which regulatory limits are set and followed in open uses amongst the Parties.

However, growth will continue as feedstock for HFC-32, with an estimated 400 ktonnes (370–430 ktonnes) of DCM production as feedstock for HFC-32 production in 2020. Production-based emissions are expected to tend to the lower end of 2% to cover the production and supply chain, leading to an estimated 10 ± 4 ktonnes of emissions in 2020, with an expectation of doubling by 2028, after which Kigali measures will begin to affect regional consumption in Article 5 parties. This is insignificant compared with emissions from DCM use as a solvent.

2.10.5 Chloroform

Global CFM production is estimated at more than 1,600 ktonnes in 2019, of which more than 90% is consumed as the feedstock in the production of HCFC-22 (ratio 1.48 units CFM to 1 unit HCFC-22, to take account of differing production units). HCFC-22 is used primarily as a refrigerant fluid and foam blowing agent, with production for emissive uses controlled by the Montreal Protocol. HCFC-22 is also used as a non-controlled feedstock in the further production of tetrafluoroethene (TFE) and hexafluoropropene (HFP), which are intermediates vital to fluoropolymers and other complex fluorocarbons, such as hexafluoropropylene oxide and tetrafluoropropanol, for pharmaceutical and agrochemical intermediate production.

A relatively recent study[86] notes a previous study in 2003, which concluded that the atmospheric flux from natural sources appeared to be constant at 660 ktonnes ±220 ktonnes, while anthropogenic sources accounted for 66 ±23 ktonnes, or around 10% of the total.[87] Fang discloses a much lower sum of global CFM emissions.[88] This paper concludes that by 2015 man-made emissions of chloroform may represent 50% of the atmospheric burden. It is noted that *"We show that emissions from eastern China grew by 49 (41–59) Gg between 2010 and 2015, a change that could explain the entire increase in global emissions.*"

This is an important conclusion, given that in 2002[89] CFM global production was estimated at about 850 ktonnes, contemporary to the above 2003 report. The CFM growth rate, largely attributed to HCFC-22 growth in China, has led to an estimated 1,500+ ktonnes CFM production in 2020, slightly lower than the 1,600+ ktonnes CFM in 2019. In China, HCFC-22 production in 2010 (550 ktonnes) and in 2015 (535 ktonnes), appeared static, with CFM requirement of about 800 ktonnes. However, in the years 2011–2014, HCFC-22 production in China averaged 620 ktonnes, with mean CFM requirement of 925 ktonnes, an increase of 15%. Following 2015, despite the reduction in emissive uses of HCFC-22, the overall production of HCFC-22 grew back to and then exceeded its 2011–2014 volumes due to rapid growth in feedstock uses.

HCFC-22 production in non-Article 5 parties in the period 2010–2015 was static, and has remained so, in the range of 180–200 ktonnes. This appears to partly align with the findings of Fang *et al*., given that much of the growth in HCFC-22 based fluoropolymers took place in China and to a lesser extent India. However, the emissions from the production and conversion of CFM to HCFC-22 would need to be far above MCTOC's emissions rates to explain why emissions rose by nearly 20%, or 53 ktonnes, between 2010 and 2015.

Notwithstanding, it is believed that globally, up to an estimated 100 ktonnes of CFM emissions (2020) may occur from emissive uses as an industrial and pharmaceutical

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[86] Fang, X., Park, S., Saito, T. *et al.*, Rapid increase in ozone-depleting chloroform emissions from China, *Nature Geosci*, 2019, **12**, 89–93. https://doi.org/10.1038/s41561-018-0278-2.

[87] A. McCulloch *et al.*, Chloroform in the environment: occurrence, sources, sinks and effects, *Chemosphere*, 2003, **50**(10), 1291–1308. https://doi.org/10.1016/S0045-6535(02)00697-5.

[88] Ibid., Fang *et al.*, 2019, Footnote 79. "*The global inversion carried out using this model shows that the annual global-total CHCl3 emissions approximately stabilised at ~271 Gg yr−1 during 2000− 2010, with a suggestion of a small decline, and then an increase after 2010 to reach 324 (261−397) Gg yr−1 (16− 84 percentile range) in 2015*" and "*We estimate that the global chloroform emissions grew at the rate of 3.5% yr−1 between 2010 and 2015 based on atmospheric model simulations.*"

[89] Article 7 data 2002 shows 514 ktonnes HCFC-22, which is equivalent to 760 ktonnes CFM, with other uses adding 80–100 ktonnes.

processing solvent. It is estimated that about 30–50 ktonnes/year chloroform may be used in emissive applications in China alone. The balance of CFM use is as feedstock, whereby an emission rate of 2–4% (30–60 ktonnes/year) may be applicable. The probability of a higher emission rate is because most of the CFM supplied to HCFC-22 production units must be transported by road, rail, or overseas shipments. It is believed that only 10–12 HCFC-22 plants globally are within the fence line of a producer of chloromethanes, with less emissive supply of CFM for HCFC-22 feedstock use.

The largest consumption regions where CFM is used as a pharmaceutical and industrial process solvent are South and East Asia. Consumption regions largely exclude Europe and the United States, where chloroform is regarded as a probable carcinogen and may be toxic to liver and kidneys, and use would be under extreme containment. Outside the most industrialised countries, emissive use for chloroform can be regarded as a relatively stable market: that is, until and if regulatory controls are applied on CFM for use in emissive applications. IARC classifies chloroform as class 2B “possibly carcinogenic to humans”

The reported increase in atmospheric chloroform emissions could either be linked to increased emissive use as a solvent or processing agent, or natural emissions from the oceans and other causes could account for a larger atmospheric burden.

2.10.6 Conclusions for dichloromethane and chloroform

In conclusion, short-term stability is expected in the chloroform market globally, with production at about 1,500–1,700 ktonnes, with the potential increase in feedstock use to HCFC-22 overriding the decline in emissive use. Increases in the production of DCM as feedstock to HFC-32 are expected, which could drive up DCM demand by a further 150–200 ktonnes relative to 2020, while the recently seen high growth rate of DCM into Asian solvents markets might abate and begin to reduce after 2025. The DCM market in China is already saturated, and high (>140 ktonnes) levels of exports from China to South Asia, Middle East and Africa have tended to displace exports from the United States and Europe.

Considering ratio management of higher chloromethanes, the current (2020) ratios of more than 1,800 ktonnes DCM to 1,500 ktonnes CFM means chloromethanes plants are running at a relatively comfortable ratio of 55:45. Looking forward, DCM is likely to be produced at around 2,000 ktonnes in 2025, whereas CFM will largely remain around 1,600 ktonnes. This would correspond to a DCM: CFM production ratio of around 56:44 DCM: CFM, well within the normal range limits of modern chloromethanes plants.

For reference, Table 2.13 presents an assessment of global chloromethanes capacity from 2010 to 2020, indicating the proportions for the country/region with the highest proportion globally.[90]

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[90] Information compiled by NSA Ltd, provided via David Sherry, MCTOC member, personal communications.

Table 2.13 Global capacity of chloromethanes, 2010–2020 (ktonnes)

Year	2010	2012	2014	2016	2018	2020
China	1,500	1615	2035	2375	2700	3250
East Asia excl. China	175	145	145	145	145	145
Europe	660	660	660	500	480	480
United States	360	360	360	360	360	360
India	150	190	210	230	260	320
Total	**2845**	**2970**	**3410**	**3610**	**3945**	**4555**
% China	53%	54%	60%	66%	68%	71%

2.10.7 Ethylene dichloride (EDC)

1,2-Dichloroethane, commonly known as ethylene dichloride (EDC), is a chlorinated hydrocarbon, principally used in the manufacture of vinyl chloride monomer (VCM, chloroethene), the major precursor for PVC production. Ethylene dichloride is also used as an intermediate to produce other organic chemicals, such as vinylidene chloride, ethyleneamines, and solvents such as trichloroethylene. It is also used itself as a chlorinated solvent. A key indicator for PVC production, and hence EDC, is the construction industry, for sidings, tubes, piping, and electronics.

EDC is produced through the reaction of ethylene and chlorine ($H_2C{=}CH_2 + Cl_2 \rightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}Cl$). This is called direct chlorination, or EDC-DC. In subsequent reactions, notably to vinyl chloride (chloroethene), hydrogen chloride is formed and re-used to produce more EDC in reaction with ethylene and oxygen. ($H_2C{=}CH_2 + 2\ HCl + \frac{1}{2}\ O_2 \rightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}Cl + H_2O$). This is called oxy-chlorination or oxy-EDC. The process is entirely closed loop. Figure 2.6, section 2.8, shows a flow chart of the closed loop production process of ethylene to EDC-DC to VCM to oxy-EDC. The end of the process is the polymerisation of VCM to PVC, with the route of polymerisation producing different qualities of PVC for various end uses.

There is no chemical distinction between EDC-DC and oxy-EDC. The total global capacity to produce EDC is more than 62,000 ktonnes/year, with the largest production arising in the United States, Southeast and East Asia, Europe, and Middle East. Global EDC production is running very close to capacity. About 90% of EDC production supports the vinyl chain; this means that EDC is linked to the fortune of the PVC industry. The global VCM market is about 55,000 ktonnes, with China (25,000 ktonnes) having the largest capacity of global regions. However, most of the VCM in China is produced by the reaction of acetylene with HCl, which avoids the requirement for EDC: this is the only country producing by this route, which is effective only with the economics of the massive scale of coal production and high energy content used to make calcium carbide, which reacts to acetylene in the presence of water.

Many VCM producers globally operate in a closed cycle, that is, the production of 1.6 units EDC by direct chlorination of ethylene yields 1.0 units of VCM and 0.6 units of HCl, which is recycled to react with ethylene in the presence of oxygen to oxy-EDC for further cracking to VCM. In countries that are ethylene limited, such as India, EDC is imported from the Middle East (or Europe or the United States), and the HCl derived reacts with local ethylene: this way the local ethylene component in VCM is reduced by 50%. In addition, EDC is the most efficient way of storing chlorine, enabling large bulk quantities to be built up for export markets. The largest exporters of EDC in 2020 were the United States, with 1,250 ktonnes, slightly down from 2019; Middle East, at about 700 ktonnes; Indonesia (280 ktonnes); and the Republic of Korea (340 ktonnes). The largest importers were India (over 700 ktonnes); East Coast China (640 ktonnes); Brazil (over 350 ktonnes, but likely to reduce with increased local capacity); Thailand (600 ktonnes); Egypt (300 ktonnes); and Japan (130 ktonnes).

In calculating emissions from this annual consumption, the tight controls imposed on the industry, in recognition of the toxicity of vinyl chain products, and the closed loop manufacturing system of integrated EDC to VCM to oxy-EDC plants are taken into account. Discussions with vinyl chain producers suggest an 0.1% emission factor from production, and that elongated supply chains involving bulk transfers, to and from ships' tanks, and onward transport, storage and use at the end-user would be subject to an additional 0.075% emission rate. With these assumptions, total 2020 EDC emissions are estimated to be around 60–105 ktonnes.

However, trade statistics often reveal small shipments of EDC, in the range 10–200 tonnes, being made to countries without VCM, solvent, or ethyleneamines production. Low volumes do not sustain high volume continuous production. These small shipments could be for use as solvent or paint thinner if local distributors are selling it as such, despite EDC having a similar toxicity profile to DCM, CFM and PCE[91], highly flammable, not commonly recommended as a solvent by producers. It is not illegal to do so, although EDC is a chemical subject to Prior Informed Consent, where trans-border shipment agreement is required. EDC has also been suggested by at least one of the Implementing Agencies as a suitable replacement for CTC as a process agent in pharmaceutical production. It is possible that even in the best-case scenario with very limited solvent use, emissions from solvent use might be 2–3 ktonnes/year globally, but could be much more, as this assessment has only considered cross-border trade. Up to 20 ktonnes/year EDC emissions from solvent uses should not be excluded.

2.10.8 Trichloroethylene (TCE)

Concerns about the toxicity of TCE[92] have reduced the global solvent market for TCE, usually used for metal degreasing, from an estimated 180 ktonnes/year in 2004 to about 100 ktonnes/year in 2020. Solvent use of TCE in Europe, the United States and Japan has virtually disappeared, and most TCE is used as solvent in South Asia and East Asia. Most of these solvent sales will be handled by local or regional distributors, largely in 200 litre drums.

Feedstock use of TCE dominates the use pattern, largely to produce HFC-134a for which global TCE use is estimated at 330–380 ktonnes in 2020. China is the largest producer of HFC-134a, and the United States is the second largest and where one of three original HFC-134a operating plants has been closed. A new 15 ktonnes/year HFC-134a plant has been proposed for Saudi Arabia, using technology from China. With HFC-134a being phased down under the Kigali Amendment, TCE producers will close production at a similar pace, rather than continue to service the very fragmented solvent market. This excludes co-product plants that can produce TCE, such as TCE/PCE units, where the ratios can be managed much as on a PCE/CTC plant. TCE production is now largely based in China and, to a smaller extent, India. One United States based company closed a 60 ktonnes/year TCE plant in 2021, leaving one U.S. producer; there are two TCE producers in Japan; there are no TCE producers remaining in Europe. Solvent based TCE emissions are likely to dominate global atmospheric TCE

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[91] IARC classifies PCE as class 2B "possibly carcinogenic to humans".

[92] IARC classifies TCE a class 1 human carcinogen.

emissions. Few HFC-134a producers also make trichloroethylene, and so the additional supply chain delivery is expected to add to a nominal 0.6–1.5% of production emissions.

Historically, there were many small companies that purchased TCE as feedstock for production of monochloroacetic acid (MCAA) by hydrolysis; however, the quality was poor, and production of high-purity MCAA by the direct chlorination of acetic acid eventually replaced the TCE process. Nevertheless, it cannot be ruled out that some small production using PCE remains. Although a feedstock use, this method of production may have had loss rates of more than 5% TCE.

In this century, it is estimated that emissions of TCE as solvent have dropped from a peak in 2002–2004 of 180 ktonnes/year to a current (2020) level of about 100 ktonnes, with current TCE feedstock use for HFC-134a production contributing an additional 3–7 ktonnes of emissions.[93]

2.10.9 Perchloroethylene (PCE)

Perchloroethylene is considered by IARC as class 2A “probably carcinogenic to humans”.

Its solvent uses mainly in dry-cleaning and metal cleaning are tightly regulated to avoid human exposure, and public uses, such as brake-pad cleaners or anti-spotting agents are not allowed. It is also used in petroleum refineries for the regeneration of catalyst, in both catalytic reformer and isomerisation operations. The consequence of human health concerns, along with generally diminishing solvent-based cleaning, has led to a slow decline in PCE dry-cleaning emissions in North America and Europe. Most of the North American and Europe PCE dry-cleaners have low-emission machines, with contracted waste removal and recycling for reuse services. France requires dry-cleaning to be conducted outside residential areas; California has a total ban on PCE use. Asia and Africa regions have relatively lower demand for PCE dry-cleaning.

Metal cleaning demand for PCE is relatively stable, despite tighter controls on metal degreasing emissions. Some 1,1,1-trichloroethane and trichloroethylene cleaning has been replaced by PCE over the years. PCE in metal cleaning is showing mild growth in some regions.

Total PCE solvent use is estimated to be in the range 170–180 ktonnes globally, with less than 40% demand in East Asia, 33% in North America and Europe, and the balance roughly evenly spread around other industrialised regions. This is a 20% reduction from one 2002 estimate for 2002 of 220 ktonnes.[94]

The greater part of PCE demand is for its use as feedstock for fluorocarbons production. Perchloroethylene is used to produce CFC-113 in the production of chlorotrifluoroethene (CTFE), an important industrial fluorinated monomer. CFC-113 is used also in the production flow of CFC-113a to CFC-114a to HFC-134a; in the principal production route to HFC-125; and in the production flow of CFC-113a via various stages to HFO-1336mzz isomers. Global PCE production as feedstock is estimated to be close to 400 ktonnes/year and declining, as the derivatives HFC-125 and HFC-134a enter Kigali phase-down schedules in non-Article 5

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[93] Information compiled by NSA Ltd, provided via David Sherry, MCTOC member, personal communications. TCE 2002–2020.

[94] Information compiled by NSA Ltd, provided via David Sherry, MCTOC member, personal communications. PCE 2002–2020.

parties. About 40% of global PCE use as feedstock is estimated for North America and 60% for East Asia, predominantly China.

Global PCE use is estimated at about 560–590 ktonnes in 2020, with emissions from solvent use (160–170 ktonnes) eclipsing emissions from the feedstock production and supply chain, which are in the range 8–16 ktonnes (2–4%).[95]

2.10.10 Methyl chloride

Methyl chloride (chloromethane, MeCl) is a colourless, odourless, and extremely flammable gas with a boiling point of -23.8°C. MeCl emissions originate largely from natural sources, including tropical and subtropical plants, biomass burning, the ocean, salt marshes, and fungi. It contributes to about 17% of the total chlorine loading of the atmosphere. Its mean molar fraction of atmospheric chlorine has risen by 2–3% since 2012, indicating that perhaps some anthropogenic activity may be contributing to the increase.[96,97]

MeCl is regarded as a potential workplace carcinogen and has an IARC rating of 3, meaning not classifiable as to its carcinogenicity in humans due to lack of evidence. The stratospheric ODP of MeCl has been determined as 0.02, based on its short atmospheric lifetime.

In 2017 Li *et al.*[98] noted that "*The annual average of industrial CH_3Cl emissions for 2008–2012 (363 ±85 Gg yr.(-1)) in China is comparable to the known total global anthropogenic CH_3Cl emissions accounting only for coal combustion and indoor biofuel use. This may suggest that unless emissions from the chemical industry are accounted for, global anthropogenic emissions of CH_3Cl have been substantially underestimated.*" In 2020, Ding *et al*. noted that the steelmaking industry was a potentially large emitter of VSLS, including methyl chloride, but that robust abatement techniques, including modifying the flue gas desulphurisation, could reduce the emissions of chlorinated substances by up to 84% efficiency.[99]

A more recent study (pre-proof publication) of MeCl emissions suggests that it may be appropriate to consider anthropological emissions of methyl chloride.[100] A major atmospheric source of MeCl is attributed to biomass burning. A significant decreasing trend ($p < 0.01$) in global methyl halide emissions from biomass burning was found between 2003 and 2021, with MeCl emissions decreasing from 302 to 220 ktonnes/year. The non-biomass burning emissions of MeCl increased from 4,749 ktonnes/year in 2003 to 4,882 ktonnes/year in 2020, implying that further research should focus on non-biomass burning emissions studies, and include investigation of new emission sources and better estimates of known sources of MeCl.

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[95] Ibid.

[96] WMO (World Meteorological Organization), 2018, *Scientific Assessment of Ozone Depletion: 2018*, Global Ozone Research and Monitoring Project–Report No. 58, 588 pp., Geneva, Switzerland, 2018.

[97] Li, S., Park, MK., Jo, C.O. *et al*., Emission estimates of methyl chloride from industrial sources in China based on high frequency atmospheric observations, *J Atmos Chem*, 2017, 74, 227–243. https://doi.org/10.1007/s10874-016-9354-4.

[98] Ibid.

[99] Ding, X., Q. Ling, Y. Huo, Y. Liang, H. Wang, J. Zhang, S. Wang, T. Wang, X. Ye, J. Chen, Gaseous and particulate chlorine emissions from typical iron and steel industry in China, *J. Geophys. Res. Atmos*., 2020, **125**(15), e2020JD032729. https://doi.org/10.1029/2020JD032729.

[100] Xiaoyi Hu, Di Chen, Liting Hu, Bowei Li, Xinhe Li, Xuekun Fang, Global methyl halide emissions from biomass burning during 2003–2021, *Environmental Science and Ecotechnology*, 2023, **14**, 100228. https://doi.org/10.1016/j.ese.2022.100228 (pre-proof publication, accessed December 2022).

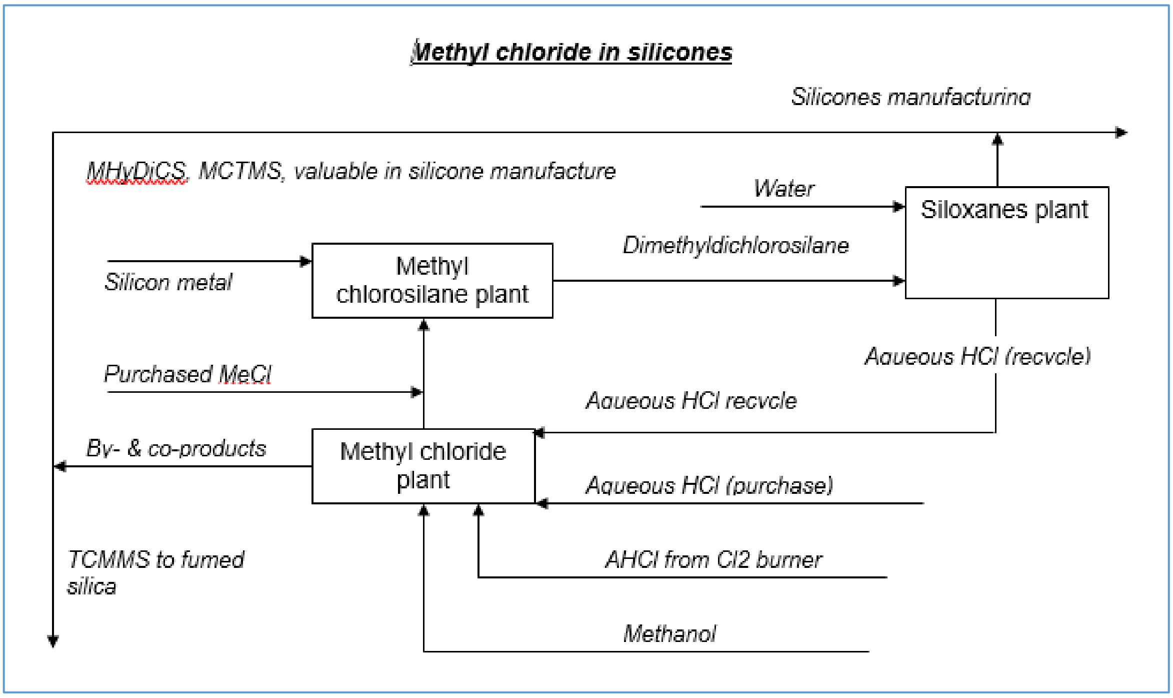
The European Union has recently added methyl chloride as a “new substance” to its Regulation (EC) No. 1005/2009 (known as the Ozone Regulation), requiring member states to report annually on their production, consumption, imports, and exports.

2.10.10.1 Production and uses of methyl chloride

Industrially, MeCl is produced by the reaction of HCl with methanol. Its only use for many years has been as an industrial feedstock, although historically it had been used as a refrigerant gas (R-40) prior to the advent of the much safer CFCs. MeCl is the initial reactant in the production of chloromethanes (by chlorination to DCM, CFM and CTC). HCl is recovered from the process and returned to produce further MeCl (see earlier sections).

Although chloromethane manufacturing represents a large use of MeCl, organic silicone production is even larger. MeCl reacts with silicone metal to make dichlorodimethylsilane (DMDCS). DCDMS reacts with water to produce methyl siloxane, with the co-product HCl released and recovered for further reaction with methanol. A graphic of the silicone process can be seen in Figure 2.9.

Figure 2.9 Use of methyl chloride in silicones[101]



The silicones and chloromethanes sectors represent by far the largest production and consumption of MeCl. Other main industrial uses are the reaction of MeCl with cellulose to make methyl cellulose, and other uses include the production of cationic polymers for paper treatment, the production of cationic surfactants, and the production of butyl rubber.

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[101] Information compiled by NSA Ltd, provided via David Sherry, MCTOC member, personal communications.

2.10.10.2 Quantification of methyl chloride used in chloromethanes

It is possible to quantify the amount of methyl chloride consumed by the chloromethanes industry by comparing the use of MeCl in the higher chloromethanes with the estimated annual production levels of chloromethanes, as seen in the following table.

Table 2.14 Calculation of MeCl use in typical chloromethane production

Product	MeCl % in product	Production ratio of 100%*	% By Weight MeCl per ktonne CMs
Dichloromethane	60	52	31.2
Chloroform	43	43	18.5
Carbon tetrachloride	33	5	1.6
MeCl %/ktonne CMs			***51.3***

** Equal to the assessed 55:45 ratio between global DCM and CFM in 2020 and adding 5% CTC.*

2.10.10.3 Global methyl chloride used in chloromethanes

Earlier in this chapter, the global consumption of DCM was estimated to be greater than 1,800 ktonnes for 2020, and chloroform 1,500 ktonnes. In section 2.8, the 2020 volume of CM-CTC was estimated at about 200 ktonnes in 2020. By using the characteristics of Table 2.14, the total amount of methyl chloride used captively by chloromethane producers globally can be estimated, which amounts to about 1,800 ktonnes.

Table 2.15 Calculation of global MeCl to chloromethanes, 2020

Product	MeCl % in product	Global CMs production (ktonnes)	MeCl (ktonnes)
Dichloromethane	60	1,850	1,100
Chloroform	43	1,500	645
Carbon tetrachloride	33	200*	66
Total MeCl			***1,811***

** More CTC is produced on PCE/CTC plants.*

It is now possible to calculate the evolution of MeCl use in chloromethanes from 2010. The following table considers the amount of methyl chloride that would be required as the initiator for all higher chloromethanes production.

Table 2.16 Global chloromethanes production and methyl chloride consumption, 2010–2020 (ktonnes)[102]

Year	**2010**	**2012**	**2014**	**2016**	**2018**	**2020**
Production CM2	1050	1190	1370	1500	1600	1850
Production CM3	1360	1480	1445	1360	1600	1500
Production CM-CTC	140	155	160	180	190	200
Total CMs	***2550***	***2825***	***2975***	***3040***	***3390***	***3550***
MeCl at ~51%	**1301**	**1441**	**1517**	**1550**	**1729**	**1810**

It should be taken into account that some chloromethane processes are initiated by the direct chlorination of methane gas, in which MeCl is created but not isolated: this may reduce the overall global consumption of MeCl by chloromethanes to about 1,600 ktonnes in 2020. In addition, global consumption of MeCl by methyl cellulose and other specialised downstream uses might add an additional 300–400 ktonnes annually.

It can be concluded that, excepting silicones demand, production, and consumption of MeCl for chloromethanes and other uses of MeCl is more than 2,000 ktonnes. In 2010, China and East Asia accounted for some 50% of global chloromethanes production; and in 2020 this proportion had increased to 70%. It could be expected that annual production of MeCl in East Asia, excluding for silicones, would currently indicate about 1,500 ktonnes.

2.10.10.4 Europe

The European Environment Agency (EEA) notes that "*The Ozone Regulation is more stringent than the rules of the Montreal Protocol and encompasses new substances (halon 1202,* n*-PB, EB, TFIM and MC (methyl chloride)). In 2020, the production of new substances amounted to 1,005,677 metric tonnes, less than a 1% increase compared with 2019. The production of new substances was almost exclusively for feedstock use and comprised MC (more than 99% of total production) and* n*-PB. Expressed in ODP tonnes, the production of MC was also largest (about 98% of total production)*."[103] From this, is it can be inferred that methyl chloride production in Europe was 1,000 ktonnes in 2020.

On the assessment that the European Union, including the United Kingdom, produced about 380 ktonnes of all higher chloromethanes (DCM, CFM, CTC) in 2020, this would indicate European MeCl demand to CMs as (380*51.3%) 195 ktonnes. The actual proportions of the higher chloromethanes are likely to differ from this table, as European Union exports relatively large quantities of CM-CTC, but the percentage of MeCl will not change greatly. In addition to this, the captive use and market sales of MeCl to methyl cellulose producers, and other minor uses in methylated polymers, cationic surfactants and butyl rubber production, could add another 90 (70–110) ktonnes/year.

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[102] Information compiled by NSA Ltd, provided via David Sherry, MCTOC member, personal communications.

[103] EEA, 2022, *Ozone-depleting substances 2022*, 16 September 2022. www.eea.europa.eu/themes/climate/ozone-depleting-substances-and-climate-change-1/ozone-depleting-substances-2022.

All other consumption, and most of the production, of methyl chloride in Europe is for the silicone industry. There are four producers of dimethyldichlorosilane, and its large chain of silicone derivatives, in Europe, and the consumption of MeCl by the silicones business in Europe appears to have been about 715 (700–730) ktonnes in 2020.

2.10.10.5 Global methyl chloride used in silicones

It is not possible to estimate the total consumption of MeCl by the silicones industry. There are five major players globally; four have bases in Europe, two have bases in the United States, and all have joint ventures with partners in China: and there are other independent producers of chlorosilanes/silicones in China. All the major players have recently increased capacity in China. There is also a large producer in Japan. A very rough estimation, based on the number of plants, is that MeCl production for silicones in the United States might be some 800 ktonnes, and in East Asia about 1,000 ktonnes, leading to a total of about 2,600–3,000 ktonnes globally.

2.10.10.6 Emissions of methyl chloride

As has been noted, a very large percentage of MeCl is consumed directly on the production site. The limited external trade for MeCl is to serve the methyl cellulose and other speciality sectors, some of which are also captively used, and topping up the silicones industry, which does not necessarily involve shipments of MeCl. Based on discussions with MeCl producers, emissions from plants are estimated at ≤0.1%, at the very low end of the TEAP production emission range. The very small fraction of methyl chloride that is shipped in the supply chain, noting that it is a highly flammable liquefied gas, would be expected to show emissions from charging and discharging at ≤0.1%.

Total global anthropogenic current production of MeCl of over 4,500–5,000 ktonnes is expected for all use sectors. Emissions are likely to be in the range of 4.8–8.7 ktonnes (0.1–0.175% emission rate). However, emissions in China alone during 2008–2012 (363 ±85 ktonnes/year), as cited by Li *et al.*, would represent a 12% loss factor, based on likely 3,000 ktonnes anthropogenic production in that period from known chemical use. It is expected that gaps in anthropological sources may be influenced by emissions from other than the chemical industry, such as coal production and biomass burning.

2.11 Response to decision XXIX/12: HFCs not listed in Annex F

The Twenty-Ninth Meeting of the Parties decided in decision XXIX/12, Consideration of hydrofluorocarbons not listed as controlled substances in Annex F to the Protocol:

> *Recalling decision XXVIII/1, by which the Meeting of the Parties adopted the amendment to the Montreal Protocol on phasing down hydrofluorocarbons listed in Annex F to the Protocol,*
>
> *Acknowledging that the substances listed in Annex F to the Protocol include those hydrofluorocarbons that are at present commercially in use,*
>
> *Noting, however, that there are other hydrofluorocarbons not listed in Annex F to the Protocol, which at present have minimal or no known production or consumption, which have global warming potential no less than the lowest global warming potential of the hydrofluorocarbons listed in Annex F,*
>
> *To request the assessment panels under the Montreal Protocol to provide in their quadrennial reports to be presented to the Thirty-Fifth Meeting of the Parties, in 2023, and every four years thereafter, information on the consumption and production of*

> *hydrofluorocarbons not listed in Annex F of the Protocol which have global warming potential no less than the lowest global warming potential of the hydrofluorocarbons listed in Annex F, noting that this is for information purposes only, given that the substances referred to in the present paragraph are not included in Annex F.*

2.11.1 The development of the Annex F list of HFCs

Annex F references 100-year GWP values from IPCC AR4, which is interpreted here as the basis for the GWP threshold mentioned in decision XXIX/12 as the lowest GWP of Annex F HFCs, i.e., GWP 53 for HFC-152 listed in Annex F.

In 2007, Table 2.14 of IPCC AR4[104] listed 11 HFCs, and the report noted that "*The species in Table 2.14 are those for which either significant concentrations or large trends in concentrations have been observed or a clear potential for future emissions has been identified.*" In 2012, an expanded IPCC AR4 Table 2.14 (errata) (AR4) was published[105], and the Montreal Protocol's Annex F includes all HFCs that were assigned 100-year GWPs in AR4 Table 2.14 (errata), excluding HFC-161 (AR4 GWP 12).

The European Union F-gas Regulation 517/2014 includes HFC-161 in the list of HFCs subject to phase-down.

Some of the HFCs listed in Annex F have not had significant commercial use (to date) consistent with data reported at this time, to the Ozone Secretariat. These are listed in Table 2.17 with comments about their lack of commercial use.

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[104] IPCC 2007, *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Chapter 2 Changes in Atmospheric Constituents and in Radiative Forcing.

[105] IPCC, 2012, *AR4 Climate Change 2007, The Physical Science Basis*, *The Working Group I Contribution to the IPCC Fourth Assessment Report Summary for Policymakers*, Technical Summary and Frequently Asked Questions, Table 2.14 (Errata), 15 June 2012.

Table 2.17 HFCs listed in Annex F having little or no significant commercial use to date

Group I		Comments
CHF_2CHF_2	HFC-134	Similar to HFC-134a, except HFC-134a had a closer match to the boiling point (b.p.) of CFC-12. CFC-12 b.p. -29.8°C. HFC-134a b.p. -26.3°C. HFC-134 b.p. -19.7°C. Reported to be available in China as a fluorine containing fine chemical.
CH_2FCHF_2	HFC-143	HFC-143 was assumed to be similar to HFC-152 (toxicology) and have the potential to metabolise to generate monofluoroacetate, due to its structure. However, in 1995 it was proposed as a foam blowing agent due to its b.p. 5°C but does not appear to have been used.[106]
$CH_2FCF_2CF_3$	HFC-236cb	Evaluated as a replacement for CFC-114 in chillers[107], but HFC-236fa also proposed for this use and 236fa is also used as a fire extinguishant.
$CH_2FCF_2CHF_2$	HFC-245ca	An assessment of HFC-245ca as a possible alternative to CFC-11 and HCFC-123 in low-pressure chillers. It was concluded that chillers designed for HFC-245ca can provide efficiencies comparable to those of HCFC-123 and CFC-11 chillers. However, hurdles applying to HFC-245ca in centrifugal chillers include flammability, toxicity, unknown heat-transfer characteristics, uncertain thermodynamic properties, high refrigerant cost and high construction costs of HFC-245ca production plants. Moreover, it is unlikely that a large market will develop for converting existing chillers from CFC-11 or HCFC-123 to HFC-245ca.[108]
CH_2FCH_2F	HFC-152	HFC-152 has a high acute toxicity and generates monofluoroacetate during its metabolism.[109]

2.11.2 HFCs not listed in Annex F

There is no definition for “Hydrofluorocarbons” in the Montreal Protocol.

SAP 2018[110], Appendix A, separates saturated HFCs (i.e., those included in Annex F) from unsaturated HFCs (generally known commercially as HFOs). IPCC AR6[111] (AR6) in the comprehensive table for substance metrics groups saturated HFCs and unsaturated HFCs together as hydrofluorocarbons.

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[106] Barthelemy, P.P., Leroy, A., Franklin, J.A., Zipfel, L., Krücke, W., 1,1,2-Trifluoroethane (HFC-143): Zero-ODP Blowing Agent for Rigid Polyurethane Foams Using Conventional Dispensing Equipment, *Journal of Cellular Plastics*, 1995, **31**(6), 513–531. https://doi.org/10.1177/0021955X9503100602.

[107] Gui, F., Back, D., Scaringe, R., Grzyll, L. *et al.*, *Zero-ODP Refrigerants for Low Tonnage Centrifugal Chiller Systems*, SAE Technical Paper 961320, 1996, https://doi.org/10.4271/961320.

[108] International Institute of Refrigeration, 1996, *An evaluation of HFC-245ca for use in low-pressure chillers*, Oct. 7, 1996. An evaluation of HFC-245ca for use in low-pressure chillers. (iifiir.org).

[109] European Centre for Ecotoxicology and Toxicology of Chemicals, 2008, *Toxicity of possible impurities and by-products in fluorocarbon products, Technical Report No.103*, Brussels, December 2008. https://www.ecetoc.org/wp-content/uploads/2014/08/ECETOC-TR-103.pdf.

[110] WMO (World Meteorological Organization), 2018, *Scientific Assessment of Ozone Depletion: 2018,* Global Ozone Research and Monitoring Project–Report No. 58, 588 pp., Geneva, Switzerland, 2018.

[111] IPCC, 2021, *Climate Change 2021, The Physical Science Basis*, *Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, Chapter 7 Supplementary Material, Table 7.SM.7, contains metrics for substances including greenhouse gas lifetimes, radiative efficiencies and Global Warming Potentials (GWPs).

Even if unsaturated HFCs (the HFOs) are included within the scope of the hydrofluorocarbons, most would have GWPs that are lower than the GWP threshold of 53 defined through decision XXIX/12. AR6 provides 100-year GWPs for a greater number of HFCs (HFCs and HFOs) compared to AR4, which did not include any HFOs. The AR6 list of HFC substances has been used to identify additional HFCs that have 100-year GWPs exceeding the defined threshold and available information about their commercial use. However, 100-year GWP values for these substances are not listed in AR4 Table 2.14 (errata), which therefore requires AR6 GWP values to be used to determine if those substances exceed the defined threshold of GWP 53 (HFC-152). The comparison of AR4 and AR6 GWPs shows significant differences for some HFCs, including for existing Annex F HFCs, in part due to changes in how GWPs are calculated. Table 2.18 lists HFCs (saturated HFCs and HFOs) and their AR6 and AR4 GWPs, where available.

In addition, there is only one substance (3,3,4,4-tetrafluorocyclobutene) that has a GWP between 21.5 (AR6 GWP for HFC-152) and 53 (AR4 GWP for HFC-152), and no commercial use information was found for this substance. From this table, those HFCs not listed in Annex F with GWPs above the threshold of 53 are presented in Table 2.19, with available commercial use information.

There are a wide range of other fluorinated substances that are not HFCs but have GWPs above the decision XXIX/12 threshold of 53. These include the PFCs (such as CF_4, C_2F_6, C_3F_8 c-C_4F_8), hydrofluoroethers (HFEs) used as solvents (see section 4.1.1), anaesthetics, SF_6, and NF_3. Sources and emissions of these substances are discussed in SAP 2022.[112] The use of PFCs, SF_6 and NF_3 for semi-conductor manufacturing are discussed in Chapter 5. Emissions of PFC c-C_4F_8 from the production of TFE are discussed in Section 2.3.1. The use of SF_6 in electronics manufacturing and as a cover gas for magnesium production are discussed in Chapters 5 and 6.

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[112] World Meteorological Organization (WMO), 2022, *Scientific Assessment of Ozone Depletion: 2022*, GAW Report No. 278; WMO: Geneva, 2022. Laube, J. and Tegtmeier, S., (Lead Authors), Fernandez, R.P., Harrison, J., Hu, L., Krummel, P., Mahieu, E., Park, S., Western, L., Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1, section 1.5.3, Other Fluorine-Containing species (SF6, Perfluorocarbons, NF3, SO2F2, SF5CF3, Hydrofluoroethers).

Table 2.18 Hydrofluorocarbons and their 100-year GWPs

Hydrofluorocarbons 100-year GWPs from AR6 7.SM.7[113]

Includes substances not in AR6

Annex F HFCs

Other HFCs

Unsaturated HFC (HFOs)

Above GWP threshold 53

Saturated HFCs	**Formula**	**GWP AR6**	**GWP AR4**
HFC-23	CHF_3	14600	14800
HFC-32	CH_2F_2	771	675
HFC-41	CH_3F	135	92
HFC-125	CHF_2CF_3	3740	3500
HFC-134	CHF_2CHF_2	1260	1100
HFC-134a	CH_2FCF_3	1530	1430
HFC-143	CH_2FCHF_2	364	353
HFC-143a	CH_3CF_3	5810	4470
HFC-152	CH_2FCH_2F	21.5	53
HFC-152a	CH_3CHF_2	164	124
HFC-161	CH_3CH_2F	4.84	12
HFC-227ca	$CF_3CF_2CHF_2$	2980	
HFC-227ea	CF_3CHFCF_3	3600	3220
HFC-236cb	$CH_2FCF_2CF_3$	1350	1340
HFC-236ea	CHF_2CHFCF_3	1500	1370
HFC-236fa	$CF_3CH_2CF_3$	8690	9810
HFC-245ca	$CH_2FCF_2CHF_2$	787	693
HFC-245cb	$CF_3CF_2CH_3$	4550	
HFC-245ea	$CHF_2CHFCHF_2$	255	
HFC-245eb	$CH_2FCHFCF_3$	325	
HFC-245fa	$CHF_2CH_2CF_3$	962	1030
HFC-263fb	$CH_3CH_2CF_3$	74.8	
HFC-272ca	$CH_3CF_2CH_3$	599	
HFC-329p	$CHF_2CF_2CF_2CF_3$	2890	
HFC-365mfc	$CH_3CF_2CH_2CF_3$	914	794
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	1600	1640
HFC-52-13p	$CHF_2CF_2CF_2CF_2CF_2CF_3$	Not listed, 2000[114]	
HFC-76-13sf	$CH_3CH_2(CF_2)_5CF_3$	Not listed 136[115]	

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[113] Smith, C., Nicholls, Z.R.J., Armour, K., Collins, W., Forster, P. , Meinshausen, M., Palmer, M.D., Watanabe, M., 2021: The Earth's Energy Budget, Climate Feedbacks, and Climate Sensitivity Supplementary Material, *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change* [Masson-Delmotte, V., P. Zhai, A. Pirani, S.L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M.I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T.K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, and B. Zhou (eds.)]. https://www.ipcc.ch/report/ar6/wg1/downloads/report/IPCC_AR6_WGI_Chapter07_SM.pdf.

[114] Value reported as calculated by the National Institute of Advanced Industrial Science and Technology (AIST). Atmospheric lifetime reported as 31 years. Chen, L., Tokuhashi, K., Kutsuna, S., Sekiya, A., Rate constants for the gas-phase reaction of $CF_3CF_2CF_2CF_2CF_2CHF_2$ with OH radicals at 250–430 K, *International Journal Of Chemical Kinetics*, 2003, **36**(1), 26–33. https://doi.org/10.1002/kin.10170.

[115] Value reported as calculated by the National Institute of Advanced Industrial Science and Technology (AIST).

Hydrofluorocarbons GWPs from AR6 7.SM.7

Includes substances not in AR6	Annex F HFCs		
	Other HFCs		
	Unsaturated HFC (HFOs)	*Above GWP threshold 53*	
	Formula	**GWP AR6**	**GWP AR4**
Cyclic Saturated HFCs			
1,1,2,2,3,3-hexafluorocyclopentane	Cyclic (-$CF_2CF_2CF_2CH_2CH_2$-)	120	
1,1,2,2,3,3,4-heptafluorocyclopentane HFC-c447ef	Cyclic (-$CF_2CF_2CF_2CHFCH_2$-)	231	
(4s,5s)-1,1,2,2,3,3,4,5-octafluorocyclopentane	*trans*- cyclic (-$CF_2CF_2CF_2CHFCHF$-)	258	
cis-1,1,2,2,3,4-hexaflurorocyclobutane	Cyclic (-CFH-CF_2CF_2CFH-)	Not listed	
Cyclic unsaturated HFCs (HFOs)			
1,3,3,4,4,5,5-heptafluorocyclopentene	Cyclic (-$CF_2CF_2CF_2CF$=CH-)	45.1	
1,3,3,4,4-pentafluorocyclobutene	Cyclic (-CH=$CFCF_2CF_2$-)	92.4	
3,3,4,4-tetrafluorocyclobutene	Cyclic (-CH=$CHCF_2CF_2$-)	25.6	
Unsaturated linear HFCs (HFOs)			
All AR6 listed linear HFOs have GWPs less than 20			

Table 2.19 Hydrofluorocarbons with 100-Year GWPs above the threshold of 53

Saturated HFCs	Formula	GWP AR6	Information about commercial use
HFC-227ca	$CF_3CF_2CHF_2$	2980	Evaluated as a replacement for CFC-114 in chillers[116], but HFC-227ea was also investigated.
HFC-245cb	$CF_3CF_2CH_3$	4550	An intermediate or feedstock in the process to produce HFO-1234yf from HCFC-225ca.[117] Evaluated in the 1990s as a replacement for CFC-114 in chillers.[118]
HFC-245ea	$CHF_2CHFCHF_2$	255	No information available.
HFC-245eb	$CH_2FCHFCF_3$	325	An intermediate or feedstock in a two-step process to prepare HFO-1234yf comprises the fluorination of 3,3,3-trifluoropropene to yield HFC-245eb and the dehydrohalogenation of HFC-245eb to afford HFO-1234yf.[119]
HFC-263fb	$CH_3CH_2CF_3$	74.8	No information available.
HFC-272ca	$CH_3CF_2CH_3$	599	No information available.
HFC-329p	$CHF_2CF_2CF_2CF_3$	2890	No information available.
HFC-52-13p	$CHF_2CF_2CF_2CF_2CF_2CF_3$	2000	Used as a solvent.
HFC-76-13sf	$CH_3CH_2(CF_2)_5CF_3$	136	Used as a solvent.
Cyclic Saturated HFCs			
1,1,2,2,3,3-hexafluorocyclopentane	Cyclic $(-CF_2CF_2CF_2CH_2CH_2-)$	120	No information available.
1,1,2,2,3,3,4-heptafluorocyclopentane (HFC-c447ef)	Cyclic $(-CF_2CF_2CF_2CHFCH_2-)$	231	One manufacturer in China produces HFC-c447ef, with production capacity about 300 tonnes/year and all product exports to Japan. HFC-c447ef is listed as an acceptable solvent under U.S. EPA SNAP alternatives for metals, precision, and electronics cleaning. The 2012-2019 U.S. public records show annual volumes less than ~450 tonnes.
(4s,5s)-1,1,2,2,3,3,4,5-octafluorocyclopentane	*trans*- cyclic $(-CF_2CF_2CF_2CHFCHF-)$	258	No information available.
cis-1,1,2,2,3,4-Hexafluorocyclobutane	Cyclic $(-CFH-CF_2CF_2CFH-)$	not listed	Exported from China in recent past, with annual volume of around 5,000 tonnes in 2018-2019.[120] Used as a solvent.
Cyclic unsaturated HFCs (HFOs)			
1,3,3,4,4-pentafluorocyclobutene	Cyclic $(-CH=CFCF_2CF_2-)$	92.4	No information available.

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[116] Gui, F., Back, D., Scaringe, R., Grzyll, L. *et al.*, *Zero-ODP Refrigerants for Low Tonnage Centrifugal Chiller Systems*, SAE Technical Paper 961320, 1996, https://doi.org/10.4271/961320.

[117] David Sherry and Maria Nolan (Nolan Sherry & Associates, NSA), Stephen Seidel (Center for Climate and Energy Solutions – C2ES) and Stephen O. Andersen (Institute for Governance & Sustainable Development, IGSD), 2017, *HFO-1234yf: An Examination of Projected Long-Term Costs of Production*, April 2017.

[118] Gui, F., Back, D., Scaringe, R., Grzyll, L. *et al.*, *Zero-ODP Refrigerants for Low Tonnage Centrifugal Chiller Systems*, SAE Technical Paper 961320, 1996. https://doi.org/10.4271/961320.

[119] https://www.epo.org/law-practice/case-law-appeals/recent/t170813eu1.html

[120] *cis*-1,1,2,2,3,4-Hexafluorocyclobutane, CAS No. 22819-47-2 Guide – ECHEMI. https://www.echemi.com.

Parties may wish to consider any actions that they might wish to take concerning those HFCs not listed in Annex F with GWPs above 53 with known commercial use (HFC-245cb, HFC-245eb, HFC-52-13p, HFC-76-13sf, HFC-c447ef, *cis*-1,1,2,2,3,4-hexafluorocyclobutane).

HFEs used as solvent replacements for controlled substances (see Chapter 4, Table 4.1) have GWPs (AR4 values) between 59 and 580. HFE solvents have relatively high boiling points in the range 56°C to 98°C, high cost and are most likely used in equipment where emissions are minimised to avoid losses.

Some fluorinated ethers are used as inhalation anaesthetics where emissions are more likely to occur. SAP 2022 reports that there is little new information on the emissions of anaesthetics since the publication by Vollmer in 2014.[121]

Table 2.20 summarises estimated emissions, GWPs, and ODPs for the inhalation anaesthetics. Methoxyflurane ($CH_3CF_2OCHCl_2$) is not included in this table, as it has limited use mainly for pain relief in a few countries and has a very low GWP (SAP 2018[122]). Enflurane (AR6 GWP 654, HCFE-235ca2, CHF_2OCF_2CHFCl) has largely been supplanted by newer agents.

Table 2.20 Inhalation anaesthetics GWPs and global emissions

		Desflurane	**Sevoflurane**	**Isoflurane**
		$CHF_2OCHFCF_3$	$(CF_3)_2CHOCH_2F$	$CF_3CHClOCHF_2$
		HFE-236ea2	HFE-347mmz1	HCFE-235da2
GWP AR6		2590	195	539
Atmospheric Lifetime years AR6		14.1	1.9	3.5
ODP SAP 2018		0	0	0.03
Atmospheric abundance 2014 Vollmer 2014		0.3 ppt	0.13 ppt	0.097 ppt
From 2014 global emissions	**Gg/yr**	0.96	1.2	0.88
	Tonnes	960	1200	880
	Emissions $MMTCO_2e$	2.5	0.23	0.47
	Emissions ODP tonnes	0	0	26.4

EEAP 2022 reports the yields of TFA from inhalation anaesthetics. There are already local or national healthcare initiatives to reduce emissions of inhalation anaesthetics, particularly desflurane (and nitrous oxide). In addition, in the European Union, the proposal to revise the F-gas Regulations may result in a requirement to limit the use of high-GWP desflurane: "*The use of desflurane as inhalation anaesthetic is prohibited as from 1 January 2026, except when such use is strictly required and no other anaesthetic can be used on medical grounds. The user shall provide evidence, upon request, on the medical justification to the competent authority of the Member State and the Commission.*"

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[121] World Meteorological Organization (WMO), 2022, *Scientific Assessment of Ozone Depletion: 2022*, GAW Report No. 278; WMO: Geneva, 2022. Laube, J. and Tegtmeier, S., (Lead Authors), Fernandez, R.P., Harrison, J., Hu, L., Krummel, P., Mahieu, E., Park, S., Western, L., Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1, section 1.5.3, Other Fluorine-Containing species (SF_6, Perfluorocarbons, NF_3, SO_2F_2, SF_5CF_3, Hydrofluoroethers).

[122] WMO (World Meteorological Organization), 2018, *Scientific Assessment of Ozone Depletion: 2018,* Global Ozone Research and Monitoring Project–Report No. 58, 588 pp., Geneva, Switzerland, 2018.

Reported production and consumption could be a valuable data set for anaesthetics that could be correlated with related emissions of substances, either from their production, use, or with the expected impact of emission abatement measures.

Several halogenated ethers with GWPs greater than 53 are in commercial use, including as solvent replacements for controlled substances. The primary use is as anaesthetic gases, which are not historically related to controlled substances under the Montreal Protocol, some are also ozone-depleting substances. Anaesthetic gases are estimated to contribute up to 0.1% of total greenhouse gas emissions[123] and account for around 5% of total healthcare emissions.[124]

Parties may wish to consider any actions that they might desire to take concerning anaesthetics that are halogenated ethers and other halogenated ethers, (e.g., HFEs) with known commercial use with GWPs (IPCC AR6) greater than 53.

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[123] Sherman, J.D., Chesebro, B.B. Inhaled anaesthesia and analgesia contribute to climate change, *BMJ (Clinical research ed.)*, 2022, **377**, o1301. https://doi.org/10.1136/bmj.o1301.

[124] Sustainable Markets Initiative, 2022, *Decarbonising patient care pathways: how choices in patient care can drive reductions in carbon emissions*, Sustainable Markets Initiative Health Systems Task Force, in collaboration with BCG, November 2022. https://a.storyblok.com/f/109506/x/bdade0cd92/smi-health-systems-pcp-whitepaper.pdf. Accessed December 2022.

3 Process Agents

3.1 What are process agents

Process agents have been characterised as controlled substances that, because of their unique chemical and/or physical properties, facilitate an intended chemical reaction and/or inhibit an unintended (undesired) chemical reaction.[125] Process agent uses can be differentiated from feedstock uses, where controlled substances undergo transformation in processes in which they are converted from their original compositions except for insignificant trace emissions as allowed by decision IV/12.

Parties have made a range of decisions relating to the use of controlled substances as process agents. Decisions were taken to clarify certain chemical process uses that were being confused with feedstock uses; some parties had interpreted the use of controlled substances in certain applications, where they were used as process agents, as feedstock applications, while other parties had interpreted similar applications as use and thereby subject to phase-out. TEAP had also been unable to recommend production and consumption of controlled substances for these uses because they could not meet the essential use criteria established under decision IV/25.

Decision VI/10 sought to clarify the situation by instructing parties to treat chemical process agents in a manner similar to feedstock for a limited duration and requesting TEAP to identify uses of ODS as chemical process agents, to estimate emissions, and to elaborate available alternatives.

Following further technical elaboration, decision X/14 clearly delineated that:

- the term “process agents” should be understood to mean the use of controlled substances for applications listed in Table A in that decision, and

- to treat process agents in a manner similar to feedstock, and not to include them in the calculation of production and consumption provided that emissions from these processes were reduced to insignificant levels, as defined by Table B in that decision.

Subsequent decisions updated Tables A and B with new information.

To qualify as a process agent use, TEAP’s Task Force on Process Agents used a working definition where the ODS in a specified process must meet at least two of the following technical criteria:

i) Chemical inertness during the process
ii) Physical properties, such as boiling point, vapour pressure, or specific solvency
iii) Action as a chain-transfer reagent in free radical reactions
iv) Control of product physical properties, such as molecular weight or viscosity
v) Ability to increase yield
vi) Non-flammable/non-explosive

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[125] UNEP, 2004, *Report of the Technology and Economic Assessment Panel Process Agents Task Force*, October 2004. Definition taken from the 1997 Process Agents TEAP Task Force Report, as reproduced in the Report of the TEAP Process Agents Task Force, pg. 27.

vii) Minimisation of by-product formation.

Most of the process agent uses are long-standing processes, where the ODS are used as solvents to create unique yields, selectivity and/or resistance to harsh chemical environments, with the result that production is achieved with high efficiency. Legacy processes built around these properties make it difficult or impossible to convert to alternatives in a cost effective and timely manner, and only a few examples are known. In this regard, the process agent uses have much in common with feedstock uses, which are covered separately in this report.

3.2 Applications defined as process agent uses

The process agent uses first defined in Table A of decision X/14 included 25 applications of ODS, including carbon tetrachloride, CFC-113, CFC-11, and CFC-12, with total maximum emissions limits of about 200 tonnes for 4,500 tonnes of make-up or consumption.

In subsequent decisions, Table A grew to more than 40 applications, adding Halon 1011 (bromochloromethane, BCM) to the group of controlled substances used in these applications. Table B emissions reached a maximum of 511 tonnes in decision XXIII/7 in 2011. From 2010 onwards, Article 5 parties were included in the measures for process agent uses.

By 2019, when Table A was last updated, decision XXXI/6, the number of process agent applications had reduced to 10 across 4 parties (China, the European Union, Israel and the United States).

Most of the removals of process agents from Table A have resulted from plant closures, rather than substitution of other substances for the ODS process agent.

Since the 2018 MCTOC Assessment Report, one process agent application ceased:

- Preparation of perfluoropolyether diols with high functionality in the European Union

Also, one party indicated that the use of ODS for a process agent application ceased in their region:

- Recovery of chlorine by tail gas absorption in chlor-alkali production in the European Union

In 2019, parties amended the list of process agent uses in decision XXXI/6 to reflect these changes to Table A, which is shown in Table 3.1 below. Since 2019, there has been no change to process agent uses in parties.

Table 3.1 List of process agent uses of controlled substances in Table A[126]

No.	Process agent applications Decision XXIX/7 Table A	Substance	Permitted Parties Decision XXIX/7 Table A
1	Elimination of NCl_3 in chlor-alkali production	CTC	European Union, Israel, United States of America
2	Recovery of chlorine by tail gas absorption in chlor-alkali production	CTC	United States of America
3	Production of chlorinated rubber	CTC	European Union
4	Production of chlorosulfonated polyolefin (CSM)	CTC	China
5	Production of aramid polymer (PPTA)	CTC	European Union
6	Production of synthetic fibre sheet	CFC-11	United States of America
7	Photochemical synthesis of perfluoropolyetherpolyperoxide precursors of (*Z*)-perfluoropolyethers and difunctional derivatives	CFC-12	European Union
8	Production of cyclodime	CTC	European Union
9	Bromination of a styrenic polymer	BCM[127]	United States of America
10	Production of high modulus polyethylene fibre	CFC-113	United States of America

In considering continued process agent use, it is worth noting that the lifetime of a chemical production plant could be up to 50 years. If the product is important enough to warrant continued production, and the plant is maintained in good condition and not in need of renewal, then the large investment required to put into operation a new process that does not use ODS is unlikely to be justified.

While each of the process agent applications is unique, there exists a suite of measures that can be applied to minimize make-up/consumption and emissions and each one needs to be considered by an operator. These measures include limiting make-up/consumption to the essential minimum, ensuring tight systems (no leaking valves and joints); evacuation and purging with recovery, prior to opening equipment; closed-loop transfer systems; proximity of production and use of the ODS; monitoring sensors at potential leak locations to provide alerts for prompt repair; use of absorbents such as activated charcoal on vents; and destruction of vent gases.

3.3 Make-up and emissions

Table B defines the maximum quantities of make-up and emissions associated with process agents defined in Table A. The quantity of make-up is the quantity of controlled substance, per year, needed to continue the manufacture of products in a process agent use, owing to

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[126] Table A was last updated in 2019 with decision XXXI/6: Use of controlled substances as process agents.

[127] Bromochloromethane.

transformation, destruction, and inadvertent losses (i.e., emissions and residual amounts in final product. Under decisions XXI/3(1) and X/14(4), parties submit information to the Ozone Secretariat on quantities of make-up/consumption and emissions from applications for which process agent exemptions exist.

The maximum quantities of make-up and emissions in Table B of decision XXXI/6 are shown in Table 3.2 below.

Table 3.3 presents an overview of the quantities of make-up or consumption reported by parties for 2009 to 2021. Table 3.4 presents an overview of the emissions reported by parties for 2009 to 2021.

Table 3.2 Maximum make-up and emissions for process agent uses in Table B (in metric tonnes per year)[128]

Party	**Make-up or consumption Table B Decision XXXI/6**	**Maximum emissions Table B Decision XXXI/6**
China	1,103	313
European Union	921	15
Israel	3.5	0
United States of America	2,300	181
Total	4,327.5	509

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[128] Table B was last updated in 2019 in Decision XXXI/6: Use of controlled substances as process agents.

Table 3.3 Data reported by parties on make-up or consumption associated with process agent uses for 2009–2021

Party	**Reported make-up or consumption (metric tonnes)**							
	2009	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**
Brazil	0	-	-	-	-	-	-	-
China	313	179.3	179.92	179.24	88.92	178.44	179.84	177.42
Colombia	-	0.64	-	-	-	-	-	-
European Union	669	1116.231	954.42	547.178	622.101	508.741	283.313	365.28
Israel	2.4	3.3	2.1	3.6	2.4	2.4	1.8	0
Mexico	-	40.9954	-	-	-	-	-	-
United States of America	NR	NR	NR	NR	NR	NR	NR	NR
Nominal Total	984.4*	1340.4664*	1136.44*	730.018*	713.421*	689.581*	464.953*	542.70*

* Nominal totals exclude data not reported by parties, as indicated by NR. The United States reports emissions data in ODP tonnes and does not report make-up/consumption data.

Party	**Reported make-up or consumption (metric tonnes)**				
	2017	**2018**	**2019**	**2020**	**2021**
Brazil	-	-			
China	175.96	176.74	179.8	179.22	179.16
Colombia	-	-			
European Union	324.301	351.675	273.876	292.39	290.712
Israel	0	0	0	5.665	NR
Mexico	-	-			
United States of America	NR	NR	NR	NR	NR
Nominal Total	500.261*	528.415*	453.676*	477.275*	469.872*

Table 3.4 Data reported by parties on emissions associated with process agent uses for 2009–2021

Party	**Reported emissions in metric tonnes *[ODP tonnes given in square brackets]***							
	2009	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**
Brazil	0	-	-	-	-	-	-	-
China	-	179.3	179.2	179.24	52.64	105.63	106.46	105.05 *[115.56]*
Colombia	-	-	-	-	-	-	-	-
European Union	1.6	1.287	116.428	27.192	15.808	7.338	6.414	3.81 *[4.15]*
Israel	0	-	-		0.000038	0.1794	0.0617	0.0143 *[0.016]*
Mexico	-	40.9954	-	-	-	-	-	-
United States of America	*[47.1]*	*[59.79]*	*[44.35]*	*[34.63]*	*[34.5]*	*[34.1]*	*[33.2]*	*[31.2]*
Total	1.6*	221.5824*	295.628*	206.432*	68.448038*	113.1474*	112.9357*	108.86* *[150.92]*

*Nominal totals in metric tonnes exclude data reported in ODP-weighted metric tonnes by the United States. Nominal totals exclude data not reported by parties, as indicated by NR.

Party	**Reported emissions in metric tonnes *[ODP tonnes given in square brackets]***				
	2017	**2018**	**2019**	**2020**	**2021**
Brazil	-	-			
China	104.19 *[114.6]*	104.65 *[115.12]*	106.46 *[117.106]*	106.116 *[116.728]*	106.080 *[116.688]*
Colombia					
European Union	4.143 *[4.548]*	2.619 *[2.87]*	3.529 *[3.874]*	3.629 *[3.984]*	2.795 *[3.070]*
Israel	0.0055 *[0.006]*	0.0042965 *[0.0047]*	0	0.09 *[0.099]*	NR
Mexico					
United States of America	*[24.65]*	*[34.01]*	*[28.79]*	*[25.7]*	*[28.99]*
Total	108.34* *[143.8]*	107.27* *[149.19]*	109.99* *[149.95]*	109.84* *[146.51]*	108.875* *[148.748]*

3.4 Progress in reducing controlled substances in process agents uses

The number of applications using ODS as process agents decreases slowly, while the emissions and make-up quantities from process agents are stabilizing. For some of the remaining applications, no alternatives are available to date.

3.4.1 Reduction in make-up quantity of controlled substances

The information reported in Table 3.3 demonstrates that the total reported make-up or consumption quantities of ozone depleting substances used for the reported processes has decreased from its peak in 2010 for those parties reporting these data (China, the European Union and Israel). These reductions could be the result of a reduction in the number of processes using ozone-depleting substances as process agents or implementation of improvements in the processes. The quantities of make-up/consumption of controlled substances are considerably lower when compared with the maximum quantity of make-up/consumption contained in decision XXXI/6.

3.4.2 Progress made in reducing emissions from process agent uses

The information reported in Table 3.4 demonstrates that the quantities of ozone depleting substances emitted from the reported processes have stabilised over the past years and are lower than the maximum quantity of emissions contained in decision XXXI/6 Table B. These reductions could be the result of a reduction in the number of processes using ozone-depleting substances as process agents or/and implementation of improvements in the processes to further reduce emissions.

3.4.3 Implementation and development of emissions reduction techniques

Several emission reduction techniques are operational and new techniques are being developed and implemented. For example, Israel has noted that it uses compression and purification systems obtained from Krebs Swiss and has continuous chlorine analysers that activate the safety interlockers system when the chlorine concentration in the air is 0.5 ppmv.

The United States has also provided a list of containment technologies that are used to minimise emissions of controlled substances. These are as follows: continuous air monitoring of stacks; fugitive emission monitoring and repair; vent emission recycling back into process; bio-treatment and carbon bed filtration; stack gas sent to vent incineration; nitrogen used to clear the transfer lines; used material sent to THROX incineration unit; solvent recovery system; carbon absorption system; wastewater treatment system; emergency discharge system routed through a blow-down collection tank; air sweep to a carbon absorption system from suspected leak areas; redundant process controls to minimize mis-operation; full system drainage and vapour purge prior to maintenance; refrigerated vent condensers to minimize BCM emissions; multi-disciplined conservation team overseeing leak detection technology and process optimization; mechanical seal pumps replaced by seal-less pumps for CTC transfer lines; compressor suction automation valves and heat exchangers to improve recovery control; recycling and recovery operations to maximize material reuse; internal mechanisms for rapid response to threshold shifts in daily emission values.

The European Union has provided an analysis of the containment technologies by application as detailed in Table 3.5.

Table 3.5 Containment Technologies to reduce emissions

Substance	Process agent application	Containment technologies used to minimize emissions
CTC	(1) Elimination of nitrogen trichloride in chlorine and caustic soda (chloralkali) production	*Emissions to water* Waste CTC containing NCl3 is kept in tanks placed over retention before being sent for destruction. CTC is next destroyed in an incineration plant. *Emissions to air* Chlorine concentration in stack is not monitored because there is no potential presence of CTC in stack gas.
CTC	(3) Production of chlorinated rubber	*Emissions to water* Solvent recovery system consisting of: 1) steam stripping column, 2) evaporation unit. *Emissions to air* Gas purification system consisting of a carbon adsorption system (active carbon beds adsorb CTC, active carbon is regenerated with steam, the condensed CTC is recycled). Chlorine concentration in stack is continuously monitored. If >3 ppmv then action is taken.
CTC	(5) Manufacture of aramid polymer, poly-phenylene-terephtalamide (PPTA)	*Emissions to water* Solvent recovery system consisting of: 1) separator, 2) steam stripping column. *Emissions to air* Gas purification system consisting of carbon adsorption system (active carbon beds adsorb CTC, active carbon is regenerated with steam, the condensed CTC is recycled). CTC concentration in the emitted gas is continuously monitored. If the CTC concentration is >5 mg/Nm3 then action is taken.
CFC-12	(7) Photochemical synthesis of perfluoro-polyetherpolyperoxide precursors of (*Z*)-perfluoropolyethers and difunctional derivatives	*Emissions to water* No emissions to water because the process is anhydrous. *Emissions to air* Gas purification system consisting of a thermal oxidation unit (1500°C, at least 0.4 sec residence time as order of magnitude) where CFC-12 is converted to CO_2, HF and HCl.

		Chlorine (Hydrochloric Acid) concentration in stack is continuously monitored. If >15 mg/Nm^3 (hourly average) then action is taken.
CTC	(8) Production of cyclodime	*Emissions to water* Stripping in a column with air. *Emissions to air* Gas purification system consisting of: 1) an absorption system in a column with water, 2) a condensation system in thermal exchangers with chilled water at 5°C, 3) a carbon adsorption system (active carbon beds adsorb CTC, active carbon is regenerated with steam, the condensed CTC is recycled), 4) a thermal oxidation unit (1000°C, 2 sec residence time) where CTC is converted to HCl. HCl is recovered by absorption in water and then recycled to the process. HCl concentration in stack is analysed every 3 months. If flowrate >0.05 kg/h (annual average) or flowrate >0.6 kg/h (acceptable limit value) then action is taken.

3.4.4 Alternative processes and products not using ozone-depleting substances

Alternative processes are investigated and implemented where possible. For example, the European Union provided information on its process agent applications and the availability of alternatives. It reported that a company has introduced a process to remove the ammonium impurity using NaClO, putting an end to the use of CTC for the elimination of nitrogen trichloride in the production of chlorine and caustic soda at one production unit in France. It has also noted that the use of CTC in the recovery of chlorine in tail gas from the production of chlorine has been eliminated through the introduction of gas burners, through which the tail gas circulates. Work is also underway to eliminate the use of CFC-12 in the photochemical synthesis of perfluoropolyetherpolyperoxide precursors of (*Z*)-perfluoropolyethers and di-functional derivatives within the European Union, and HFE-449s1 has replaced the use of CFC-113 in the preparation of perfluoropolyether diols with high functionality.

Table 3.6 presents a summary of available information on the industrial application of alternative technologies employed by parties that have already eliminated the use of controlled substances as process agents in the processes listed in Table A, as in decision XXXI/6.

Table 3.6 Available information on alternative technologies employed for process agent applications listed in Table A (as in decision XXXI/6)

No.	Process agent application Decision XXXI/6	Substance	Permitted Parties in Decision XXXI/6	Reason for process agent application using ODS	Status of process agent use (including as reported by parties in 2020)
1	Elimination of NCl_3 in chlor-alkali production	CTC	European Union, Israel, United States of America	CTC is used for quality of final product and safety in production, transport, and use of liquid chlorine. At concentrations above approximately 3%, NCl_3 has a high explosion potential.	The European Union noted that NaClO has been introduced as the alternative and CTC is no longer used at one site. CTC use was expected to cease shortly at the other site in the European Union. In Europe, very few plants used CTC for elimination of NCl_3 in chlor-alkali production. The majority now use either very pure salt and water or NaClO to avoid the formation of NCl_3, or UV destruction in the gas phase. CTC phase-out was initiated by other changes that were required.
2	Recovery of chlorine by tail gas absorption in chlor-alkali production	CTC	United States of America	CTC is used as a process agent to separate the residual chlorine from the inert vapours present in the chlorine gas and recover it in a usable form. CTC is a practical solvent suitable for use in this type of gas recovery process.	This process agent application ceased in the European Union due to introduction of gas burners through which tail gas circulates. In Europe, very few plants used CTC for this purpose, and mainly because of the type of chlorine liquefaction process employed at those plants in the past. Today, chlor-alkali plants have reduced chlorine in the tail gas with compression/ condensation and because of the higher chlorine purity from the processes used. CTC phase-out was initiated by other changes that were required.
3	Production of chlorinated rubber	CTC	European Union	Chemical inert solvent for high quality product for heavy duty anti-corrosives and adhesives.	The European Union noted that alternatives do not exist.
4	Production of chlorosulfonated polyolefin (CSM)	CTC	China	In China, this CTC-based process has been optimised to minimise CTC emissions. Chlorobenzene was evaluated as an alternative unsuccessfully due to energy	The United States has previously eliminated this CTC use. Information is not available on how this was achieved.

No.	Process agent application Decision XXXI/6	Substance	Permitted Parties in Decision XXXI/6	Reason for process agent application using ODS	Status of process agent use (including as reported by parties in 2020)
				consumption, chemical stability and in-plant safety.	
5	Production of aramid polymer (PPTA)	CTC	European Union	CTC is used for the following reasons: to avoid side reactions during chlorination, which is crucial for the polymerisation; to reduce explosion and fire risks during chlorination; to reduce waste and increase yield by acting as a carrier for recycling of incomplete chlorination products; and to clean HCl emerging from the reactors (the cleaning solution is recycled). CTC is the only option that satisfies safety, waste reduction, and quality purposes under the various conditions of the process because: CTC is inert in all process steps; CTC prevents side reactions in the reactor; CTC has the right vapour pressure to prevent explosions in the gas cap of the reactor; CTC is easy to recover and re-use; and CTC has a low solubility in HCl.	The European Union noted that alternatives do not exist.
6	Production of synthetic fibre sheet	CFC-11	United States of America	The use of CFC-11 is primarily due to safety, yield and cost, but also product quality. The unique process agent properties are low	No information available.

No.	Process agent application Decision XXXI/6	Substance	Permitted Parties in Decision XXXI/6	Reason for process agent application using ODS	Status of process agent use (including as reported by parties in 2020)
				toxicity; non-flammable; physico-chemical properties e.g., boiling point, critical temperature/pressure, solvency power (capability to enter polymer matrix), and control of solution viscosity and process operating pressures; chemical stability to high temperature and pressure; and non-corrosivity.	
7	Photochemical synthesis of perfluoropolyetherpolyperoxide precursors of (*Z*)-perfluoropolyethers and difunctional derivatives	CFC-12	European Union	CFC-12 is liquid at the reaction temperatures (–50 °C to –90 °C); it dissolves both reactants tetrafluoroethylene and oxygen (whose mixture would otherwise explode); is transparent and inert to UV radiation, apart from a minimal release of radicals that are responsible for initiation and regulation of the molecular weight in case of UV initiated synthesis. Should the breakdown be more than minimal, degradation products would make it impossible to achieve commercial results.	Work is currently being undertaken on replacing CFC-12 with an alternative.
8	Production of cyclodime	CTC	European Union	The CTC is used in this process because it is the only solvent compatible with the raw	The European Union noted that alternatives do not exist.

No.	Process agent application Decision XXXI/6	Substance	Permitted Parties in Decision XXXI/6	Reason for process agent application using ODS	Status of process agent use (including as reported by parties in 2020)
				materials; it is very stable, non-reactive, and non-flammable. Evaluation of numerous other solvents under process conditions has led to unsatisfactory results. Only, chloroform seemed to be a potential alternative solvent. However, due to the different behaviour of this solvent (volatility, reactivity), chloroform resulted in other process safety and hygiene issues, major loss of yield, and greater solvent consumption. Moreover, a large part of the plant would have to be re-designed and re-built in other materials compatible with chloroform. For these reasons, this would be a less safe and uneconomical solution.	
9	Bromination of a styrenic polymer	BCM	United States of America	This process uses bromochloromethane (BCM) as an inert solvent in the bromination of styrenic polymer. The 2002 TEAP Report indicated that BCM was used as a solvent for its inertness, for safety reasons, and for waste reduction. Brominated styrenic polymers are useful as	No information available.

No.	Process agent application Decision XXXI/6	Substance	Permitted Parties in Decision XXXI/6	Reason for process agent application using ODS	Status of process agent use (including as reported by parties in 2020)
				flame retardants for thermoplastic polymers.	
10	Production of high modulus polyethylene fibre	CFC-113	United States of America	The interaction of the spinning solvent with the fibre plays an important role in the unusual strength of the end-product. Hundreds of non-ODS materials had been tested as replacements for CFC-113, but none had been able to achieve the technical performance of CFC-113 in respect of flammability, boiling point, toxicity, compatibility with materials of construction, economy, and recoverability while retaining required product properties and performance.	No information available.

3.5 Decision XVII/6(4): Assessment of any new plant using controlled substances as process agents

Decision XVII/6(4) states, “Where Parties install or commission new plant after 30 June 1999, using controlled substances as process agents, to request Parties to submit their applications to the Ozone Secretariat and the TEAP by 31 December 2006, and by 31 December every subsequent year or otherwise in a timely manner that allows the TEAP to conduct an appropriate analysis, for consideration subject to the criteria for essential uses under decision IV/25, in accordance with paragraph 7 of decision X/14;”. No applications were submitted by parties by 31 December 2021.

4 Solvents

4.1 Solvent uses of controlled substances and their alternatives

Controlled substances (CFC-113, 1,1,1-trichloroethane, CTC, CFC-11, HCFC-141b and -225ca/cb, and HFC-43-10mee, -365mfc, and to a limited extent HFC-245fa) were chosen due to their favourable chemical and physical properties in various solvent applications, including metal, electronics, and precision cleaning, and in formulations for adhesives[129], coatings, and inks. HCFCs and HFCs have been used to a much lesser extent than the high ODP ODS solvents that were phased out, with other alternatives substituting many of those previous solvent uses of ODS. The use of controlled substances as solvents has been or will be phased out (HCFCs[130]) or phased down (HFCs) under the Montreal Protocol and its Kigali Amendment.

The main applications of HCFC and HFC solvents are metal cleaning, where metal working oil, grease, pitch wax, etc., are cleaned from metals, electronics cleaning, where flux is cleaned, precision cleaning, where particulate or dust is cleaned from precision parts (e.g., military equipment and aerospace components), and coating deposition, where coatings are dissolved in solvent to deposit onto surfaces e.g., medical devices such as syringe needles.

HFCs are commonly used as azeotropic mixtures, which are mixtures of two or more liquids that have the same mixture concentration in liquid and vapour phases. Fluorinated solvents, like HFC-43-10-mee, HFC-365mfc, and HFC-245fa (a solvent used in aerosols), have poorer solvency than chlorinated solvents because of the lower dipole of the fluorine-carbon covalent bond compared with the chlorine-carbon bond. As a result, HFCs are often mixed with chlorinated chemicals to boost the solvency.

Many alternative solvents and technologies developed as ODS alternatives are also the candidates for alternatives to HCFCs and high-GWP HFCs. These include not-in-kind technologies, such as aqueous cleaning, semi-aqueous cleaning, hydrocarbon and oxygenated solvents, and in-kind solvents, such as chlorinated solvents and fluorinated solvents, including high-GWP HFCs not listed in Annex F and low-GWP HFOs, HCFOs and HFEs, with various levels of acceptance. Alternatives to HCFCs and HFCs that are controlled substances are being used for electronics defluxing/cleaning and precision cleaning in several industries automotive, aerospace, medical device, and optical components where high levels of cleanliness are required.[131]

Choices for alternative technologies to controlled substances used as solvents include:

- Aqueous/hydrocarbon-surfactant cleaning
- Organic solvent cleaning (with solvents less toxic, *iso*-propyl alcohol, acetone than halogenated solvents)

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[129] Adhesive uses no longer use controlled substances, which were phased out with 1,1,1-trichloroethane.

[130] Between 1 January 2020 and 1 January 2030, in any non-Article 5 party, Article 2F, paragraph 6, allows HCFC consumption and production up to 0.5% of the allowance in any year under Article 2F, paragraph 1, for restricted applications including solvent applications in rocket engine manufacturing.

[131] Several reports that describe the use of ODS and their alternatives in solvent applications have been published in the past. These include the IPCC/TEAP Special Report: Safeguarding the Ozone Layer and the Climate System, the Decision XXI/9 TEAP Task Force Report, the Decision XXIII/9 TEAP Task Force Report, the Decision XXIV/7 TEAP Task Force Report, the Decision XXV/5 TEAP Task Force Reports, and STOC and CTOC Assessment Reports.

- Halogenated solvents (e.g., HFEs, trichloroethylene (TCE), perchloroethylene (PCE), dichloromethane, chloroform, *n*-propyl bromide, *trans*-1,2-dichloroethylene (TDCE, a hydrochloroolefin (HCO)), hydrofluoroolefins (HFOs), HCFOs, chlorofluoroolefins (CFOs))

- Organic solvent cleaning (with some solvents, e.g., toluene, *n*-methyl pyrrolidone (NMP), dimethyl formamide (DMF), more toxic than halogenated solvents)

Solvents using HCFCs and HFCs have been used in several different industries, for example, in aerospace, micro-mechanical part manufacturing, plating, aerosol cleaners, circuit flushing, electronics defluxing/cleaning, oxygen service cleaning and the medical industry in coating deposition. Each of these industries has its own set of specific solvent requirements and associated test procedures, e.g., to ensure cleaned parts are acceptable for use. The consequences of incomplete cleaning can be anything from poor performance in the next step, which can be seen in applications like plating, decreased product lifetime or performance in electronics cleaning, and even large potential safety concerns, such as when parts are cleaned for use in oxygen services.

As manufacturers transition away from using HCFC-based solvents, such as HCFC-141b and HCFC-225ca/cb, and HFC-based solvents, such as mixtures containing HFC-43-10-mee and HFC-365mfc, it is important that manufacturers match their cleaning requirements with the new solvent or cleaning system. Typically, when manufacturers seek to transition, they evaluate alternative solvents, aqueous cleaners, no clean solutions, or complete system changes. Each of these alternatives will be evaluated to assess how they meet the specific cleaning or coating deposition requirements, as well as cost and health and safety requirements.

HCFC-141b is used for syringe/needle coating in Article 5 parties. This solvent application coats silicone oil on the surface of the needle/syringe to reduce pain at injection. The solvent properties required are non-flammability, good solvency with the silicone oil, and quick solvent evaporation after coating. Alternative non-ozone-depleting substances (ODS) solvents are used in Europe, Japan, and the United States (e.g., HFEs). Topical creams are also available as alternative pain relief for injections.

Medical grade HFC-134a is used in relatively minor quantities in sub-critical liquid solvent extraction (under pressure) of bio-organics from biomass in the production of food flavours, fragrances, cannabinoids, and other bio-organics (e.g., hop extracts[132], artimesinin for malaria treatment[133]). HFC-134a is an approved solvent for this use, e.g., approved in the European Union under EC Directive 2009/32. Emissions can be kept low during the process through closed system design of solvent extraction and recirculation. Emissions could arise from residual HFC-134a in the solute and/or biomass at completion, although these can be minimised through vacuum extraction and compression. Alternative solvent extractants include super-critical carbon dioxide, ethanol, hexane, and butane, which, compared with HFC-134a, are considered disadvantageous in either lack of specificity in the alternative solvent (hydrocarbons) extraction of target solutes, solvent (hydrocarbons) physical properties leading to solute decomposition during isolation, solvent (supercritical carbon dioxide) chemical properties creating acidic environments within the biomass leading to solute

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[132] Colucci Cante R, Gallo M, D'Avino A, Garella I, Nigro R., Using Hydrofluorocarbon Extracts of Hop in a Pilot Scale Brewing Process, *Applied Sciences*, 2022, **12**(14), 6959. https://doi.org/10.3390/app12146959.

[133] Lelono, A., Simanungkalit, S., Umarudin, I., Herdiawan, H., Screening of Active Compounds from Artemisia annuausing HFC-134a Subcritic Extraction System, *J. Trop. Pharm. Chem.*, 2018, **4**(3), 114–121. https://doi.org/10.25026/jtpc.v4i3.149.

decomposition, cost, complexity of equipment and operator training, or flammability.[134] Medical grade HFC-152a is being investigated as an alternative; it would require process precautions to address flammability issues. HFOs or HCFOs could be suitable as alternatives if none of the bio-organic materials being extracted were reactive with the double bonds in the HFO/HCFO.

4.1.1 Halogenated solvents

This section focuses on halogenated solvents that can be used as substitutes for HCFCs and high-GWP HFCs and that comprise the available in-kind alternative technologies. Table 4.1 lists some of the important solvent properties that a manufacturer considers when evaluating an alternative solvent in their process.

Table 4.1 HCFC and HFC solvents and halogenated alternatives

Solvent	Solvent Class	100-Year GWP[135]	Boiling Point (ºC)	Flash Point (ºC)	KB value	Surface Tension (dynes/cm)
HCFC-141b	HCFC	725	32	none	56	19
HCFC-225ca/cb		122/595	54	none	31	16
HFC-43-10mee	HFC	1640	55	none	13	14
HFC-365mfc		794	40.2	-24	14	15
HFC-245fa[136]		1030	15	none	6	14
HFC-c447ef[137]		231[138]	82	none	14	20
HFC-52-13p[139]		2610[140]	71	none	5	13
HFC-76-13sf[141]		136[142]	114	none	7	16
HFE-449s1	HFE	297	61	none	10	14
HFE-569sf2		59	76	none	10	14
HFE-64-13s1		210[143]	98	none	7	15
HFE-347pc-f2		580	56	none	13	16

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[134] Medical Cannibis Network, 2020, *PURE5 R134a extraction vs CO_2 for extraction of cannabis*, 19th February 2020, https://www.healtheuropa.com/pure5-r134a-extraction-vs-co2-for-extraction-of-cannabis/97894/. Accessed August 2022.

[135] IPCC 4th Assessment Report (AR4) GWP, unless indicated otherwise.

[136] Used in aerosols.

[137] Heptafluorocyclopentane; an HFC not listed in Annex F.

[138] IPCC 6th Assessment Report (AR6) GWP.

[139] 1-Hydroperfluorohexane, $CF_3(CF_2)_4CHF_2$; an HFC not listed in Annex F.

[140] World Meteorological Organization (WMO), 2022, *Scientific Assessment of Ozone Depletion: 2022*, GAW Report No. 278; WMO: Geneva, 2022.

[141] 1,1,1,2,2-Pentahydroperfluorooctane, $CF_3(CF_2)_5CH_2CH_3$; an HFC not listed in Annex F.

[142] GWP is a value calculated by the National Institute of Advanced Industrial Science and Technology (AIST), Japan. AGC Chemicals, Environmentally Friendly Fluorinated Fluids, ASAHIKLIN, https://agc-asiapacific.com/product/solvent/?attachment_id=10883&download_file=ddegduh3axk9b. Accessed September 2022.

[143] UNEP, 2012, *May 2012 Report of the Technology and Economic Assessment Panel, Volume 2, Decision XXIII/9 Task Force Report: Additional Information on Alternatives to Ozone-Depleting Substances*, May 2012.

Solvent	Solvent Class	100-Year GWP[144]	Boiling Point (ºC)	Flash Point (ºC)	KB value	Surface Tension (dynes/cm)
HFO-1336mzz(Z)	HFO	2[145]	33	none	11	13
HFO-74-13[146]		<2.5[147]	110	none	6	18
HCFO-1233zd(E)[148]	HCFO	4[149]	19	none	25	13
HCFO-1233zd(Z)[150]		<1[151]	39	none	34	19
HCFO-1233yd(Z)[152]		<1[153]	54	none	48	23
TDCE	HCO	1[154]	48	-6	117	28

Several blends of HFEs, HCFOs and HFOs are available as HFC and HCFC alternatives. These blends take advantage of key properties of the solvent alternatives, for example, blending a non-flammable solvent with one that has high solvency while also reducing the cost. For example, chlorinated solvents with stronger solvency, such as TDCE, are added to improve the solvency of the mixtures. Examples of these blends are shown in Table 4.2.

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[144] IPCC 4th Assessment Report (AR4) GWP, unless indicated otherwise.

[145] World Meteorological Organization (WMO), 2022, *Scientific Assessment of Ozone Depletion: 2022*, GAW Report No. 278; WMO: Geneva, 2022. IPCC 6th Assessment Report (AR6) GWP.

[146] Methoxytridecafluoroheptene (MPHE) isomers, used in non-mechanical heat transfer, solvent cleaning, aerosol solvents, and adhesives and coatings.

[147] GWP, which is not listed in AR5, is calculated using the AR5 method, as referenced by the U.S. EPA in the Federal Register, Vol. 80, No. 136, July 16, 2015, 42053. https://www.govinfo.gov/content/pkg/FR-2015-07-16/pdf/2015-17469.pdf.

[148] ODP <0.0004

[149] World Meteorological Organization (WMO), 2022, *Scientific Assessment of Ozone Depletion: 2022*, GAW Report No. 278; WMO: Geneva, 2022.

[150] ODP <0.00034

[151] Ibid., WMO, 2022.

[152] ODP <0.00003

[153] Kazuaki, T., Tadafumi, U., Kenji, T., *et al.*, Rate constants for the reactions of OH radical with the (E)/(Z) isomers of $CF_3CF=CHCl$ and $CHF_2CF=CHCl$, *The Journal of Physical Chemistry A*, 2018, **122**, 3120–3127. https://doi.org/10.1021/acs.jpca.7b11923.

[154] UNEP, 2018, *2018 Report of the Medical and Chemical Technical Options Committee, 2018 Assessment Report*, December 2018.

Table 4.2 Examples of fluorinated solvent mixtures in use

Solvent Mixtures	Solvent Class	100-year GWP[155]	Boiling Point (ºC)	Flash Point (ºC)	KB value	Surface Tension (dynes/cm)
HFC-43-10mee with 38 wt% *trans*-1,2-dichloroethylene	HFC	1017	39	none	23	15
HFC-365mfc with 30 wt% *trans*-1,2-dichloroethylene		556	36	none	25	18
HFE-449s1 with 50 wt% *trans*-1,2-dichloroethylene	HFE	149	41	none	27	17
HFE-569sf2 and HFE-449s1 with 70 wt% *trans*-1,2-dichloroethylene		42	43	none	52	19
HFE-64-13s1 with 85 wt% *trans*-1,2-dichloroethylene		32	48	none	83	20
HFE-347pcf2 with 50 wt% *trans*-1,2-dichloroethylene		291	38	none	32	18
HFO-74-13 with ≥95 wt% t*rans*-1,2-dichloroethylene	HFO	<2.5	47	none	99	21
HCFO-1233yd(Z) with 63.5 wt% *trans*-1,2-dichloroethylene	HCFO	<1	47	none	118	23

The major trend in the development of solvents is the introduction of substances with unsaturated molecules, and thus short atmospheric lifetimes, near zero-ODP and low-GWP, such as HFOs, HCFOs, CFOs and hydrobromofluoroolefins (HBFOs). HFOs, with zero ODP and ultra-low GWP, are being commercialised for the replacement of high-GWP HFC and low- or moderate- GWP HFE solvents. HCFOs, CFOs and HBFOs are unique in their balanced solvency due to the presence of chlorine (or bromine) and fluorine atom in the molecule. Those with appropriate boiling points, low toxicity and sufficient stability may replace HCFCs and HFCs totally in the future. For example, HCFO-1233zd(E) (CF_3-CH=CH-Cl, *trans* isomer) has boiling point 19ºC and useful solvency property.

The main groups of new substances are unsaturated HFCs (HFOs, such as HFO-1336mzz(Z)) and unsaturated HCFCs (HCFOs). Such substances are expected to replace HCFCs and HFCs in several uses and to compete with HFEs in the solvent sector.

4.1.2 Solvents market profile

The global solvents market used around 27 million tonnes of solvents in 2021.[156] The solvents market value is expected to grow at a compound annual growth rate of 7.5% from 2022 to 2030, driven by increasing demand for environmentally friendly solvents (as replacements for petroleum-based organic solvents), and increasing demand from the agriculture and other applications sectors, such as adhesives and sealants that have transitioned away from using controlled substances. Restraining market growth are regulatory requirements for mitigating workplace exposure to solvents.

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[155] GWPs of mixtures are calculated based on the GWPs cited in Table 4.1.

[156] Research and Markets, 2022, *Global Solvents Market, By Type, By Application, By Source, Estimation & Forecast, 2017–2030*, January 2022. https://www.researchandmarkets.com/reports/5547463/global-solvents-market-by-type-by-application#src-pos-1. Accessed October 2022.

Controlled substances make up a small portion overall of the global solvents market. The fluorinated (including HCFCs, HFCs, HFOs, HFEs) solvents market value is expected to grow at a compound annual growth rate of 5.8% from 2021 to 2029.[157] Next generation fluorinated solvents, such as HFOs and HFEs, are gaining traction globally due to their zero ODP and low GWPs. Restraining market growth are factors such as high cost, flammability, possible toxic by-products, and non-fluorinated alternatives. The price of fluorinated solvents is relatively high compared with chlorinated, petroleum-based, glycol and glycol ether, and formulated hydrocarbon solvents.[158] An advantage of fluorinated solvents is their chemical stability, allowing solvent recovery and recycling.

HFCs dominated the fluorinated solvents market in 2020; however, HFEs are replacing many high GWP solvents for precision cleaning, coating deposition, and heat transfer fluids (see chapter 5), and are expected to be the fastest growing of the fluorinated solvents in the period 2021 to 2029.[159] HFOs are also expected to grow relatively strongly due to their low-GWPs. Where there are strict regulations to phase down specific fluorinated solvents, the solvents market is trending towards increased consumption of HFO, HCFO, and HFE-based solvents compared with the rest of world.[160]

The solvent markets of Asia Pacific, North America and Europe are the predominant regions for the consumption of fluorinated solvents due to their regional alignment with end-use industries. The Asia-Pacific region was the largest regional market for fluorinated solvents in 2020, with strong solvents market growth expected to continue due to increasing electronics manufacturing in China, the Republic of Korea, Japan, and other East Asian countries, and increasing automotive manufacturing in China, India, Indonesia, and Malaysia. North America and Europe are also large regional markets for fluorinated solvents.

Electronics component cleaning was the major end-use application in the global fluorinated solvents market in 2020, and precision cleaning the fastest growing market segment.[161] Other significant applications include coating deposition solvent and lubricant carrier solvent.

4.1.3 Consumption of controlled substances

Among controlled substances, trichlorotrifluoroethane (CFC-113) and 1,1,1-trichloroethane (TCA) use as solvents has been phased out in both of Article-5 and non-Article 5 parties, with the exception being the use of CFC-113 as a cleaning solvent in aerospace applications until stockpiles are depleted.

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[157] Research and Markets, 2021, *Fluorinated Solvents Market Size, Market Share, Application Analysis, Regional Outlook, Growth Trends, Key Players, Competitive Strategies and Forecasts*, 2021 to 2029, November 2021. https://www.researchandmarkets.com/reports/5614463/fluorinated-solvents-market-size-market-share. Accessed October 2022.

[158] Persistence Market Research, 2018, *Asia Pacific North America Europe Fluorinated Solvents Market*, August 2018. https://www.persistencemarketresearch.com/market-research/asia-pacific-north-america-europe-fluorinated-solvents-market.asp. Accessed October 2022.

[159] Research and Markets, 2021, *Fluorinated Solvents Market Size, Market Share, Application Analysis, Regional Outlook, Growth Trends, Key Players, Competitive Strategies and Forecasts, 2021 to 2029*, November 2021. https://www.researchandmarkets.com/reports/5614463/fluorinated-solvents-market-size-market-share. Accessed October 2022.

[160] Ibid., Persistence Market Research, 2018.

[161] Ibid., Research and Markets, 2021.

The use of 1,1-dichloro-1-fluoroethane (HCFC-141b) and dichloropentafluoropropane (HCFC-225) for solvent cleaning has been largely phased out in non-Article 5 parties, except in aerospace and military applications.

In Article 5 parties, solvent uses of hydrochlorofluorocarbon (HCFC) have declined and will continue to reduce as more critical uses of HCFCs are given priority and as available quantities decline under the HCFC phase-out schedule of the Montreal Protocol. HCFC consumption for solvents in Article 5 parties includes for electronics, metal cleaning, for coatings deposition in the manufacture of disposable medical devices and solvent formulations.

It is difficult to obtain accurate figures of the total manufacture, import, and use of solvents using controlled substances, particularly in Article 5 parties because of the nature of the market, with distribution and sales to supply many smaller users. Small- and medium- sized enterprises (SMEs) collectively make up a major portion of the solvents market. Alternatives are generally readily available in Article 5 parties, except the unsaturated chemicals (e.g., HFOs) that are relatively more expensive. Economic factors are a major determinant for Article 5 parties in the selection of alternatives. SMEs that do not have enough investment tend to use chlorinated solvents as they are cheaply available and existing facilities can be used with minimum modifications.

As an example, China has reported HCFC-141b as the most widely consumed HCFC for solvent uses, with a much smaller amount of HCFC-225ca/cb imported for these uses. Total consumption was 4433 tonnes (485 ODP tonnes) in 2014 and was expected to decrease to 321 ODP tonnes in 2021 under consumption targets. In 2014, solvent uses for HCFCs in China were mainly for medical device manufacture (40%), solvent formulation (25%), metal cleaning (21%), and electronics (14%) sectors. The solvent sector in China is dominated by SMEs; in a survey, over 70% of total consumption was by enterprises using less than 10 tonnes annually. The phase-out of HCFC-141b was expected to be challenging, among other reasons, due to decreasing availability of HCFC-141b from reduced consumption in foam blowing applications.[162]

Recent estimates for the consumption of Annex F HFCs used in the solvents sector for Article 5 parties were included in TEAP's assessment of the funding requirement for the replenishment of the Multilateral Fund for the period 2021–2023.[163] This study estimated HFC consumption for solvent uses in Article 5 parties to be 1,208 tonnes (1.98 $MMTCO_2e$) as an annual average for the replenishment period 20212023.

4.1.4 Availability of HCFCs

HCFC production and consumption (as defined) in non-Article 5 parties was required to be phased out by 1 January 2020, with allowance for essential use exemptions if authorised by the Montreal Protocol. Between 1 January 2020 and 1 January 2030, for any non-Article 5 party, Article 2F, paragraph 6, allows HCFC consumption and production in any year up to 0.5% of the baseline consumption allowance, for restricted applications including solvent applications in rocket engine manufacturing. Otherwise, use of HCFC solvents can continue

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[162] Executive Committee of the Multilateral Fund, Meeting Document: UNEP/OzL.Pro/ExCom/76/25, *Project Proposals: China*, 22 April 2016.

[163] UNEP, 2021, *September 2021 Report of the Technology and Economic Assessment Panel, Volume 6: Assessment of the Funding Requirement for the Replenishment of the Multilateral Fund for the Period 2021–2023*, September 2021.

in non-Article 5 parties from recycled or stockpiled sources, for as long as those sources remain.

HCFC production and consumption (as defined) in Article 5 parties will be phased out by 1 January 2030, with allowance for essential use exemptions if authorised by the Montreal Protocol. Between 1 January 2030 and 1 January 2040, for any Article 5 party, Article 5, paragraph 8 *ter*, allows HCFC consumption and production in any year up to 2.5% of the baseline consumption allowance, for restricted applications including solvent applications in rocket engine manufacturing. Otherwise, use of HCFC solvents would be allowed to continue in Article 5 parties from recycled or stockpiled sources, for as long as those sources remain.

In decision XXX/2, parties asked TEAP to provide information on the amounts of HCFCs available from recovery, recycling and reclamation, and stocks and availability of alternative options for solvent applications in rocket manufacturing.

The following section describes solvent applications using HCFCs in non-Article 5 parties, where recycling and use from existing stockpile may be on-going in small quantities.

Aerospace and military applications may require small quantities of CFCs or HCFCs globally to service existing equipment (e.g., CFC-113, HCFC-122, -122a, -141b, -225) in non-Article 5 parties, which would be sourced from stockpiles.

For example, HCFC-225 replaced CFC-113 in precision cleaning and cleanliness verification of sensitive equipment, such as oxygen systems, in aerospace and military applications. Small quantities of CFC-113 from existing stocks are still used for this purpose. HCFC-225 was used widely in space and aerospace as a substitute for CFC-113 in oxygen system cleaning. These HCFC solvent uses are unlikely to exceed several hundred metric tonnes (i.e., several ODP tonnes) annually for the period 2020–2030. CFC-113 solvent uses are also unlikely to exceed several hundred metric tonnes per year. Stockpiled sources of controlled substances can become unsuitable over time for these precision cleaning uses due to the formation of chemical impurities, which in these critical uses can result in the compromised safety of humans and vehicles.

It can be difficult to prove the efficacy of replacement solvents under actual conditions of use. When making solvent substitutions, rigorous qualification or certification testing of critical materials is needed, which is accomplished on relatively small scales. However, in some cases, full-scale testing is needed under expected loads and use environments.

Chemicals like HCFO-1233zd, which is relatively oxygen-compatible, have been qualified as a replacement for solvent cleaning and verification sampling of NASA propulsion oxygen systems hardware, ground support equipment, and associated test systems.[164] One U.S. military application is also known to be moving to HFEs over the next two years.

Challenges remain with substitution, including with oxygen compatibility for aerospace applications that can manifest adversely as solvent flammability or reactivity in an oxygen-rich environment. Legacy systems designed for CFCs and HCFC cleaning solvents can be degraded by replacement chemicals, e.g., softening of non-metallic components such as seals and gaskets.

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[164] NASA, 2015, *Replacement of Hydrochlorofluorocarbon (HCFC)-225 Solvent for Cleaning and Verification Sampling of NASA Propulsion Oxygen Systems Hardware, Ground Support Equipment, and Associated Test Systems*, April 1, 2015. https://ntrs.nasa.gov/citations/20150006941. Accessed October 2022.

4.1.5 Emissions of controlled substances and mitigation

Solvent end users work to control emissions to every extent possible since this directly affects their operating costs. For example, solvent cleaning systems (often referred to as vapor degreasers) will contain not only primary cooling coils for condensation of the boiling solvent but also secondary coils operated at much lower temperature to reduce solvent vapor concentrations and emissions. Many users will also recycle solvent for reuse. Only the largest solvent equipment installations would typically find the use of additional solvent capture and recovery equipment, such as carbon adsorption, to mitigate fugitive emissions to be cost effective.

IPCC Guidelines for National Greenhouse Gas Inventories assume solvents used for cleaning are emitted during, or shortly after, use; typically, 100 per cent of total use over 2 years. Solvent emissions can be reduced by up to an estimated 80 per cent using improved housekeeping and recycling practices.[165,166] Recycling practices reduce consumption and prolong the period over which 100 per cent emissions occur; there is an economic incentive for solvent conservation with the high price of some speciality chlorinated and fluorinated cleaning and coating deposition fluids. Destruction is not commonly practised, and so eventually 100% of solvent uses will be emitted over time.

4.2 Technical and economic assessment of solvent uses of controlled substances and their alternatives

An assessment follows of the technical and economic feasibility of HFC alternatives in solvent uses. The assessment criteria referenced in decision XXVIII/2 have been slightly modified to remain relevant to this application, using the following criteria:

i. Commercially available
ii. Technically proven
iii. Environmentally sound
iv. Economically viable and cost effective
v. Safe to use in industrial applications considering flammability and toxicity issues
vi. Easy to use and maintain

"Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization" has been adjusted to *safe to use in industrial applications considering flammability and toxicity issues*. "Easy to service and maintain" has been adjusted to *easy to use and maintain*. Technically proven is interpreted to mean the technology has been proven to work for that application, or an aspect of it; not necessarily commercialised for that application.

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[165] IPCC, 1996, *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories: Reference Manual, Volume 3*. https://www.ipcc-nggip.iges.or.jp/public/gl/guidelin/ch3ref1.pdf.

[166] IPCC, 2006, *2006 IPCC Guidelines for National Greenhouse Gas Inventories: Volume 3, Industrial Processes and Product Use*, Chapter 7 Emissions of Fluorinated Substitutes for Ozone-depleting Substances. https://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/3_Volume3/V3_7_Ch7_ODS_Substitutes.pdf.

Table 4.3 Technical and economic assessment of solvent uses of controlled substances and their alternatives

Controlled Substances and Alternatives	**Characteristics**	**Commercially available**	**Technically proven**	**Environmentally sound**	**Economically viable**	**Safe to use**	**Easy to use**
HCFCs (-141b, -225ca/cb)	HCFCs were implemented as in-kind alternatives to CFCs and 1,1,1-trichloroethane. The compounds are non-flammable, effective cleaning agents with defined ODPs.	🟨	🟩	🟥	🟩	🟩	🟩
HFCs (43-10-mee, 365mfc)	HFCs have limited utility in cleaning applications due to their mild solvent strength. They are most often used in blends and azeotropic mixtures with compounds such as *trans*-1,2-dichloroethylene and/or alcohols. These formulations are effective cleaning agents but can often be more expensive than other in-kind alternatives.	🟨	🟩	🟥	🟨	🟩	🟩
	Alternatives						
Aqueous and semi-aqueous cleaning	Water-based cleaning processes often use surfactants and saponifiers and in the case of semi-aqueous high boiling hydrocarbon solvents followed by several water rinses. These processes can present challenges to maintain water purity and typically consume more energy to dry water.	🟩	🟩	🟩	🟩	🟩	🟨
Organic solvents	Organic solvents, such as alcohols, ethers, ketones, esters, aromatics, can be low cost, effective solvents but users must address flammability and/or toxicity concerns and the fact that most are precursors to smog formation which are regulated as volatile organic compounds (VOCs).	🟩	🟩	🟨[1]	🟩	🟨	🟨
n-Propyl bromide	*n*-Propyl bromide has been used in several solvent applications but has a non-zero ODP and occupational exposure limits as low as 0.1 ppmv in some parties. *n*-Propyl bromide is considered a suspected carcinogen and mutagen. This compound is listed as a hazardous air pollutant in some parties, e.g., the United States.	🟩	🟩	🟨	🟩	🟨	🟨
Trichloroethylene, perchloroethylene, dichloromethane, chloroform	Chlorinated solvents are non-flammable, low cost, effective cleaning agents with relatively low occupational exposure limits ($\leq$ 50 ppmv) and classified as confirmed or suspected carcinogens in many parties. These compounds are listed as hazardous air pollutants in some parties, e.g., the United States.	🟩	🟩	🟨	🟩	🟨	🟨
HFCs	Saturated HFCs not listed as controlled substances in Annex F are used in low volume quantities in solvent applications, including HFC-c447ef (5-carbon cyclic HFC, ($-CHFCH_2(CF_2)_3-$), HFC-52-13p ($CF_3(CF_2)_4CHF_2$) and HFC-76-13sf ($CF_3(CF_2)_5CH_2CH_3$).	🟩	🟩	🟨[2]	🟩	🟩	🟩

Controlled Substances and Alternatives	**Characteristics**	**Commercially available**	**Technically proven**	**Environmentally sound**	**Economically viable**	**Safe to use**	**Easy to use**
Alternatives							
HFEs	Hydrofluoroethers have limited utility in cleaning applications due to their mild solvent strength. They are most often used in blends and azeotropic mixtures with *trans*-1,2-dichloroethylene and/or alcohols. These formulations are effective cleaning agents but can often be more expensive than other in-kind alternatives.	🟩	🟩	🟩[3]	🟨	🟩	🟩
HCFOs	HCFO-1233zd(E), -1233zd(Z), and -1233yd(Z) are emerging as effective cleaning agents with negligible ODPs and GWPs. HCFO-1233zd(E) alone can present technical challenges in some solvent applications due to its 19°C boiling point (b.p.). HCFO-1233zd(Z) (b.p. 39ºC), and HCFO-1233yd(Z) (b.p. 54ºC) have more suitable boiling points and do not present these same challenges.	🟩	🟩	🟩	🟩	🟩	🟨
HFOs	Like HFEs, hydrofluoroolefins have limited utility in cleaning applications due to their mild solvent strength. They are most often used in blends and azeotropic mixtures with *trans*-1,2-dichloroethylene. These formulations are effective cleaning agents but can often be more expensive than other in-kind alternatives.	🟩	🟩	🟩	🟨	🟩	🟩

🟩 Yes or More acceptable; 🟨 Not always or Less acceptable; 🟥 No or Unacceptable.

1. Most organic solvents are VOCs, which are regulated in some regions due to their potential for photochemical smog generation.
2. HFC-c447ef is reported to have a 100-year GWP of 231 (IPCC AR6). HFC-52-13p is calculated to have a 100-year GWP of 2000. HFC-76-13sf is calculated to have a 100-year GWP of 136. HFC-52-13p has a GWP higher than those for HFC-43-10-mee and HFC-365mfc and would be rated as red. When used as solvents, these HFCs can be used neat or with a co-solvent, which would lower the overall GWP.
3. HFEs, including HFE-449s1, HFE-569sf2, HFE-64-13s1, and HFE-347pc-f2 have 100-year GWPs ranging from around 59–580. However, being most often used in mixtures with lower GWP chemicals, HFE solvents can be rated as being environmentally sound.

Commercial availability and accessibility— In-kind and not-in-kind alternatives are commercially available and accessible for solvent applications. By comparison, HCFCs and HFCs have decreasing commercial availability and accessibility due to Montreal Protocol control measures to phase out or phase down these controlled substances.

Technically proven— All alternatives have been technically proven in specific solvent applications.

HFC (and HCFC) solvents using have been used in several different industries, for example, in aerospace, micro-mechanical part manufacturing, plating, aerosol cleaners, circuit flushing, electronics defluxing/cleaning, oxygen service cleaning, and the medical industry in coating deposition. Each of these industries has its own set of specific solvent requirements and associated test procedures, e.g., to ensure cleaned parts are acceptable for use. The consequences of incomplete cleaning can be anything from poor performance in the next step, which can be seen in applications like plating, decreased product lifetime, performance in electronics cleaning, or even large potential safety concerns, such as when parts are cleaned for use in oxygen services. It is important for manufacturers to match their cleaning requirements with the new solvent or cleaning system. Typically, when seeking an alternative, manufacturers will evaluate alternative solvents, aqueous cleaners, no clean solutions, or complete system changes. Each of these alternatives will be evaluated to assess how they meet the specific cleaning or coating deposition requirements, as well as cost and health and safety requirements.

Aqueous and semi-aqueous cleaning can present challenges in maintaining water purity and consume more energy to dry water.

Environmentally sound— Trichloroethylene, perchloroethylene, dichloromethane, chloroform, and *n*-propyl bromide have been listed as hazardous air pollutants in some parties, e.g., the United States. These halogenated solvents have low ODPs; they are not controlled substances.

HFC-52-13p is calculated to have a 100-year GWP of 2000, which is higher than the GWPs for HFC-43-10-mee (1640) and HFC-365mfc (794). HFC-c447ef is reported to have a 100-year GWP of 231. HFC-76-13sf is calculated to have a 100-year GWP of 136. When used as solvents, these HFCs can be used neat or with a co-solvent that lowers the overall GWP.

HFEs, including HFE-449s1, HFE-569sf2, HFE-64-13s1, and HFE-347pc-f2 have 100-year GWPs ranging from around 59–580. HFEs are most often used as azeotropic mixtures with lower GWP chemicals, meaning HFE solvents are considered environmentally sound.

HCFO-1233zd(E), 1233zd(Z), and 1233yd(Z) are emerging as effective cleaning agents with negligible ODPs and GWPs.

Economically viable and cost effective— HFEs and HFOs are more expensive than other in-kind solvent options. For this reason, they can often find their way into high value and/or specialist applications.

Safe to use in industrial applications considering flammability and toxicity issues— Organic solvents require consideration of flammability concerns. Most organic solvents are photochemical smog precursors that are regulated as volatile organic compounds (VOCs)

Trichloroethylene, perchloroethylene, dichloromethane, chloroform, and *n*-propyl bromide are confirmed or suspected carcinogens in many parties. They have been listed as hazardous air pollutants in some parties, e.g., the United States. They have relatively low (≤50 ppmv) or very low (*n*-propyl bromide, 0.1ppmv) occupational exposure limits in some parties.

Easy to use and maintain—Due to their different technical or chemical/physical properties, or safety profiles, aqueous and semi-aqueous cleaning, organic solvents, trichloroethylene, perchloroethylene, dichloromethane, chloroform, *n*-propyl bromide can be options that are more difficult to use. HCFO-1233zd(E) alone can present technical challenges in some solvent applications due to its low boiling point. HFEs, HFOs, and HCFO-1233zd(Z), and HCFO-1233yd(Z) are easier to use than the other alternatives.

4.3 *n*-Propyl bromide

n-Propyl bromide (1-bromopropane, $CH_3CH_2CH_2Br$, *n*-PB, CAS No. 106 94 5) is being used as a solvent in a range of applications. Its boiling point, 71ºC, is comparable to those of CFC-113 (48ºC), hexane (69ºC), methyl chloroform (TCA, 74ºC) and trichloroethylene (87ºC), making it attractive as a solvent with similar physical properties. Its solvent properties are typical of those of lower molecular weight hydrocarbons and organohalogen compounds. *n*-Propyl bromide is classified as a highly flammable liquid and vapour.

n-Propyl bromide is used as an electrical cleaning agent, degreaser, or carrier solvent, as an intermediate in chemical manufacture, in spray adhesives, dry cleaning, insulation for building and construction material, and as a refrigerant flushing agent. Consumer uses include degreasers, cleaners, adhesives, sealants, and automotive care products. *n*-Propyl bromide is also used in consumer aerosol products for electronics cleaning and degreasing, dusters, adhesives, textile spot removers, and paintable mould release agents.

n-Propyl bromide is not a controlled substance under the Montreal Protocol. Due to the presence of bromine in the molecule, however, there are concerns regarding its use based both on its potential for ozone depletion and its toxicity. *n*-Propyl bromide may also contribute to photochemical smog and is regulated as a volatile organic compound.

The atmospheric lifetime, and impact on ozone depletion, of *n*-propyl bromide have been evaluated in several studies, with derivations dependent on emissions location. In 2011, using a current-generation chemistry-transport model of the troposphere and stratosphere, Wuebbles *et al*. derived an atmospheric chemical lifetime of 19.6 days, and ODP of 0.011, for the global emissions case, and 24.7 days, and an ODP of 0.0049 at northern hemisphere mid-latitudes.[167] At tropical latitudes, *n*-propyl bromide has a higher ODP, closer to that of HCFC-141b.[168]

Regarding its toxicity, the National Toxicology Program report (NTP TR 564, August 2011) and the American Conference of Governmental Industrial Hygienists (ACGIH®) (February 2012) established a threshold limit value (TLV®) for *n*-propyl bromide of 0.1 ppm. The Japan Society for Occupational Health set a TLV of 0.5ppm for *n*-propyl bromide in 2013. In 2013, the U.S. National Toxicology Program concluded that *n*-propyl bromide is reasonably anticipated to be a human carcinogen.[169] In 2014, ACGIH published a time-weighted average exposure limit (TWA) of 0.1ppm for *n*-propyl bromide.

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[167] Wuebbles, D.J., Patten, K.O., Wang, D., Youn, D., Martinez-Avile, M., and Francisco, J.S., Three-dimensional model evaluation of the Ozone Depletion Potentials for *n*-propyl bromide, trichloroethylene and perchloroethylene, *Atmos. Chem. Phys.*, 2011, **11**, 2371–2380. https://doi.org/10.5194/acp-11-2371-2011.

[168] National Center for Biotechnology Information, PubChem Annotation Record for 1-Bromopropane, Source: Hazardous Substances Data Bank (HSDB). https://pubchem.ncbi.nlm.nih.gov/source/hsdb/1068. Accessed October 2022.

[169] U.S. Department of Health and Human Services, National Toxicology Program, 2013, *Report on Carcinogens Monograph on 1-Bromopropane*, NIH Publication No. 13-5982, September 23, 2013. https://ntp.niehs.nih.gov/ntp/roc/thirteenth/monographs_final/1bromopropane_508.pdf. Accessed December 2022.

Primarily due to health and safety risk characterisations for *n*-propyl bromide, several countries regulate its use (see section below).

4.3.1 Regulatory status

The European Chemical Agency (ECHA) has classified *n*-propyl bromide as a Substance of Very High Concern (SVHC), and it is included in the list of substances included in Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Annex XIV to Regulation (EC) No 19078/2006 ("Authorisation List"). *n*-Propyl bromide is now subject to authorisation, meaning it cannot be placed on the market or used, e.g., for solvent uses, after 4th July 2020, unless an authorisation is granted. There are no exempted (categories of) uses for *n*-propyl bromide.[170] The European Union has also extended its reporting requirements for ozone-depleting substances to *n*-propyl bromide.

According to the harmonised classification and labelling (CLP00) approved by the European Union, *n*-propyl bromide *"...may damage fertility and may damage the unborn child, is a highly flammable liquid and vapour, causes serious eye irritation, may cause damage to organs through prolonged or repeated exposure, causes skin irritation, may cause respiratory irritation and may cause drowsiness or dizziness*". In addition, the classification identifies that *n*-propyl bromide "*...may cause damage to organs, is harmful to aquatic life with long lasting effects and harms public health and the environment by destroying ozone in the upper atmosphere*".[171]

Under U.S. EPA's SNAP program, *n*-propyl bromide is listed as an acceptable substitute for ozone-depleting substances in metals, electronics, and precision cleaning, subject to use conditions, such as the use of personal protective equipment and compliance with permissible exposure limits.

Under the Toxic Substances Control Act (TSCA), the U.S. EPA has established a chemical risk evaluation process. In performing risk evaluations for existing chemicals, U.S. EPA is directed to "*determine whether a chemical substance presents an unreasonable risk of injury to health or the environment, without consideration of costs or other non-risk factors, including an unreasonable risk to a potentially exposed or susceptible subpopulation identified as relevant to the risk evaluation by the Administrator under the conditions of use*." In December 2016, *n*-propyl bromide was identified as one of ten chemicals designated by U.S. EPA for chemical risk evaluation, based on high hazard concerns due to its toxicity profile and high exposure concerns due to its use in consumer products.

In June 2017, U.S. EPA published the scope of the risk evaluation to be conducted for *n*-propyl bromide, as part of the public consultation process.[172] The scope of risk evaluation stated that in the United States *n*-propyl bromide is primarily used as a solvent cleaner in vapour and immersion degreasing operations to clean optics, electronics, and metals. It has also been used as an alternative solvent carrier for other ozone-depleting substances and chlorinated solvents, e.g., in industries using spray adhesives such as foam cushion

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[170] European Chemicals Agency (ECHA) authorisation list entry for *n*-propyl bromide, https://echa.europa.eu/authorisation-list/-/dislist/details/0b0236e1804d5364. Accessed March 2018.

[171] European Chemicals Agency (ECHA), 2022, *Brief Profile of* n-*propyl bromide*. https://echa.europa.eu/brief-profile/-/briefprofile/100.003.133. Accessed December 2022.

[172] U.S. EPA, Office of Chemical Safety and Pollution Prevention, 2017, *Scope of the Risk Evaluation for 1-Bromopropane*, CASRN: 106-94-5, EPA Document # EPA- 740-R1-7009, June 2017. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-evaluation-1-bromopropane-1-bp. Accessed April 2018.

manufacturing. *n*-Propyl bromide is also used in aerosols, such as contact cleaners and dusters, in the United States.

Following a statutory process of risk evaluation[173] and associated public consultation, in December 2022, U.S. EPA released a final revised risk determination for *n*-propyl bromide. The final revised risk determination finds that *n*-propyl bromide, as a whole chemical, presents an unreasonable risk of injury to the health of workers, occupational non-users, consumers, and bystanders to consumer use, under its conditions of use. The primary health risks identified were developmental toxicity from short-term and long-term inhalation and dermal exposure to the chemical and cancer from long-term inhalation and dermal exposure. The risk determination did not make the assumption that all workers always and appropriately wear personal protective equipment, recognising the unreasonable risk to sub-populations who may be highly exposed if they are not protected by occupational safety and health standards.[174]

n-Propyl bromide is listed on the United States' Toxics Release Inventory (TRI), with data on environmental releases of *n*-propyl bromide to air, landfills, or water. In February 2022, U.S. EPA also added *n*-propyl bromide to the list of hazardous air pollutants under the Clean Air Act, meaning emissions will be evaluated and controlled.

In China, *n*-propyl bromide is identified as one of nearly 3,000 hazardous chemicals controlled under the Regulation on the Safety Management of Hazardous Chemicals. Based on this regulation, stakeholders handling *n*-propyl bromide must prevent and reduce hazardous chemical accidents and guarantee the use of *n*-propyl bromide will not impact the life and safety of the public and the environment during its production, storage, use, dealing and transport.

4.3.2 Consumption estimates

Manufacture is occurring in a small number of countries, including China, Israel, and the United States. Chemical manufacturers do not publicise their *n*-propyl bromide production data for commercial reasons. Parties to the Montreal Protocol are not required under Article 7 to report the production and consumption because *n*-propyl bromide is not a controlled substance.

- East Asia is believed to be the largest growth market for *n*-propyl bromide in part because of its use as a feedstock in the manufacture of profenofos, an acaricide used in cotton treatment, and propylphos.

- There are six major producers of *n*-propyl bromide in China, with total production capacity about 15,000 tonnes/year. In 2021, production of *n*-propyl bromide was about 8,000 tonnes, of which about 1,500 tonnes were for solvent use (about half exported, mainly to Japan and the United States). Most *n*-propyl bromide produced and used in China is as an intermediate in pharmaceuticals manufacture.

- India imported around 1,000 tonnes in 2021 and 2,000 tonnes in 2020 and 2019.

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[173] U.S. EPA, Office of Chemical Safety and Pollution Prevention, 2020, *Risk Evaluation for 1-Bromopropane (*n-*Propyl Bromide)*, EPA Document #740-R1-8013, August 2020. https://www.epa.gov/sites/default/files/2020-08/documents/risk_evaluation_for_1-bromopropane_n-propyl_bromide.pdf. Accessed October 2022.

[174] U.S. EPA, 2022, *1-Bromopropane (1–BP); Revision to Toxic Substances Control Act (TSCA) Risk Determination; Notice of Availability*, Federal Register, 87 FR 77603, December 19, 2022. Accessed December 2022.

- Japan imported about 5,000 tonnes *n*-propyl bromide in 2015. The amount imported into Japan has decreased year on year; in 2020, Japan imported around 1,500 tonnes *n*-propyl bromide. *iso*-Propyl bromide, with an ODP of 0.018[175], is also imported into Japan, which has been increasing in recent years, with around 2,500 tonnes imported in 2020.

- In 2018, the European Union imports about 2,000 tonnes *n*-propyl bromide, with maximum production of 3,600 tonnes. By 2022, the European Union imports between 1 to 10 tonnes *n*-propyl bromide per annum, as reported under REACH.

- The United States manufactured and imported about 8,500 tonnes *n*-propyl bromide in 2012, which had increased to nearly 12,000 tonnes in 2015 and 2016.[176,177] Nationally aggregated production volumes reported for 2019 are between 5,000 and 23,000 tonnes (given as a range for commercial business reasons).[178] These quantities are relevant for all uses, including as an intermediate in chemical manufacturing. According to information from public sources, the pharmaceutical and agrochemical industries have become the largest consuming sector, accounting for nearly half.

4.3.3 Future demand

The relatively low workplace exposure standards indicate that use of *n*-propyl bromide in solvent applications is likely to be problematic, and its use will likely be limited to applications where worker exposure is controlled and will require significant emission control. Nevertheless, *n*-propyl bromide continues to appear as a marketed solvent at trade exhibitions with demand in several markets (e.g., China, Japan, and the United States).

4.3.4 Assessment of alternatives

Alternatives to *n*-propyl bromide are the same as, or similar to, other solvent alternatives to controlled substances, as outlined in the section above.

n-Propyl bromide is relatively cheap to produce and can be seen as a cheap solvent. However, if the costs of appropriate measures surrounding its use to protect worker health and safety were included, *n*-propyl bromide would likely not be considered an inexpensive choice for end-users. That it remains an attractive cheaper solvent choice in some circumstances is indicative that appropriate worker exposure controls might not always be implemented, that worker health and safety might be compromised, and that the true costs of using *n*-propyl

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[175] Nordic Council of Ministers, 2005, *Potential Ozone Depleting Substances: Uses and Alternatives in the Nordic Countries*, Copenhagen 2005, reference Huie R.E., Orkin, V.L., Louis, F., Kozlov, S., Kurylo, M.J., Effect of bromine substitution on the lifetimes and ozone depletion potentials of organic compounds, *Halon Options Technical Working Conference*, 2002, 12th. Proceedings. HOTWC 2002. http://norden.diva-portal.org/smash/get/diva2:701223/FULLTEXT01.pdf. Accessed October 2022.

[176] U.S. EPA, Office of Chemical Safety and Pollution Prevention, 2017, *Scope of the Risk Evaluation for 1-Bromopropane*, CASRN: 106-94-5, EPA Document # EPA- 740-R1-7009, June 2017. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-evaluation-1-bromopropane-1-bp. Accessed April 2018.

[177] U.S. EPA, Office of Chemical Safety and Pollution Prevention, 2017, *Preliminary Information on Manufacturing, Processing, Distribution, Use, and Disposal: 1-Bromopropane*, CASRN: 106-94-5, Support document for Docket EPA-HQ-OPPT-2016-0741, February 2017. https://www.epa.gov/sites/production/files/2017-02/documents/1-bromopropane.pdf. Accessed April 2017.

[178] U.S. EPA, 2020, Chemical Data Reporting, https://www.epa.gov/chemical-data-reporting/access-cdr-data#2020.

bromide are being evaded by some solvent end-users and then being externalised to society, e.g., resulting human health costs paid for by individuals or society.

5 Semiconductor and other electronics manufacturing

5.1 Semiconductor manufacturing uses of controlled substances

Semiconductors are fabricated by forming circuit patterns on wafers.

In 1970, 1 kbit dynamic random-access memory (DRAM[179]) was fabricated, when the transistor size was 10 microns, and wet etching with chemicals was used to form the pattern. Miniaturisation of patterns was pursued to achieve higher performance, both reducing cost and achieving higher processing speeds. While it was possible to achieve sizes down to 1 micron, further miniaturisation was difficult with traditional wet etching. Subsequently, dry etching was developed using reactive ion etching (RIE), which dramatically improved miniaturisation with line widths of the order of several nanometres now achieved.

In semiconductor and other electronics manufacturing, fluorinated gases/liquids such as HFCs are used for three purposes:

- Etching—selective etching for fine circuit patterns
- Chamber cleaning—to reset the chamber conditions by removing deposited silicon materials from the chamber walls
- As a heat transfer fluid—to control the etching performance.

Dry etching using RIE utilises plasma-generated fluorine radicals and other reactive fluorine-containing ions that react with the substrate or thin-film to be etched. For example, when HFC-23 (CHF_3) is used as the etching gas and silicon (Si) as the substrate to be etched, in RIE the CHF_3 forms ions, such as CF_3+, and fluorine (F) radicals by electron collision. These active species arrive at the substrate surface and react with the Si surface to form SiF_4, which is volatile, resulting in the Si being etched.

$$Si + 4F \rightarrow SiF_4$$

If the substrate to be etched is a silicon compound, SiO_2 or Si_3N_4, it is etched in the same way, through the formation of volatile SiF_4.

$$SiO_2 + 4F \rightarrow SiF_4 + O_2$$

$$Si_3N_4 + 12F \rightarrow 3\ SiF_4 + 2\ N_2$$

Fluorinated gases are used in dilute concentrations in combination with inert species, such as argon and other gases, such as oxygen, that can modify etching rates and fluorine atom concentration.[180] Etch recipes are optimised for characteristics, such as desired selectivity, etch rate, anisotropy (directionality) and homogeneity. Plasma etching is widely used due to the selectivity, reproducibility, and anisotropy that it provides, e.g., producing reproducible, very deep vertical sidewalls with no

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[179] Dynamic random-access memory (DRAM) is a type of memory that is typically used for the data or program code needed by a computer processor to function.

[180] Mogab, C.J., Adams, A.C., Flamm, D.L., Plasma etching of Si and SiO_2—The effect of oxygen additions to CF_4 plasmas, Journal of Applied Physics, 1978, **49**, 3796. https://doi.org/10.1063/1.325382.

undercut.[181] Depending on the complexity of the device being manufactured, the manufacturing process may require upwards of 100 steps that use fluorinated gases.[182]

The fluorinated gases used in dry etching include PFCs, HFCs, sulphur hexafluoride (SF_6) and nitrogen trifluoride (NF_3). PFCs such as PFC-14 (CF_4), PFC-c318 (cyclic C_4F_8) are used. The most commonly used HFCs for dry etching are HFC-23 (CHF_3), HFC-32 (CH_2F_2) and HFC-41 (CH_3F).

HFC-23 is commonly used for selective etching of silicon dioxide (SiO_2) and silicon nitride (SiN).[183] PFC-c318, and more recently used gases like HFC-32, HFC-41 and C_4F_6 (perfluoro-1,3-butadiene), are utilised in high aspect hole etching (e.g., for manufacturing DRAM and NAND[184]).[185,186] Gases such as PFC-c318, perfluorobuta-1,3-diene, and HFC-32 are used to form polymer films (CF_x) to protect the sidewalls during high aspect hole etching.[187,188]

Not all the fluorinated gas breaks down, or is consumed, in the plasma. Radicals and molecules can also recombine in the plasma. Unreacted gas (or recombined molecules) accounts for most emissions of fluorinated gases from electronics manufacturing. A small fraction of the gas will also be converted into fluorinated by-products. For example, PFC-116 (C_2F_6) is typically a by-product in all etching processes that use a carbon-containing fluorinated gas as the etchant, like HFCs.[189] HFCs themselves can be formed as by-products.

The walls of the chemical vapour deposition chamber, electrodes, and chamber hardware are also cleaned using fluorinated chemicals. Plasma-generated fluorine radicals and other reactive fluorine-containing ions are used to remove the build-up of silicon materials on the chamber walls and tools. HFCs are only minimally used for chamber cleaning. PFC-116 (C_2F_6), SF_6 and NF_3 are the most commonly used gases for chamber cleaning.

Fluorinated heat transfer fluids are used for thermal management. PFCs, perfluoroalkyl amine, hydrofluoroether, and perfluoropolyether are commonly used fluorinated chemicals used as heat transfer fluids.[190] They can control the temperature of the wafer during etching, which is an important factor in high aspect ratio hole etching. HFCs are not commonly used as heat transfer fluids. In the

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[181] Sarangan, A., Chapter 5, *Nanofabrication*, in *Fundamentals and Applications of Nanophotonics*, Editor: Haus, J.W., Woodhead Publishing, 2016, pp. 149–184, ISBN 9781782424642. https://doi.org/10.1016/B978-1-78242-464-2.00005-1.

[182] U.S. EPA, 2022, *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2020*. https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2020.

[183] Dhungana, S., Nordell, B. J., *et al.*, Combinatorial survey of fluorinated plasma etching in the silicon-oxygen-carbon-nitrogen-hydrogen system, Journal of Vacuum Science & Technology A, 2016, **34**, 061302. https://doi.org/10.1116/1.4964648.

[184] NAND flash memory is the most common type of memory being used in solid state drives (SSD), smartphones and Universal Serial Bus (USB) memory. NAND is not an acronym; the term drives from an operator 'and' logic.

[185] Fuji Keizai Corporation, 2020, *Current status and future prospects of the semiconductor materials market in 2020*.

[186] Kondo, Y., Ishikawa, K., Hayashi, T., Miyawaki, Y., Takeda, K., Kondo, H., Sekine, M., Hori, M., Silicon nitride etching performance of CH_2F_2 plasma diluted with argon or kypton, *Jpn. J. Appl. Phys*., 2015, **54**, 040303. DOI 10.7567/JJAP.54.040303.

[187] Yoon, M.Y., Yeom, H.J., Kim, J.H, *et al.*, Discharge physics and atomic layer etching in Ar/C_4F_6 inductively coupled plasmas with a radio frequency bias, *Physics of Plasmas*, 2021, **28**, 063504. https://doi.org/10.1063/5.0047811.

[188] Sung-Woon Cho, *et al*., Reduction in the Diameter of Contact Holes with a High Anisotropy and Aspect Ratio, *ECS J. Solid State Sci. Technol*., 2015, **4**(7), P226. DOI 10.1149/2.0161507jss.

[189] IPCC, 2019, *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories.* Calvo Buendia, E., Tanabe, K., Kranjc, A., Baasansuren, J., Fukuda, M., Ngarize S., Osako, A., Pyrozhenko, Y., Shermanau, P. and Federici, S. (eds). Published: IPCC, Switzerland, 2019.

[190] U.S. EPA, 2016, *Uses and Emissions of Liquid PFC Heat Transfer Fluids from the Electronics Sector*. https://www.epa.gov/sites/default/files/2016-02/documents/pfc_heat_tranfer_fluid_emission.pdf.

United States, HFCs (not including HFEs and perfluorotrialkylamine) account for 0.33% of heat transfer fluid emissions (GWP-weighted) and the highest emitted HFCs as heat transfer fluids are HFC-125, HFC-134a and HFC-143a.[191]

Some parties appear to treat production and consumption of HFCs in semiconductor manufacturing in the same way as other emissive uses; while other parties appear to treat the production and consumption of HFCs in semiconductor manufacturing as feedstock use, excluding the portion that results in emissions of HFCs in the process.

Parties may wish to consider how to treat HFC production and consumption for semiconductor uses for the purposes of Article 7 data reporting.

5.1.1 Consumption of controlled substances

Global consumption of HFCs for electronics manufacturing has increased significantly since 2013. According to the World Semiconductor Council (WSC), since 2013, the average annual growth rate of HFC-23 (CHF_3) consumption for semiconductor manufacturing (etching and chamber cleaning) has been approximately 15%, from a total global consumption of 277 tonnes in 2013 to 720 tonnes in 2020. Historically, HFC-41 (CH_3F) and HFC-32 (CH_2F_2) have been consumed in much smaller quantities.[192,193] For example, in 2019 in the United States, HFC-41 and HFC-32 only accounted for 9% and 6%,[194] respectively, of the HFCs consumed for etching and cleaning in semiconductor manufacturing. However, global consumption of “new” gases (defined by the WSC as including HFC-32, C_5F_8, C_4F_8O and C_4F_6) reported by the WSC had an annual average growth rate of 41% since 2013 (when total consumption was less than 160 tonnes per year).[195] Data reported by the WSC did not include HFC-41. In 2020, the consumption of “new” gases (HFC-32, C_5F_8, C_4F_8O and C_4F_6) totalled more than 1,000 tonnes per year. Disaggregated data for HFC-32 alone was not available; however, based on available gas consumption patterns[196,197] and market data[198], HFC-32 is expected to be a significant portion (at least one-third, ~300 tonnes, and likely greater than 50%, 500 tonnes) of the total in 2020. Consumption of all three HFCs are expected to increase with increasing semiconductor production and the increasing complexity of semiconductor devices. The global

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[191] U.S. EPA, 2022, Greenhouse Gas Reporting Program (GHGRP) Envirofacts, Subpart I: Electronics Manufacture. https://enviro.epa.gov/query-builder/ghg. Accessed September 2022.

[192] World Semiconductor Council, 2014, *Annex III: Revision of 2013 World Semiconductor Council (WSC) PFC Data*, November 5, 2014, and corrections received via private communication. http://www.semiconductorcouncil.org/public-documents/joint-statements-from-prior-wsc-meetings/.

[193] U.S. EPA, 2021, prepared by ICF, *Market Characterization of the U.S. Semiconductor Industry*, EPA-hq-oar-2021-0044-0002, August 2021. https://www.epa.gov/sites/default/files/2021-03/documents/epa-hq-oar-2021-0044-0002_attachment_3-semiconductors.pdf.

[194] Ibid., U.S. EPA, 2021.

[195] World Semiconductor Council, 2014, *Annex III: Revision of 2013 World Semiconductor Council (WSC) PFC Data*, November 5, 2014, and corrections received via private communication. http://www.semiconductorcouncil.org/public-documents/joint-statements-from-prior-wsc-meetings/.

[196] SIA, 2012, *Report to EPA on Etch Factor Proposal for Fab GHG Emissions Reporting*, February 28, 2012. https://www.regulations.gov/document/EPA-HQ-OAR-2011-0028-0074.

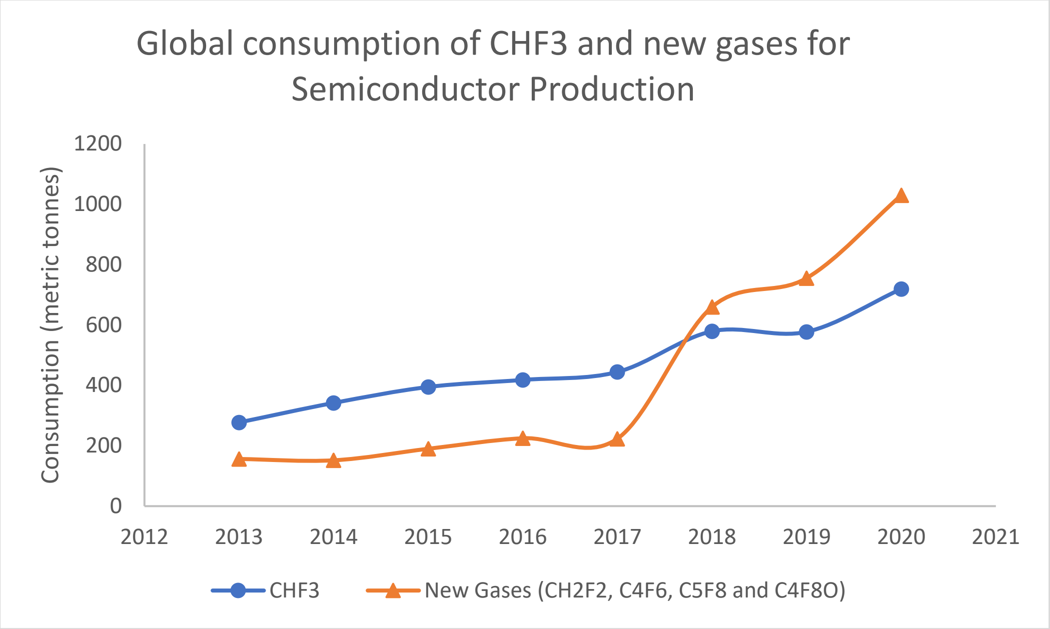
[197] U.S. EPA, 2021, prepared by ICF, *Market Characterization of the U.S. Semiconductor Industry*, EPA-hq-oar-2021-0044-0002, August 2021. https://www.epa.gov/sites/default/files/2021-03/documents/epa-hq-oar-2021-0044-0002_attachment_3-semiconductors.pdf.

[198] Fuji Keizai Corporation, 2020, *Current status and future prospects of the semiconductor materials market in 2020*.

consumption of HFC-32 and HFC-41 are also expected to continue to increase at a high rate due to their use in high aspect hole etching (e.g., used in manufacturing DRAM, NAND).[199,200]

There was insufficient data available to estimate global HFC consumption for use as heat transfer fluids.

Figure 5.1 Global consumption of HFC-23 and "new" gases (HFC-32, C_5F_8, C_4F_8O and C_4F_6) (tonnes)[201]



World Semiconductor Council (based on annual reports and corrections received via private communication.[202]

HFCs are consumed in regions that manufacture semiconductors, with the highest consumption in the regions of East Asia and North America. HFCs are also consumed for semiconductor production in the regions of China mainland, Southeast Asia and Europe.[203]

5.1.2 Emissions of controlled substances

Emissions from electronics manufacturing consist of the unutilised portion of the process gas and gases formed as a by-product during the process from other process gases. Some facilities have implemented emissions control technologies that significantly reduce emissions of HFCs and other fluorinated gases during semiconductor manufacturing.

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[199] Ibid., Fuji Keizai Corporation, 2020.

[200] Kondo, Y., Ishikawa, K., Hayashi, T., Miyawaki, Y., Takeda, K., Kondo, H., Sekine, M., Hori, M., Silicon nitride etching performance of CH_2F_2 plasma diluted with argon or kypton, *Jpn. J. Appl. Phys*., 2015, **54**, 040303. DOI 10.7567/JJAP.54.040303.

[201] Excludes HFC-41.

[202] Consumption as reported by the World Semiconductor Council (based on published reports and corrections received via private communication). WSC members account for the vast majority of semiconductor manufacturers and consumption by WSC members is expected to be approximately equal to global consumption.

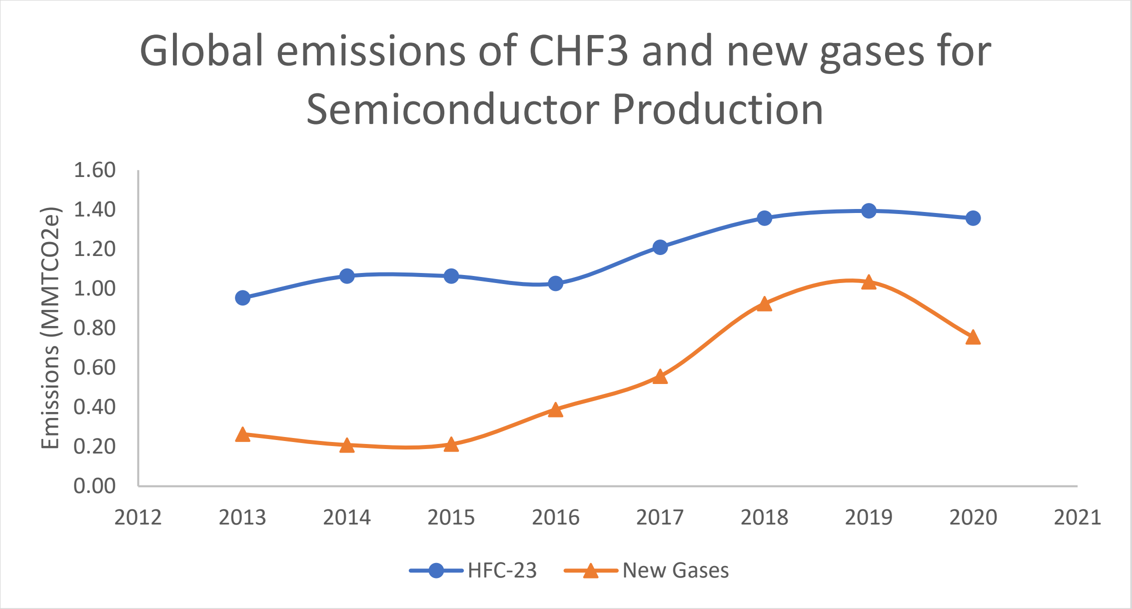
[203] Fuji Keizai Corporation, 2020, *Current status and future prospects of the semiconductor materials market in 2020.*

In the 2019 IPCC Refinement[204], the default emission factor [205] for HFCs used in plasma etching or chamber cleaning in semiconductor manufacturing ranged from 0.13 to 0.7, depending on the gas and wafer size.

HFCs can also be produced as by-products from other process gases. HFC-23, HFC-32 and HFC-41 are all commonly produced as by-products during the etch process when fluorinated gases are used as the etchant. Out of the HFCs, HFC-23 is the by-product generally produced in the largest quantities (with by-product emission factors ranging from 0.002 to 0.03), but HFC-41 and HFC-32 are also produced as by-products in small quantities (with by-product emission factors ranging from <0.001 to 0.014) during plasma etching.[206] There was insufficient data available to estimate global HFC emissions from use as HTFs.

Emissions of HFC-23 from semiconductor manufacturing have increased from 0.9 MMTCO$_2$e in 2013 to 1.4 MMTCO$_2$e in 2020, with an average annual growth rate of 6%.[207] This is a much smaller growth rate than the growth rate in consumption (see section 5.1.1), indicating an increase in the percentage of HFC-23 destroyed by abatement systems. Disaggregate emissions data for HFC-32 was not available.

Figure 5.2 Global emissions of HFC-23 and "new" gases (HFC-32, C_5F_8, C_4F_8O and C_4F_6) (tonnes)[208]



World Semiconductor Council (based on annual reports and corrections received via private communication.[209]

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[204] IPCC, 2019, *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories.* Calvo Buendia, E., Tanabe, K., Kranjc, A., Baasansuren, J., Fukuda, M., Ngarize S., Osako, A., Pyrozhenko, Y., Shermanau, P. and Federici, S. (eds). Published: IPCC, Switzerland.

[205] Without abatement.

[206] Ibid., IPCC, 2019.

[207] Data compiled from the Joint Statements of the World Semiconductor Council published between 2014 and 2021 and corrections received via private communication. http://www.semiconductorcouncil.org/public-documents/joint-statements-from-prior-wsc-meetings/.

[208] Excludes HFC-41.

[209] Emissions as reported by the World Semiconductor Council (based on published reports available at http://www.semiconductorcouncil.org/public-documents/joint-statements-from-prior-wsc-meetings/ and corrections received

In the 2019 IPCC Refinement, emission factors and by-product emission factors for semiconductor manufacturing were updated. It is expected that the update will increase reported emissions of HFC-32 (CH_2F_2), reflecting the inclusion of more HFC by-product emission factors and a higher etch emission factor (due to additional data becoming newly available) compared with the 2006 IPCC Guidelines.

5.1.2.1 Emissions from HFC purification

Raw HFCs produced by suppliers typically have purity lower than the high-grade purity required in electronics manufacturing (99.9999%). The raw product is then passed through one or more purifiers to achieve the required high-grade purity. The purification process results in emission losses, with estimates in the range of 5-10%.[210]

5.1.3 Future demand for controlled substances

HFC use in semiconductor manufacturing is expected to increase with increases in semiconductor production and increases in device complexity. It is difficult to replace fluorinated gases with non-fluorinated gases as fluorinated gases are needed to etch surfaces such as silicon wafers, SiO and SiN thin films. According the WSC, the annual growth rate of HFC-23 consumption since 2013 has been 14%.[211] Consumption of HFC-23 is expected to continue to increase as semiconductor production continues to increase. Consumption of "new" gases, including but not limited to HFC-32, have increased significantly since 2017, when consumption was still reported to be around 200 tonnes per year, with consumption in 2020 totalling more than 1,000 tonnes per year. Consumption of both HFC-32 and HFC-41 is expected to continue to increase at a rapid pace due to their use in high aspect hole etching (e.g., used in manufacturing DRAM, NAND).[212,213]

Future demand for HFCs used as heat transfer fluids is expected to remain limited or decrease, as countries move to phase out non-essential uses of HFCs.

5.2 Other electronics manufacturing uses of controlled substances

Like semiconductor manufacturing, etching and chamber cleaning are the key processes that use fluorinated chemicals in other electronics manufacturing, including flat panel display (FPD), photovoltaics (PV) and microelectromechanical systems (MEMS).

The FPD industry primarily uses PFCs, such as PFC-14 (CF_4) and PFC-c318 (cyclic C_4F_8), SF_6, NF_3 and HFC-23.[214] HFC-23 is used in plasma etching.

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via private communication). WSC members account for the vast majority of semiconductor manufacturers and emissions by WSC members is expected to be approximately equal to global emissions.

[210] U.S. EPA, 2021, prepared by ICF, *Market Characterization of the U.S. Semiconductor Industry*, EPA-hq-oar-2021-0044-0002, August 2021. https://www.epa.gov/sites/default/files/2021-03/documents/epa-hq-oar-2021-0044-0002_attachment_3-semiconductors.pdf.

[211] Data compiled from the Joint Statements of the World Semiconductor Council published between 2014 and 2021 and corrections received via private communication. Available at http://www.semiconductorcouncil.org/public-documents/joint-statements-from-prior-wsc-meetings/

[212] Fuji Keizai Corporation, 2020, *Current status and future prospects of the semiconductor materials market in 2020*.

[213] Kondo, Y., Ishikawa, K., Hayashi, T., Miyawaki, Y., Takeda, K., Kondo, H., Sekine, M., Hori, M., Silicon nitride etching performance of CH_2F_2 plasma diluted with argon or kypton, *Jpn. J. Appl. Phys*., 2015, **54**, 040303. DOI 10.7567/JJAP.54.040303.

[214] World LCD Industry Cooperation Committee, 2011, *WLICC WG1 Activity Report on the 2010 FCs Emissions Reduction*, November 10, 2011, Tokyo. https://home.jeita.or.jp/device/committee/kankyou/pdf/20111110WLICG_e.pdf.

Fluorinated gases have been used in photovoltaic manufacturing for texturing, phosphorus silicate glass removal (PSG), edge isolation and chamber cleaning.[215] However, HFCs are not commonly used for this purpose. In the United States, only one facility reported emissions of HFC-23 that implied consumption of HFC-23 for PV manufacturing in 2011 and 2012; another facility that reported fluorinated GHG emissions to the U.S. Environmental Protection Agency reported no HFC consumption but a small amount of HFC-23 emissions as a by-product.[216] Since consumption of HFCs by photovoltaic manufacturers are expected to minimal, their consumption and emissions are not further addressed in this assessment.

5.2.1 Consumption of controlled substances

Although emissions of HFCs from flat panel display manufacturing have been surveyed in a series of flat panel display supplier profiles developed by the U.S. EPA[217], there is limited available information on HFC consumption by the flat panel display industry. Not all companies reported their emissions to U.S. EPA; however, if reported emissions of HFCs were extrapolated to the entire global industry using the reporting companies share of global production, global HFC emissions from the flat panel display manufacturing industry can be estimated to be approximately 0.12 MMTCO$_2$e per year on average. Based on default emission factors in the 2006 IPCC Guidelines[218], and assuming that all the HFC emissions are HFC-23 and from consumption (not formed as by-products), global consumption would be around 30–80 tonnes per year. However, this is likely an underestimate, with global consumption of HFC-23 for LCD manufacturing likely to be several hundred tonnes per year, as many flat panel display manufacturers abate fluorinated greenhouse gases, which is not taken into account in the above estimate of 30–80 tonnes.

Emissions of HFC-23 are reported from MEMS manufacturing in the United States, implying HFC-23 consumption[219] because there are no HFC-23 by-product emission factors for MEMs in the emission factors companies are required to use when reporting to U.S. EPA. There is insufficient global data on consumption of HFCs for MEMS manufacture to develop an estimate of global consumption.

5.2.2 Emissions of controlled substances

Emissions of HFCs from flat panel display manufacturing have been surveyed in a series of flat panel display supplier profiles developed by the U.S. EPA.[220] Although not all flat panel display manufacturers reported, emissions can be estimated by extrapolating the total reported emissions to the remaining manufacturers. From this data, we estimate that global emissions of HFCs from display manufacturing have been approximately 0.1–0.2 MMTCO$_2$e per year.

There is insufficient global data on consumption of HFCs for MEMS manufacture to develop an estimate of global consumption. Emissions from MEMS manufacture are often reported to the

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[215] M.J. de Wild-Scholten, *et al.*, *Fluorinated Greenhouse Gases in Photovoltaic Module Manufacturing: Potential Emissions and Abatement Strategies*, 22nd European Photovoltaic Solar Energy Conference, Fiera Milano, Italy, September 3–7, 2007, Version: 30 August 2007.

[216] U.S. EPA, 2022, Greenhouse Gas Reporting Program (GHGRP) Envirofacts. Subpart I: Electronics Manufacture. http://www.epa.gov/enviro/facts/ghg/search.html. Accessed September 2022.

[217] U.S. EPA, 2022, F-GHG Emission Reduction Efforts: Supplier Profiles for FY2011–FY2019. https://www.epa.gov/climateleadership/sector-spotlight-electronics. Accessed December 2022.

[218] IPCC, 2006, *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. The National Greenhouse Gas Inventories Programme, The Intergovernmental Panel on Climate Change. [H.S. Eggleston, L. Buendia, K. Miwa, T. Ngara, and K. Tanabe (eds.)]. Hayama, Kanagawa, Japan.

[219] U.S. EPA, 2022, Greenhouse Gas Reporting Program (GHGRP) Envirofacts. Subpart I: Electronics Manufacture. http://www.epa.gov/enviro/facts/ghg/search.html. Accessed September 2022.

[220] U.S. EPA, 2022, F-GHG Emission Reduction Efforts: Supplier Profiles for FY2011–FY2019. https://www.epa.gov/climateleadership/sector-spotlight-electronics. Accessed December 2022.

UNFCCC aggregated with emissions from semiconductor manufacture, making it challenging to develop a global estimate of emissions of HFCs from MEMS manufacture alone.

5.3 Technical and economic assessment of semiconductor and electronics manufacturing uses of controlled substances and their alternatives

An assessment follows of the technical and economic feasibility of the alternatives to HFC use in semiconductor and electronics manufacturing. The assessment criteria referenced in decision XXVIII/2 have been slightly modified to remain relevant to this application, using the following criteria:

i. Commercially available
ii. Technically proven
iii. Environmentally sound
iv. Economically viable and cost effective
v. Safe to use in industrial applications considering flammability and toxicity issues
vi. Easy to use and maintain

“Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization” has been adjusted to *safe to use in industrial applications considering flammability and toxicity issues*. “Easy to service and maintain” has been adjusted to *easy to use and maintain*. Technically proven is interpreted to mean the technology has been proven to work for that application, or an aspect of it; not necessarily commercialised for that application

Table 5.5 Technical and economic assessment of controlled substances and alternatives for etching, chamber cleaning, and heat transfer fluids

Controlled Substances and Alternatives	Gas Category	100-year GWP	Alternative characteristics	Commercially available	Technically proven	Environmentally sound	Economically viable	Safe to use	Easy to use
Semiconductor Manufacturing									
Plasma Etching and Chamber Cleaning									
HFC-23 (CHF_3)	Saturated HFC with 2 or fewer C-H bonds	14,800	Used for etching. HFCs are minimally used for chamber cleaning. Etch SiO_2 and SiNx, sidewall passivation.	🟩	🟩	🟥	🟩	🟩	🟩
HFC-32 (CH_2F_2)	Saturated HFC with 2 or fewer C-H bonds	675	Used for etching. HFCs are minimally used for chamber cleaning. Etch SiO_2 and SiNx, sidewall passivation; good for high-aspect hole etching.	🟩	🟩	🟥	🟩	🟩	🟩
HFC-41 (CH_3F)	Saturated HFC with 3 or more C-H bonds	92	Used for etching, not known to be used for chamber cleaning. Good for high-aspect hole etching.	🟩	🟩	🟨	🟩	🟩	🟩
Alternatives									
SF_6	Fully fluorinated GHG	22,800	Used for etching and chamber cleaning. Etch Si, SiO_2, SiNx, Bosch process.	🟩	🟩	🟥	🟩	🟩	🟩
NF_3	Fully fluorinated GHG	17,200	Used for etching and chamber cleaning, including remote plasma. Etch Si, Si_3N_4.	🟩	🟩	🟥	🟩	🟩	🟩
Saturated PFCs (CF_4, C_2F_6, c-C_4F_8)	Fully fluorinated GHGs	7,390–12,200	Used for etching and chamber cleaning. Etch Si, TiN, SiO_2, SiNx, Organics, Sidewall passivation. c-C_4F_8 is good for high-aspect hole etching. More difficult to abate, esp. CF_4.	🟩	🟩	🟥	🟩	🟩	🟩
Unsaturated PFCs (C_4F_6, C_5F_8)	Unsaturated PFCs	<2	Used for etching. Good for high-aspect hole etching. Not known to be used for chamber cleaning.	🟩	🟩	🟩	🟩	🟩	🟩
PFC-1216 (C_3F_6)	Unsaturated PFC	<1	Studied as a possible etchant for SiO_2	🟩	🟨	🟩	🟩	🟩	🟩

Hexafluoroisobutylene (HFIB) (CH_2=C(CF_3)$_2$)	Unsaturated HFC	~3[221]	Can be used for etching of trench holes, trench gates, etc. for Si containing substrates. Not known to be used.	🟨	🟥	🟩	🟨	🟩	🟩
HFO-1336mzz(E) (CF_3-CH=CH-CF_3)	Unsaturated HFC	18[222]	Studied as a replacement for CF4 in semiconductor etching; not technically proven.	🟩	🟥	🟩	🟨	🟩	🟩
Trifluoroiodomethane (CF_3I)	Saturated halomethane	N/A	Used for etching of SiO_2 and SiNx	🟨	🟨	🟩	🟨	🟨	🟨
Chlorine trifluoride (ClF_3)	Interhalogen	N/A	Cleaning for Low Pressure Chemical Vapor Deposition (LPCVD) chambers	🟩	🟨	🟩	🟨	🟥	🟥
Carbonyl Sulphide (O=C=S)	-	27[223]	Etching for NAND and DRAM	🟨	🟨	🟩	🟨	🟥	🟥
F_2	Molecular Fluorine	N/A	Very aggressive, therefore more suitable for chamber cleaning. Not known to be used for etching (not technically proven; etching with F2 generally leaves a rough and pitted surface).	🟩	🟨	🟨	🟩	🟨	🟨

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[221] Papadimitriou, V.C., Spitieri, C.S., Papagiannakopoulos, P., *et al.*, Atmospheric chemistry of (CF 3) 2 CQ Q QCH 2 : OH radicals, Cl atoms and O 3 rate coefficients, oxidation end-products and IR spectra †, *Physical Chemistry Chemical Physics*, 2015, **17**(38), pp. 25607–25620. https://doi.org/10.1039/C5CP03840E.

[222] Gao, Z., *et al.*, Investigation on insulation properties of HFO-1336mzz(E) and N_2/CO_2 mixtures as SF_6 substitutes in gas-insulated electrical applications, *High Voltage*, 2021, 1–11. https://doi.org/10.1049/hve2.12181.

[223] Bruhl, C., Lelieveld, J., Crutzen1, P. J., Tost, H., The role of carbonyl sulphide as a source of stratospheric sulphate aerosol and its impact on climate, *Atmos. Chem. Phys*., 2012, **12**, 1239–1253.

Controlled Substances and Alternatives	**Gas Category**	**100-year GWP**	**Alternative characteristics**	**Commercially available**	**Technically proven**	**Environmentally sound**	**Economically viable**	**Safe to use**	**Easy to use**
Semiconductor Manufacturing									
Heat Transfer Fluids									
HFC-134a	Saturated HFC	1,430	HFCs typically have smaller temperature ranges than other HTFs	🟩	🟨	🟥	🟩	🟩	🟩
HFC-125	Saturated HFC	3,500	HFCs typically have smaller temperature ranges than other HTFs	🟩	🟨	🟥	🟩	🟩	🟩
HFC-143a	Saturated HFC	4,470	HFCs typically have smaller temperature ranges than other HTFs	🟩	🟨	🟥	🟩	🟨	🟩
HFC-245fa	Saturated HFC	1,030	HFCs typically have smaller temperature ranges than other HTFs	🟩	🟨	🟥	🟩	🟩	🟩
HFC-236fa	Saturated HFC	9,810	HFCs typically have smaller temperature ranges than other HTFs	🟩	🟨	🟥	🟩	🟩	🟩
HFC-245fa	Saturated HFC	1,030	HFCs typically have smaller temperature ranges than other HTFs	🟩	🟨	🟥	🟩	🟩	🟩
HFC-32	Saturated HFC	675	HFCs typically have smaller temperature ranges than other HTFs	🟩	🟨	🟥	🟩	🟨	🟩
HFC-43-10mee	Saturated HFC	1,640	HFCs typically have smaller temperature ranges than other HTFs	🟩	🟨	🟥	🟩	🟩	🟩
HFC-152a	Saturated HFC	124	HFCs typically have smaller temperature ranges than other HTFs	🟩	🟨	🟨	🟩	🟨	🟩
Alternatives									
Saturated PFCs	Saturated perfluoroalkanes and perfluorotrialkylamines $(C_nF_{2n+1})_3N$	9,300	Wide temperature range, high dielectric strength, high GWP.	🟩	🟩	🟥	🟩	🟩	🟩
Perfluoropolyethers (PFPE)	Saturated perfluoropolyethers $CF_3[O\text{-}CF(CF_3)CF_2]_m(OCF_2)_nOCF_3$	10,300	Wide temperature range, high dielectric strength, high GWP.	🟩	🟩	🟥	🟩	🟩	🟩
HFE	Saturated hydrofluoroethers $C_nF_{2n+1}OC_mH_{2m+1}$	59–297	Wide temperature range, dielectric strength not as high as PFC or PFPE.	🟩	🟩	🟩	🟩	🟩	🟩

Controlled Substances and Alternatives	**Gas Category**	**100-year GWP**	**Alternative characteristics**	**Commercially available**	**Technically proven**	**Environmentally sound**	**Economically viable**	**Safe to use**	**Easy to use**
Flat Panel Display									
HFC-23 (CHF_3)	Saturated HFC with 2 or fewer C-H bonds	14,800	HFC-23 can be used in plasma etching.	🟩	🟩	🟥	🟩	🟩	🟩
Alternatives									
Saturated PFCs (CF_4, C_2F_6, c-C_4F_8)	Fully fluorinated GHGs	7,390–12,200	Saturated PFCs are used for etching and chamber cleaning.	🟩	🟩	🟥	🟩	🟩	🟩
SF_6	Fully fluorinated GHG	22,800	SF_6 is used for etching and chamber cleaning.	🟩	🟩	🟥	🟩	🟩	🟩
NF_3	Fully fluorinated GHG	17,200	NF_3 is used for etching and chamber cleaning.	🟩	🟩	🟥	🟩	🟩	🟩
F_2	Molecular Fluorine	N/A	Used for chamber cleaning, not known to be used for etching.	🟩	🟨	🟨	🟩	🟨	🟨

Controlled Substances and Alternatives	**Gas Category**	**100-year GWP**	**Characteristics**	**Commercially available**	**Technically proven**	**Environmentally sound**	**Economically viable**	**Safe to use**	**Easy to use**
Photovoltaics									
HFC-23 (CHF_3)	Saturated HFC with 2 or fewer C-H bonds	14,800	HFC-23 is used in plasma etching, although is not commonly used.	🟩	🟩	🟥	🟩	🟩	🟩
Alternatives									
Saturated PFCs (CF_4, C_2F_6, c-C_4F_8)	Fully fluorinated GHG	7,390–12,200	Saturated PFCs are used for etching and chamber cleaning.	🟩	🟩	🟥	🟩	🟩	🟩
SF_6	Fully fluorinated GHG	22,800	SF_6 is used for etching and chamber cleaning.	🟩	🟩	🟥	🟩	🟩	🟩
NF_3	Fully fluorinated GHG	17,200	NF_3 is used for etching and chamber cleaning.	🟩	🟩	🟥	🟩	🟩	🟩
F_2	Molecular Fluorine	N/A	Used for chamber cleaning, not known to be used for etching.	🟩	🟨	🟨	🟩	🟨	🟨

🟩 Yes or More acceptable; 🟨 Not always or Less acceptable; 🟥 No or Unacceptable.

Commercial availability and accessibility— All alternatives are commercially available and accessible for their specific uses.

Technically proven— F_2 is a suitable replacement for CVD chamber cleaning in semiconductor manufacturing. It is however very aggressive (low selectivity and high etch rates) and not known to be used for etching. Some flat panel display manufacturers have piloted the use of F_2 to replace NF_3 in remote plasma chamber cleaning processes.[224] F_2 has also been explored as an alternative to SF_6 in photovoltaic manufacturing.[225]

HFCs, including HFC-134a, have smaller temperature ranges as heat transfer fluids compared with alternatives. Most semiconductor heat transfer processes require the material to operate over a relatively large temperature range, which is better accomplished with a liquid.

Environmentally sound— Alternatives to HFC use in semiconductor manufacturing include other fluorinated gases, such as saturated PFCs, SF_6 and NF_3, many of which have higher GWPs and lower utilization rates than HFCs, such as HFC-32 and HFC-41. Emissions from electronics manufacturing include the unutilised portion of the process gas and gases formed as a by-product during the process from other process gases. Abatement and scrubbing of process emissions is considered best practice. Pollutant emissions are required to meet local regulatory standards.

For heat transfer fluids, the HFE is relatively the best available option environmentally compared with HFCs, including HFC-134a, and the higher GWP alternatives; however, the HFE may not always be suitable due to its dielectric properties.

Economically viable and cost effective—All alternatives are economically viable and cost effective.

Safe to use in industrial applications considering flammability and toxicity issues—Whether HFCs or their alternatives, all chemicals require appropriate storage and handling. Abatement and scrubbing of process emissions is considered best practice. Pollutant emissions would be required to meet local regulatory standards.

Molecular fluorine (F_2) has challenges associated with transport, storage and use due to extremely high reactivity and oxidizing capability, which require the use of special safety precautions. Safe installation and operation procedures are required due to corrosivity and toxicity. For example, special mass flow controllers and valves are required in addition to special passivation process of the process gas lines. F_2 can be supplied in cylinders mixed with nitrogen or produced on-site, which would eliminate any transportation challenges. [226]

Easy to use and maintain— Molecular fluorine (F_2) has challenges associated with transport, storage and use. Safe installation and operation procedures are required due to corrosivity and toxicity. F_2 can be supplied in cylinders mixed with nitrogen or produced on-site, which would eliminate any transportation challenges.[227]

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[224] U.S. EPA, 2013, *F-GHG Emissions Reduction Efforts: Flat Panel Display Supplier Profiles*, May 2013, https://www.epa.gov/sites/default/files/2015-07/documents/supplier_profiles_2013.pdf. Accessed September 2022.

[225] M.J. de Wild-Scholten, *et al.*, *Fluorinated Greenhouse Gases in Photovoltaic Module Manufacturing: Potential Emissions and Abatement Strategies*, 22nd European Photovoltaic Solar Energy Conference, Fiera Milano, Italy, September 3–7, 2007, Version: 30 August 2007.

[226] Ibid., de Wild-Scholten, *et al.*, 2007.

[227] Ibid., de Wild-Scholten, *et al.*, 2007.

5.4 Mitigation of emissions of controlled substances

The electronics industry has made efforts to reduce emissions through the following:

- Process optimisation to reduce usage of fluorinated gases— the semiconductor industry has used process optimisation to decrease emissions of PFCs over time, largely by replacing PFC-116 (C_2F_6) clean processes with NF_3 remote clean processes.[228] Remote plasma cleans with NF_3 utilise a much larger percentage of the gas (>97% vs. 45%).[229] Similar examples involving HFCs are not known.

- Gas substitution— substituting gases with lower GWP values, gases that decompose during etching and do not contribute to global warming (i.e., gases with high utilisation rates), or gases that decompose more easily in the abatement equipment (gases with high abatement efficiency).

- Installation of abatement equipment.

HFCs are relatively easy to destroy with abatement equipment designed to abate fluorinated chemicals. In the 2019 Refinement to the 2006 IPCC Guidelines[230], the default destruction and removal efficiency (DRE) values for HFCs ranged from 95–98%, with most HFCs having a default of 98%. In comparison, the default DRE for CF_4 is only 89%. Space constraints can be a limiting factor for increasing abatement at older fabrication facilities with limited floor or subfab[231] space.[232]

Reclamation, recycling, and reuse of gases is not practiced by the electronics industry. The electronics industry requires gases of extremely high purity, much higher than those required by other industries, such as refrigeration, that use HFCs.[233] Additionally, some HFCs, such as, HFC-41, are not used in the refrigeration industry and not available as reclaimed gas.[234] Although it is possible to capture unreacted process gases for recycling and reuse, the reclamation, recycling and reuse of fluorinated gases used in semiconductor manufacturing is not currently economically viable. However, it could be appropriate where there are high volume emissions of a single, relatively clean, fluorinated chemical not used in plasma processing.[235] Plasma processes result in multicomponent gas streams that contain

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[228] Beu. L., 2005, *Reduction of Perfluorocompound (PFC) Emissions: 2005 State-of the-Technology Report,* International SEMATECH Manufacturing Initiative, Technology Transfer #05104693A-ENG (2005). https://www.epa.gov/sites/default/files/2016-02/documents/final_tt_report.pdf. Accessed December 2022.

[229] IPCC, 2019, *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories.* Calvo Buendia, E., Tanabe, K., Kranjc, A., Baasansuren, J., Fukuda, M., Ngarize S., Osako, A., Pyrozhenko, Y., Shermanau, P. and Federici, S. (eds). Published: IPCC, Switzerland.

[230] Ibid., IPCC, 2019.

[231] The subfab is the area located underneath the processing floor of the fab that contains support equipment (pumps, etc.) for processing tools.

[232] Beu. L., 2005, *Reduction of Perfluorocompound (PFC) Emissions: 2005 State-of the-Technology Report*, International SEMATECH Manufacturing Initiative, Technology Transfer #05104693A-ENG (2005). https://www.epa.gov/sites/default/files/2016-02/documents/final_tt_report.pdf. Accessed December 2022.

[233] U.S. EPA, 2021, prepared by ICF, *Market Characterization of the U.S. Semiconductor Industry*, EPA-hq-oar-2021-0044-0002, August 2021. https://www.epa.gov/sites/default/files/2021-03/documents/epa-hq-oar-2021-0044-0002_attachment_3-semiconductors.pdf. Accessed December 2022.

[234] Ibid., U.S. EPA, 2021.

[235] Beu. L., 2005, *Reduction of Perfluorocompound (PFC) Emissions: 2005 State-of the-Technology Report*, International SEMATECH Manufacturing Initiative, Technology Transfer #05104693A-ENG (2005). https://www.epa.gov/sites/default/files/2016-02/documents/final_tt_report.pdf. Accessed December 2022.

unused process gas, by-products produced during the process and N_2 purging gas.[236] On-site recycling of SF_6 has however been used in some PV manufacturing fabrication facilities.[237]

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[236] M.J. de Wild-Scholten, *et al.*, *Fluorinated Greenhouse Gases in Photovoltaic Module Manufacturing: Potential Emissions and Abatement Strategies*, 22nd European Photovoltaic Solar Energy Conference, Fiera Milano, Italy, September 3–7, 2007, Version: 30 August 2007.

[237] Ibid., de Wild-Scholten, *et al.,* 2007.

6 Magnesium Production

6.1 Magnesium production uses of controlled substances

Cover gases are used in magnesium production, casting processes, and recycling to prevent oxidation and combustion of molten magnesium. Without protection, molten magnesium will oxidise and ignite in the presence of air and form magnesium oxide (MgO) deposits that greatly reduce the quality and strength of the final product. An effective cover gas will modify and stabilise the MgO surface film to form a protective layer that prevents further oxidation.

Sulfur hexafluoride (SF_6) is the most widely used cover gas. A cover gas of dilute SF_6 in dry air and/or carbon dioxide protects the melt from oxidation and potential fires. SF_6 widely replaced sulfur dioxide (SO_2) and salt fluxes in the 1970s and improved operator health and safety and equipment life.[238] However, SF_6 has a very high GWP of 22,800.

Several gases with lower GWPs have been identified as alternatives to SF_6, including HFC-134a (GWP of 1,430) and a fluoroketone (GWP of 0.1). HFC-134a has been shown to have adequate melt protection; however, careful selection of the diluent gas and concentration is required to prevent damaging corrosion.[239,240] Both HFC-134a and the fluoroketone are reported as being used by the industry as a cover gas.[241] More recently, researchers have begun exploring the addition of small amounts of unique alloying elements (e.g., Be, Al, Ca) to enhance the oxidation resistance of the magnesium alloy and possibly reduce the need for a cover gas.[242]

The majority (80–90%) of primary magnesium production occurs in China, followed by the United States, Israel, and Brazil.[243]

6.2 Consumption of controlled substances

The quantity of consumption of controlled substances can be considered the same as emissions, for which estimates are provided below.

6.3 Emissions of controlled substances

Emissions from magnesium production is generally estimated to be equal to consumption.[244] However, a small portion of the gas is likely consumed/transformed and the amount destroyed is

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[238] Ricketts, N. J., Esdaile, R., Ramakrishnan, S., 2002, *Environmental Implications of using HFC-134a as a replacement for sulphur hexafluoride in the magnesium industry*, International Conference on SF_6 and the Environment, 2002.

[239] Won Ha, Young-Jig Kim, Effects of cover gases on melt protection of Mg alloys, *Journal of Alloys and Compounds,* 2006, **422**, 208–213.

[240] Ricketts, N. J., Esdaile, R., Ramakrishnan, S., 2002, *Environmental Implications of using HFC-134a as a replacement for sulphur hexafluoride in the magnesium industry*, International Conference on SF_6 and the Environment, 2002.

[241] U.S. EPA, 2022, EPA Greenhouse Gas Reporting Program (GHGRP) Envirofacts. Subpart I: Electronics Manufacture. http://www.epa.gov/enviro/facts/ghg/search.html. Accessed September 2022.

[242] D'Errico, F., Tauber, M., Just, M., 2022, Magnesium Alloys for Sustainable Weight-Saving Approach: A Brief Market Overview, New Trends, and Perspectives, in (Ed.), *Current Trends in Magnesium (Mg) Research*, IntechOpen, April 5, 2022. https://doi.org/10.5772/intechopen.102777.

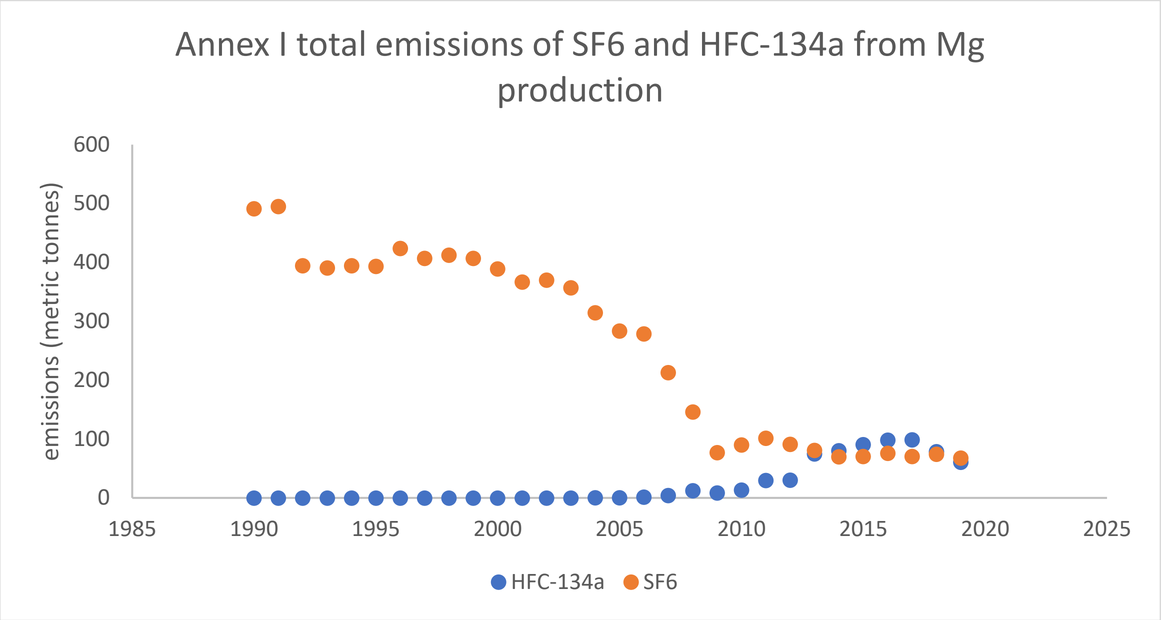
[243] U.S. Geological Survey. (2021, 2020, 2017, 2016, 2015, 2014, 2013, 2012, 2011, 2010, 2009, 2008, 2007, 2006, 2005a, 2003, 2002). Minerals Yearbook: Magnesium Annual Report. U.S. Geological Survey, Reston, VA. http://minerals.usgs.gov/minerals/pubs/commodity/magnesium/index.html#mis.

[244] IPCC, 2019, *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories*, Calvo Buendia, E., Tanabe, K., Kranjc, A., Baasansuren, J., Fukuda, M., Ngarize S., Osako, A., Pyrozhenko, Y., Shermanau, P. and Federici, S. (eds). Published: IPCC, Switzerland.

dependent upon a variety of factors, including gas flow rate, concentration of cover gas, size of reactive magnesium surface, type of carrier gas and furnace charging practices.[245] The main producer of magnesium (China) did not report any SF_6 or HFC emissions from metal production in its most recent Biennial Update Report (which covered 2014 data) for the UNFCCC, indicating that China does not use SF_6 or HFC-134a. Due to cost limitations, SF_6 has not historically been used in China.[246]

According to emissions reported to the UNFCCC[247], emissions (and consumption) of HFC-134a from Annex I reporting countries have increased from 13 tonnes in 2010 to a high of 99 tonnes in 2017. In 2020, emissions were reported to have decreased to 52 tonnes, largely due to a decrease from 71 to 40 tonnes of emissions in the United States. There may be additional consumption and emissions from countries not included in Annex I.

Figure 6.1 Annex I total emissions of SF_6 and HFC-134a from magnesium production (tonnes)



6.4 Future demand for controlled substances

The demand for HFCs and other fluorinated gases is highly dependent on whether facilities in China, the main magnesium producing country, transition to more technologies using fluorinated gases. Historically, SO_2 (gas) or sulfur powder has been the cover material used predominately in China. In the rest of the world, it is expected that there will continue to be a demand for HFC-134a, especially in locations that are phasing out higher GWP SF_6 and are not yet phasing out HFCs.

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[245] Ibid., IPCC, 2019.

[246] Dai, Q., Kelly, J., Elgowainy, A., 2016, *Update of Recycled Content and SF_6 Emissions for Magnesium in the GREET® Model*, Argonne National Laboratory, 2016.

[247] Data downloaded from the GHG Locator Tool, a web-based application showing time-series data of submitted CRF tables by UNFCCC Parties. https://rt.unfccc.int/locator. Accessed July 2022.

6.5 Technical and economic assessment of magnesium production uses of controlled substances and their alternatives

An assessment follows of the technical and economic feasibility of the alternatives to HFC use in magnesium production. The assessment criteria referenced in decision XXVIII/2 have been slightly modified to remain relevant to this application, using the following criteria:

i. Commercially available
ii. Technically proven
iii. Environmentally sound
iv. Economically viable and cost effective
v. Safe to use in industrial applications considering flammability and toxicity issues
vi. Easy to use and maintain

"Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization" has been adjusted to *safe to use in industrial applications considering flammability and toxicity issues*. "Easy to service and maintain" has been adjusted to *easy to use and maintain*. Technically proven is interpreted to mean the technology has been proven to work for that application, or an aspect of it; not necessarily commercialised for that application.

Table 6.1 Technical and economic assessment of uses of controlled substances and their alternatives for magnesium production

Controlled Substances and Alternatives	Gas Category	100-year GWP	Characteristics	Commercially available	Technically proven	Environmentally sound	Economically viable	Safe to use	Easy to use
HFC-134a	HFC	1,430	May not be suitable for all products. Cost may be a factor for using HFC-134a instead of higher priced fluoroketone. HFC-134a is less expensive than SF_6.	🟩	🟩	🟥	🟩	🟩	🟩
Alternatives									
Dodecafluoro-2-methyl-3-pentanone ($(CF_3CF_2C(O)CF(CF_3)_2)$)	Fluoroketone	~1	Suitable with N_2 or CO_2 or with dry-air/N_2 carrier or CO_2 with dry-air. Emits trace C_3F_8. Even distribution of gas is required, which sometimes requires adjustments to equipment with the use of this fluoroketone, as it is more reactive than SF_6.	🟩	🟩	🟩	🟩	🟩	🟩
SF_6	Fully fluorinated GHG	22,800	Less reactive gas. Suitable for most applications. SF_6 is relatively expensive compared to alternatives.	🟩	🟩	🟥	🟧	🟩	🟩
SO_2 (gas)	Non-GHG	0	Requires safety measures due to toxicity and SO_2 scrubber to meet environmental requirements. Corrosion issues.	🟩	🟩	🟥	🟩	🟥	🟩
CO_2	CO_2	1	May not be suitable for all products.	🟩	🟧	🟩	🟩	🟩	🟩
Salt Flux	N/A (Granular cover material)	N/A	Mixture of chlorides (KCl, NaCl, $MgCl_2$), fluorides (CaF_2) and/or oxides (MgO). Negatives: flux entrapment, release of corrosive gases, melt loss; may still need trace HFC-134a to purge moulds.	🟩	🟩	🟧	🟩	🟩	🟩
Vacuum	N/A	N/A	Not technically proven. Technically challenging and requiring significant equipment and process adjustments.	🟧	🟧	🟩	🟩	🟩	🟧
S (powder)	N/A	N/A	Older technology, with technical issues associated with potential contamination of Mg.	🟩	🟩	🟥	🟩	🟥	🟩

🟩 Yes or More acceptable; 🟧 Not always or Less acceptable; 🟥 No or Unacceptable.

Commercial availability and accessibility— Most alternatives are commercially available and accessible. Vacuum technology has not been technically proven and would require significant equipment and process adjustments.

Technically proven—Vacuum technology has not been technically proven and would require significant equipment and process adjustments.

Environmentally sound— SF_6 has a much higher GWPs than HFC-134 and other alternatives (fluoroketone, CO_2). Sulfur dioxide is a toxic air pollutant and contributor to acid rain. HFE has a higher GWP than the fluoroketone. Salt flux is less environmentally sound due to the release of corrosive gases and may still require trace HFC-134a to purge moulds.[248] The use of sulfur produces emissions of sulfur dioxide, which is a toxic air pollutant.

Economically viable and cost effective— SF_6 is relatively expensive compared with alternatives. The operating costs for other alternatives are likely to be lower than SF_6. Technologies, such as vacuum, or using sulfur dioxide or sulfur, would likely require significant capital investment to upgrade equipment and process for safe use.

Safe to use in industrial applications considering flammability and toxicity issues—Sulfur dioxide requires scrubbing to be considered environmentally sound. Sulfur powder is flammable and strongly reactive with magnesium, leading to potential contamination of magnesium.

Easy to use and maintain—Dodecafluoro-2-methyl-3-pentanone may require equipment adjustments for use in some magnesium production processes for more even distribution of the cover gas.[249] Implementation of vacuum technology would require significant modification of current processes to prevent exposure of molten magnesium to air and may not be applicable to all stages of production.

6.6 Mitigation of emissions of controlled substances

SF_6 or other gases are not regularly captured or destroyed at magnesium production facilities. However, methods have been developed to capture SF_6 from magnesium production facilities and recycle it back over the molten magnesium with up to a 95% recovery rate.[250]

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[248] California Air Resources Board, 2015, *Magnesium casters successfully retool for a cleaner future: Two firms develop climate-friendly process in response to regulation*, Release Number 15–07, February 2, 2015. https://ww2.arb.ca.gov/news/magnesium-casters-successfully-retool-cleaner-future. Accessed September 2022.

[249] Milbrath, D.S., 2004, *3M™ Novec™ 612 Magnesium Protection Fluid*, 3M Industrial Chemicals, International Conference of SF_6 and the Environment, December 1–3, 2004.

[250] Li, Y., Kapusta, J., Meimari, M, Barney, J., 1999, *Capture and recycle: A new option for emission reduction of sulfur hexafluoride in magnesium melting*, REWAS'99 Global Symposium on Recycling, Waste Treatment and Clean Technology I–III, 1999.

7 Laboratory and Analytical Uses

7.1 Background

Laboratory and analytical uses of controlled substances have included: equipment calibration; extraction solvents, diluents, or carriers for specific chemical analyses, inducing chemical-specific health effects for biochemical research; as a carrier for laboratory chemicals; and for other critical purposes in research and development where substitutes are not readily available or where standards set by national and international agencies require specific use of the controlled substances.

Decision IV/25 establishes criteria and procedures that permit the production and consumption of controlled substances beyond their production phase-out, in relation to the control measures under Article 2. A controlled substance qualifies as essential only if:

i) it is necessary for the health, safety or is critical for the functioning of society (encompassing cultural and intellectual aspects); and

ii) there are no available technically and economically feasible alternatives or substitutes that are acceptable from the standpoint of environment and health.

Production and consumption are permitted only if:

1. all economically feasible steps have been taken to minimize the essential use and any associated emission of the controlled substance; and

2. the controlled substance is not available in sufficient quantity and quality from existing stocks of banked or recycled controlled substances, also bearing in mind the developing countries' need for controlled substances.

At the 6th Meeting, parties authorised an essential use exemption for laboratory and analytical uses for the first time in decision VI/9, according to conditions set out in Annex II of the report for that meeting. Annex II authorises essential use production for laboratory and analytical purposes only if the controlled substances are manufactured to high purity and supplied in re-closable containers and in small quantities[251]: this became known as the global essential use exemption. Other than these quality specifications, Annex II also required that parties shall annually report for each controlled substance produced: the purity; the quantity; the application, specific test standard, or procedure requiring its uses; and the status of efforts to eliminate its use in each application. The Annex also required that parties shall also submit copies of published instructions, standards, specifications, and regulations requiring the use of the controlled substance.

Decision XVIII/15 authorises the production and consumption of methyl bromide subject to the conditions applied to the global essential use exemption for laboratory and analytical uses contained in annex II to the report of the 6th Meeting of the parties and adopts a category of laboratory and analytical uses of methyl bromide allowable under the global exemption.

Various decisions have subsequently extended the global laboratory and analytical use exemption under these specified conditions, excluded additional specific uses from the global exemption, and/or

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[251] The purity standards and other requirements placed on laboratory and analytical uses are given in Annex II of the report of the Sixth Meeting of the Parties, and include the following: (i) purity requirements; (ii) criteria that controlled substances for laboratory and analytical uses shall be supplied only in re-closable containers or high pressure cylinders smaller than three litres or in 10 millilitres or smaller glass ampoules; and (iii) advice concerning preparation of mixtures containing the controlled substances, labelling, recovery and reuse, and annual reporting of activities.

requested the Technology and Economic Assessment Panel (TEAP) to report on developments in alternatives to the use of controlled substances.

Decision XXI/6 extended the applicability of the global essential use exemption to countries operating under Article 5 for controlled substances subject to relevant Article 2 control measures. Decision XXII/7 allowed parties operating under paragraph 1 of Article 5 until 31 December 2011 to deviate from the existing laboratory and analytical use bans in individual cases, where a party considered that this was justified.

Decisions made by the Meeting of the Parties extended the period applicable to the global laboratory and analytical use exemption. Decision X/19 extended the global laboratory and analytical essential use exemption until 31 December 2005 under the conditions set out in annex II of the report of the Sixth Meeting of the Parties. Decision XXVI/5 extended the global laboratory and analytical use exemption until 31 December 2021.

Decision XXXI/5 further extended the global laboratory and analytical use exemption indefinitely beyond 2021, without prejudice to the parties deciding to review the exemption at a future meeting. This decision also requested the Technology and Economic Assessment Panel to report in its quadrennial report on any progress made by parties in reducing their production and consumption of ozone-depleting substances for laboratory and analytical uses, on any new alternatives to those uses, and on laboratory standards that can be performed without such substances.

Where alternatives have become available for laboratory and analytical uses of controlled substances, decisions have been made to exclude those uses from the exemption because they were no longer considered essential. Decisions VII/11, XI/15, XVIII/15, and XIX/18 have eliminated several laboratory and analytical uses from the global exemption for laboratory and analytical uses.

A compilation of relevant decisions on laboratory and analytical uses is included in Appendix 2.

7.2 Production and consumption data reported for laboratory and analytical uses

This section provides an analysis of production and import data reported by parties for laboratory and analytical uses (LAUs), which may provide a focus for the remaining priorities in this application.

7.2.1 Reported data

Parties have reported the production and import of controlled substances used for laboratory and analytical purposes to the Ozone Secretariat since 1996. Data for production and consumption by country and by the annex group of controlled substances can be downloaded from the Ozone Secretariat[252] website. More than 40 parties have reported their production and consumption data, covering more than 46 different ozone-depleting substances (ODS), with their data varying greatly from tonnes to grams. However, only 7 parties operating under non-Article 5, and one party operating under Article 5, have reported production data.

7.2.2 Global production and consumption data for LAUs

Figures 7.1 and 7.2 show the total global quantities of ODS produced and consumed as reported by parties for LAUs in the latest decade. An overall decreasing trend in the reported quantities produced and consumed from 2010 to 2020 shows the lasting efforts to eliminate the ozone depletion substances in this application.

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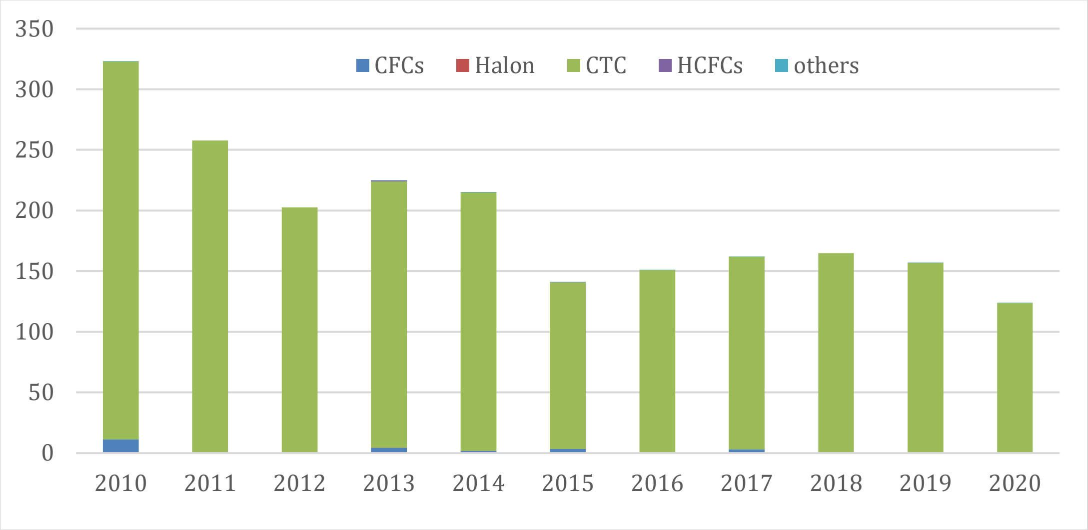
[252] UNEP, https://ozone.unep.org/countries/data-table.

In 2020, the global production of ODS produced for LAUs was 123.61 tonnes, when CTC and methyl bromide were the only two controlled substances produced for LAUs. CTC remains the predominant ODS during the years, with production of 123.59 tonnes in 2020.

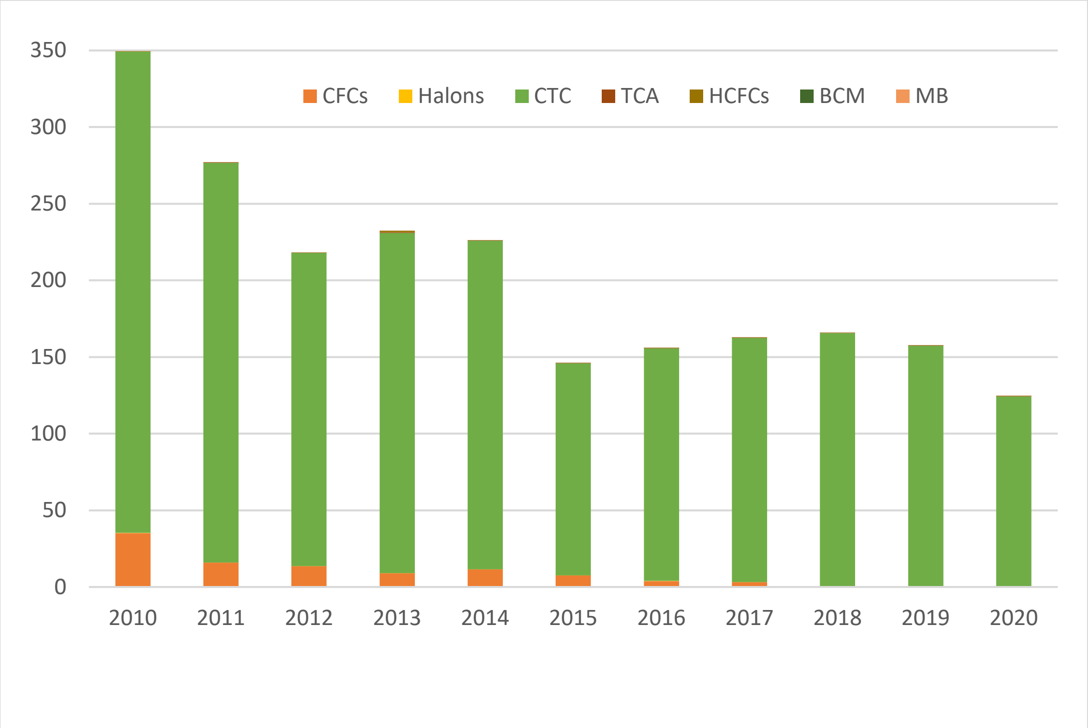
The total global consumption of ODS in 2020 for LAUs was 124.76 tonnes, with mainly CTC and a smaller proportion of CFCs as the main ODS.

Figure 7.1 Reported global ODS production for LAUs, 2010–2020 (tonnes)



Note: Others includes Annex B, Group III 1,1,1-trichloroethane (TCA) and Annex E, Group I methyl bromide (CH_3Br)

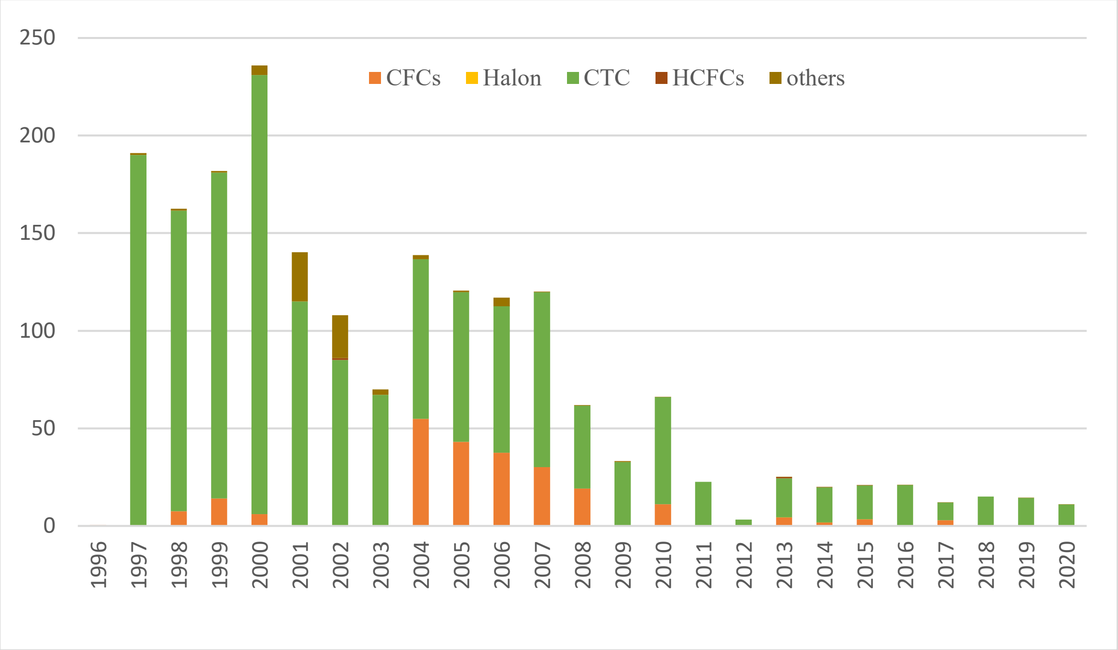
Figure 7.2 Reported global ODS consumption for LAUs, 2010–2020 (tonnes)



7.2.3 Production and consumption of ODS in non-Article 5 and Article 5 parties for LAUs

The reported production of ODS for LAUs in non-Article 5 parties is presented in Figure 7.3. Production of ODS in all non-Article 5 parties was 191 tonnes in 1997, reaching a peak of 225 tonnes in 2000, with a reduction to 11 tonnes in 2020. CTC remains the predominant ODS being produced for LAUs in non-Article 5 parties in recent years; no production of CFCs has been reported since 2018 when CFC-113 production for LAUs was reported.

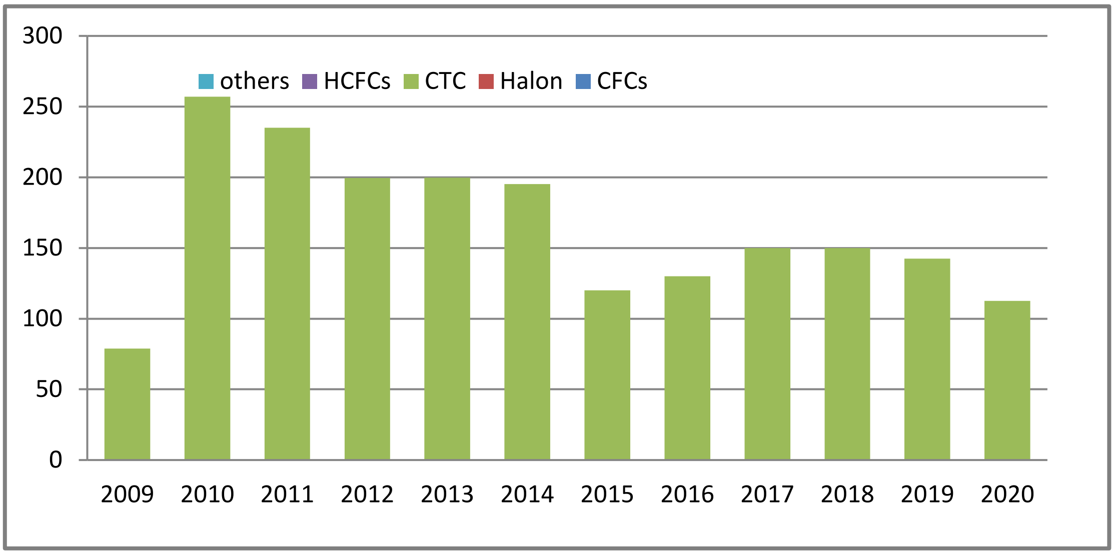
Figure 7.3 ODS production for LAU reported by non-Article 5 parties, 1996–2020 (tonnes)



Note: Others includes Annex B, Group III 1,1,1-trichloroethane (TCA) and Annex E, Group I methyl bromide (CH_3Br)

Article 5 parties began reporting production data for LAUs in 2009, as shown in Figure 7.4. CTC is the only ODS reported by Article 5 parties. An overall decrease in reported production can be seen during the period, from a peak of 257 tonnes in 2010 to 113 tonnes in 2020.

Figure 7.4 ODS production for LAUs reported by Article 5 parties, 1996–2020 (tonnes)



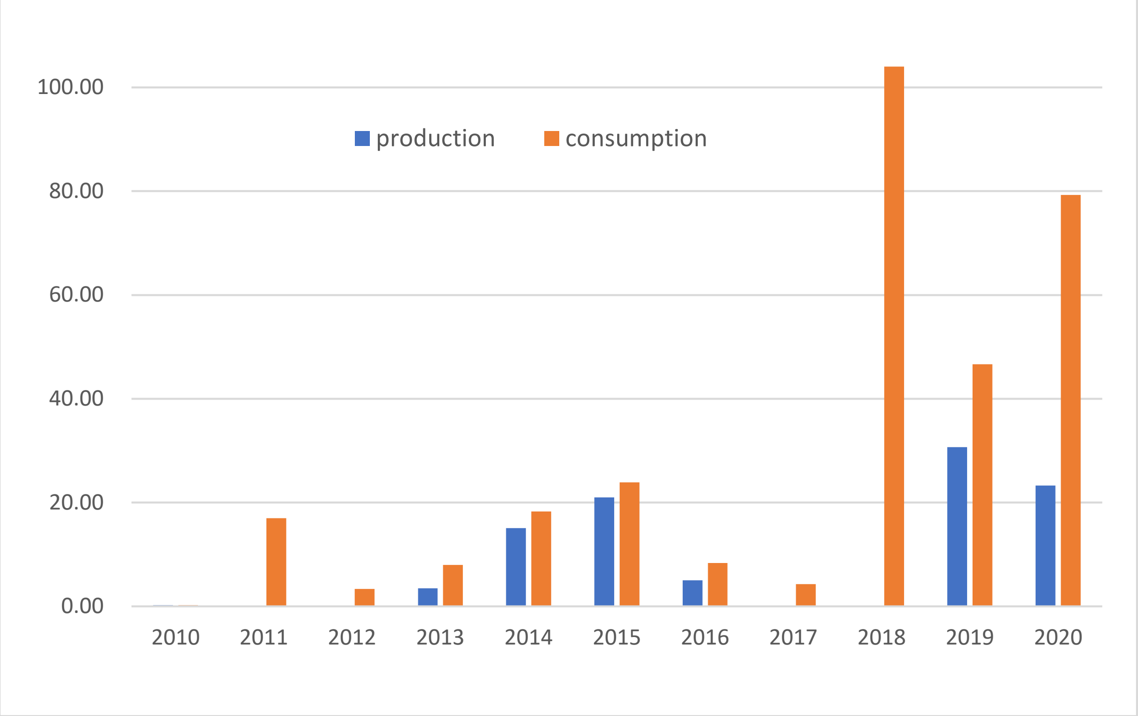
Others includes Annex B, Group III 1,1,1-trichloroethane (TCA) and Annex E, Group I methyl bromide (CH_3Br)

Consumption of ODS for LAU in both non-Article 5 and Article 5 parties generally matches with their production data. The discrepancy between the production data and consumption data might come from imported ODS or resulted from production stock in some years.

7.2.4 Production and consumption of methyl bromide for LAUs

Only 1 party has reported production data and 5 parties have reported consumption data for methyl bromide in the decade. It shows that the total reported global production and consumption of methyl bromide for LAUs has remained at a low level in the last decade (Figure 7.5). These reported quantities account for a very minor part of the total annual reported ODS production and consumption for laboratory and analytical uses. However, it shows that the consumption of methyl bromide increased from 2018. In 2020, the production of methyl bromide was 23.3 kg, and the total consumption was 79.27 kg for LAUs.

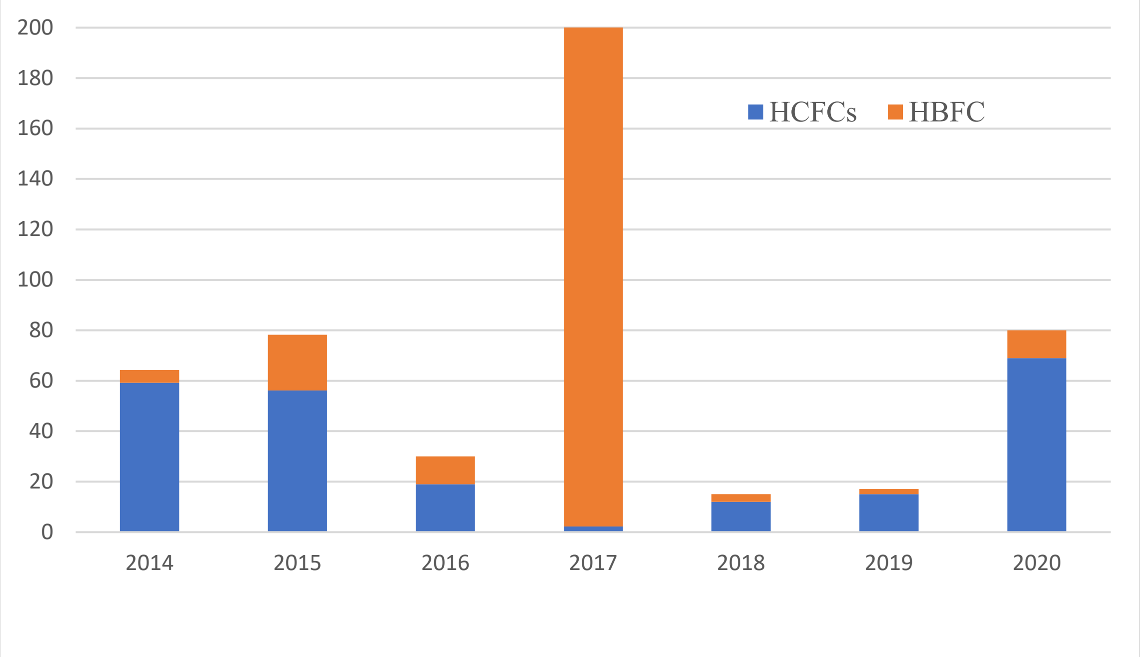
Figure 7.5 Reported global production and consumption of methyl bromide for LAUs, 2009–2020 (kilograms)



7.2.5 Production and consumption of HCFCs for LAUs

No production of HCFCs (including HBFCs) have been reported since 2016. Global consumption of HCFCs (including HBFCs) is showed in Figure 7.6.

Figure 7.6 Global consumption of HCFCs and HBFCs for LAUs, 2014–2020 (kilograms)



Since 2014, the annual consumption of HCFCs and HBFCs has generally remained below 80 kg with an exceptional higher consumption of HBFCs in 2017. No additional information on the specific chemicals was available from the Ozone Secretariat website. However, MCTOC 2018 assessment report previously identified the type of HCFCs and HBFCs, including HCFC-21, -22, -123, -141b, -233, -242, -252, HBFC-21B2, -22B1.

7.3 Laboratory and analytical uses and their alternatives

7.3.1 Background

Decision XXXI/5 requested the Technology and Economic Assessment Panel to report in its quadrennial report on any progress made by parties on any new alternatives to laboratory and analytical uses, and on laboratory standards that can be performed without such substances, on the understanding that, should new compelling information become available, including opportunities for significant reductions in production and consumption, that information should be reported in its annual progress report.

TEAP reported in detail in 2008, 2009, 2010, 2011, and 2018 on the availability of alternatives for laboratory and analytical uses of ozone-depleting substances. The 2018 MCTOC Assessment Report identified alternatives for CTC and methyl bromide as a solvent or reacting agent in laboratory uses and in operating procedures of standards. The report also proposed a list of recommendations for laboratory and analytical uses that could be performed without using controlled substances.

This report further considers available alternatives, and potential barriers to their adoption, in Article 5 and non-Article 5 parties. A brief review of laboratory solvent and reagent uses has been taken based on the earlier findings of the 2018 MCTOC Assessment Report, with a renewed search of major global standard bodies of the latest progress with standards that do not use ODS.

7.3.2 Laboratory solvent and reagent uses

Many laboratory uses of controlled substances have been phased out using alternative chemicals and/or procedures. Laboratory uses of ODS, e.g., as a common solvent or cleaning agent, have largely been phased out in non-Article 5 parties and are disappearing from laboratories in Article 5 parties, by using alternatives with similar chemical properties (e.g., polarity and solvent properties).

CTC is a useful laboratory chemical due to one or more of the following characteristics: reasonably good solvency; compatible with common materials including many elastomers used in reaction vessels; non-flammable, and not easily degraded under conditions of use; easily removed by evaporation or distillation without excessive energy consumption; readily available at affordable prices.

For the above reasons, CTC has been widely used as a solvent in synthetic organic chemistry for reactions in which two or more components are dissolved in the solvent to react under heating to form new substances. The products of these reactions are recovered by cooling, followed by appropriate ‘work up’ that often involves distillation (and potential recovery) of the CTC. Many of the industrial uses of CTC stem from patented procedures that were developed in laboratories. If such laboratory work is destined to become an industrial process, an alternative solvent should be considered from the outset.

In its progress reports, TEAP has reported the details on the use of CTC in laboratory and analysis procedures and has identified alternative procedures for which CTC can be replaced. As part of investigations made by the Chemicals Technical Options Committee (CTOC) in 2008[253], 2009[254], 2010[255] and 2011[256], TEAP recommended a list of procedures that could be removed from the global exemption for laboratory and analytical uses of CTC. In 2018, MCTOC reviewed the use of ODS in laboratory and analytical, including CTC used as a solvent in bromination reactions using *N*-bromosuccinimide (NBS). MCTOC identified several procedures where ODS can be replaced by non-ODS solvents and are no longer required for those procedures.[257,258]

Several alternative reaction procedures where CTC used as a solvent in bromination reactions using *N*-bromosuccinimide (NBS) can be replaced by non-ODS solvents are shown in Table 7.1.

Table 7.1 Alternatives, or alternative procedures, for CTC in reactions involving NBS

Reaction Procedure	**Alternatives to CTC**
Wohl–Ziegler bromination	Chlorinated solvents (chloroform, 1,2-dichloroethane, dichloromethane) Non-chlorinated solvents ((trifluoromethyl)benzene, acetonitrile, ionic liquid, etc.)
Electrophilic substitution reaction	DMF, THF, acetic acid-chloroform
Electrophilic addition reaction	DME, THF, or *t*-butanol, dichloromethane
Oxidation reaction	Cyclodextrin-water, aqueous THF-H_2SO_4

DMF: N,N-Dimethylformamide; THF: Tetrahydrofuran, H_2SO_4*: sulfuric acid.*

Methyl bromide is another ODS once widely used as a methylating agent in chemical reactions to deliver a methyl group to a chemical substrate. In 2018 MCTOC assessment report, MCTOC made a comprehensive literature review and found that there are many alternatives to methyl bromide when used as a methylating agent. These alternatives are almost always used in preference to methyl bromide. Following these findings, TEAP and its MCTOC recommended that methyl bromide used as a methylating agent in laboratories could be excluded from the global essential use exemption for laboratory and analytical uses.

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[253] UNEP, 2008, *May 2008 Report of the Technology and Economic Assessment Panel, Volume 1, Progress Report*, May 2008, pg. 54.

[254] UNEP, 2009, *May 2009 Report of the Technology and Economic Assessment Panel, Volume 1, Progress Report*, May 2009, pg. 51.

[255] UNEP, 2010, *May 2010 Report of the Technology and Economic Assessment Panel, Volume 2, Progress Report*, May 2010, pg. 53.

[256] UNEP, 2011, *May 2011 Report of the Technology and Economic Assessment Panel, Volume 1, Progress Report*, May 2011, pg. 51.

[257] UNEP, 2018, *September 2018 Report of the Technology and Economic Assessment Panel, Volume 4, Response to Decision XXVI/5(2) on Laboratory and Analytical Uses*, September 2018.

[258] UNEP, 2018, *2018 Report of the Medical and Chemical Technical Options Committee, 2018 Assessment Report*, December 2018. https://ozone.unep.org/sites/default/files/2019-04/MCTOC-Assessment-Report-2018.pdf.

It is challenging to identify alternatives to ODS for some specific laboratory uses within such a wide range of chemical reactions undertaken in laboratories. In future, MCTOC might focus its efforts mainly on identifying the available alternatives to CTC, which is the dominant ODS in LAUs.

7.3.3 Standards related to laboratory and analytical use of controlled substances and their alternatives

Standards play vital roles in leading and promoting the substitution of controlled substances in laboratory and analytical uses. As standard methods allow comparisons over time as well as between different laboratories, they have been widely adopted and followed. The use of a standard method is often required by a customer or a regulatory authority as a form of quality assurance for a product. Several factors such as the ease and reliability of the assay, workplace health and safety, or the availability of substances under inter-governmental agreements (e.g., the Montreal Protocol), can lead to the writing of new standards. The development or revision of standards must undergo a rigorous procedure, which usually takes time and comes with costs, as well as lags behind the identification of the need for change. In addition, users may be slow to adopt new standards for several reasons, including costs, familiarity with techniques, availability of equipment, and validation of the new method which covers comparability of results measured using previous and new methods.

International bodies, such as ASTM International and ISO, have been working on the development of new standard methods to replace ODS in laboratory and analytical uses. In previous reports, the former CTOC provided information on the development of standards that do not use ODS, especially in relation to standards that previously used CTC. In the 2018 MCTOC Assessment Report, MCTOC reviewed the status of standards by searching major standard-related bodies such as ISO, ASTM International, the European Committee for Standardisation (CEN), the Standardization Administration of the People's Republic of China (SAC) and U.S. EPA. Following its review of these standards, MCTOC provided a list of standards that do not use ODS.

In this report, MCTOC updated its review of standards, based on its 2018 Assessment Report. The websites of major global standard organizations were scrutinised, and the results indicated that some bodies seemed to have eliminated the use of some ODS for their standards, for example, there existed no results when searching for CTC on the CEN database. The updated list of standards that do not use ODS is included in Appendix 3.

For the test on the **determination of hydrocarbons** (oil, grease etc.) in water or soil, CTC was the most common solvent used in this standard procedure. Considering the toxicity of CTC, CFC-113 was previously selected as an alternative. A wide range of alternatives are now available for both CTC and CFC-113, such as hydrocarbons and chlorinated solvents (hexane, dichloromethane and perchloroethylene etc.).

For the test on the **determination of iodine index or bromine index**, in which CTC and 1,1,1-trichloroethane were used as solvents, a mixture of glacial acetic acid with other solvents, such as cyclohexane, methanol and chloroform, could be adopted.

For the test on the **determination of moisture and water** in animal and vegetable fats and oils, or petroleum products and bituminous materials, alternatives such as xylene, methanol, aromatic solvents, and paraffinic solvents could be selected for different analytical procedures.

For the test on the **determination of phenol in water**, chloroform is recognized as alternative for CTC by some standard-related organisations, such as ISO, ASTM, and U.S. EPA. However, ISO still allows the use of ODS for the standard, "Water quality — Determination of phenol index — 4-Aminoantipyrine spectrometric methods after distillation".

ASTM also developed a new procedure that uses methyl isobutyl ketone as an alternative for CTC in the test on the **determination of lead in gasoline**, which will facilitate the development of new analytical methods for the determination of the content of other metals in water or soil.

However, even though significant progress has been made by the international standard bodies and non-Article 5 parties in the development or revision of standards to replace ODS in analytical use, there still exist standards that allow the use of ODS, as listed in Appendix 4. For some standards, the alternative or alternative procedures may exist, but the ODS method remains as an active standard for these standard bodies, implying some barrier in adopting the alternatives or alternative procedures in standard development or revision.

It may be more challenging for Article 5 parties to adopt the alternatives or alternative procedures due to the difficulties and/or complexities in the use of the alternatives. China, for example, investigated CTC in laboratory and analytical uses in China[259] and listed more than 30 standards still using CTC that require revision. Recent information indicates that some standards for the determination of oil and grease in water, soil or sediment have been successfully revised and implemented to adopt the non-ODS alternatives (see Appendix 3), which would greatly promote the phase-out of CTC in China and further meet the international compliance requirements.

The reasons that non-ODS methods are not adopted in Article 5 parties are adherence to standard methods that use ODS, and the cost of implementing new methods including training. In the first instance, where purely national standards are involved, skilled practitioners within those countries have the capability to adopt the alternative procedures. Only in a few cases, where an international standard exists and there is no non-ODS alternative, should it be necessary to persist with the use of ODS. In the second instance, the cost of transition should be sustainable, although the cost of alternative substances or procedures may be higher than those of the ODS methods they replace. It takes a lot of time and skilled resources to implement new methods; however, in many cases, non-ODS alternatives are available and may have been adopted by international standards bodies or in non-Article 5 parties.

Therefore, international cooperation between different standards organisations and between parties should be encouraged to facilitate and accelerate the development or revision of standards for the replacement of ODS in analytical uses.

7.3.4 Methyl bromide used as a reference or standard, or in laboratory studies

Decision XVIII/15 authorizes the production and consumption of methyl bromide for laboratory and analytical uses subject to the conditions applied to the global exemption, and adopts a category of laboratory and analytical uses of methyl bromide that is allowable:

- As a reference or standard:
    - (i) To calibrate equipment which uses methyl bromide;
    - (ii) To monitor methyl bromide emission levels;
    - (iii) To determine methyl bromide residue levels in goods, plants and commodities;
- In laboratory toxicological studies;
- To compare the efficacy of methyl bromide and its alternatives inside a laboratory;

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[259] http://odslab.chinareagent.com.cn/. Accessed September 2022 (in Chinese).

- As a laboratory agent which is destroyed in a chemical reaction in the manner of feedstock;

MCTOC believes that the current usage of methyl bromide as a reference or standard, in laboratory toxicological studies, and for comparison of methyl bromide and its alternatives inside a laboratory, is likely to be minor, possibly in the kilograms range globally. The likelihood of significant amounts (or any amounts) used this way has diminished as there are very few trials done on methyl bromide, with fewer on insect mortality studies and laboratory emission studies using barrier films. Nevertheless, methyl bromide used as a reference or standard, or in laboratory studies, will likely continue for as long as methyl bromide is used in applications (e.g., QPS or horticultural uses).

7.3.5 Laboratory and analytical uses of HCFCs

HCFCs are likely to be required for laboratory and analytical uses in non-Article 5 parties, for example to be used as analytical standards for the determination of atmospheric levels of HCFCs, and for the research into and development of new substances. The following laboratory and analytical uses for HCFCs have been reported and may continue to exist post-2022 due to slow progress in moving to alternatives.

- Reference chemical (in analytical methods and for enforcement) e.g., HCFC-21, HCFC-22, HCFC-31, HCFC-122, HCFC-123, HCFC-124, HCFC-133a, HCFC-141b, HCFC-142b, HCFC 151a, HCFC-233

- Feedstock (reagent in laboratory chemical synthesis) e.g., HCFC-22, HCFC-242, HCFC-252

- Solvent (inert solvent in laboratory chemical synthesis) e.g., HCFC-31

- Reference chemical (in toxicological studies) e.g., HCFC-21

- ODS as a component in samples to be tested.

Laboratory and analytical uses of HCFCs as a reference chemical will continue for as long as HCFCs are used in applications.

7.4 Laboratory and analytical uses that can be performed without using controlled substances

In 2018 TEAP and MCTOC reports, several laboratory and analytical procedures were identified that can be performed without using controlled substances, and their exclusion from the global essential use exemption for laboratory and analytical uses was recommended.

At the 31st meeting, in decision XXXI/5, parties extended the global exemption indefinitely. In the preamble to that decision, parties noted the 2018 reports of the TEAP and the MCTOC, and the very small quantities of ozone-depleting substances consumed for laboratory and analytical uses. Parties also acknowledged that the approach, whereby the Meeting of the Parties periodically removes individual laboratory and analytical uses from the global exemption, may lead to confusion since the list of laboratory and analytical uses is not exhaustive, and entails a level of administrative effort not commensurate with the environmental benefit of phasing out the quantities of ozone-depleting substances concerned. These acknowledgements were accompanied by a decision that invited parties to consider the information provided by MCTOC on uses that could be performed without using ODS.

The procedures listed in Table 7.2 are the previously recommended laboratory and analytical uses that can be performed without using controlled substances that could be excluded from the global exemption.

Table 7.2 Laboratory and analytical procedures that can be performed without using controlled substances

ODS Type	Procedures
Methyl bromide	Laboratory uses as a methylating agent
Carbon tetrachloride (CTC)	Reaction solvents
CTC	A solvent for IR, Raman and NMR spectroscopy
CTC	Grease removal and washing of NMR tubes
CTC	Iodine partition and equilibrium experiments
CTC	Determination of hydrocarbons in water, air, soil or sediment
CTC	Determination of moisture and water
1,1,1-trichloroethane (TCA)	Determination of bromine index
CTC	Determination of iodine index

As mentioned in section 7.3, the adoption of alternatives to ODS laboratory and analytical uses is still underway in Article 5 parties, with some challenges such as adherence to standards using ODS, cost and time. In addition, in some cases, ISO and ASTM International still list standards that require the use of ODS.

Parties may wish to consider actions to facilitate the adoption of alternatives in Article 5 parties, such as international cooperation between different standards organisations and between parties. Possible actions may include sharing more information on alternatives as well as on the revision of standards that use ODS.

8 End-of-life management and destruction

8.1 Introduction

In the 2018 MCTOC Assessment Report[260], this Chapter has primarily focused on destruction technologies applicable to controlled substances either in concentrated or dilute form at the end-of-life (EOL). This encompassed controlled substances contained in equipment or products that would otherwise be emitted to the atmosphere, as well as those generated as a waste by-product in production processes. The former relates primarily to refrigerants and blowing agents and the latter, for example, to HFC-23 produced as a by-product principally during the production of HCFC-22.

Environmentally sound destruction of surplus or contaminated ODS and HFCs at end-of-life is generally encouraged by the Montreal Protocol because it avoids unnecessary emissions and helps protect the stratospheric ozone layer and/or the climate. However, the Montreal Protocol does not mandate the destruction of ODS or Annex F Group I HFCs. The exception, under Article 2J, is emissions of HFC-23 (Annex F, Group II) generated in production facilities that manufacture Annex C, Group I, or Annex F substances, where emissions must be destroyed to the extent practicable using technologies approved by parties. Otherwise, the Montreal Protocol generally encourages parties to prevent EOL emissions of controlled substances through preferential recovery for recycling and reclamation and, where that is not feasible or no longer suitable, through environmentally sound destruction.

The Montreal Protocol provides a list of destruction technologies approved for the purposes of Article 7 data reporting and for the destruction of HFC-23 under Article 2J. Article 7 data reporting requires production to be reported by parties, including the amounts of controlled substances destroyed by technologies approved by parties. The use of destruction technologies approved by parties applies to the amounts of controlled substances destroyed and accounted for within the Protocol's definition of 'production'. The Protocol also allows Parties to manufacture an amount of controlled substance almost equivalent (e.g., in ODP tonnes) to the quantity destroyed with technology listed as approved, within the same year as destruction, and within the same group of substances.

The 2018 MCTOC Assessment also reports the application of these approved destruction technologies in the selection of destruction options beyond its application to the narrow obligation associated with Article 7 data reporting. It also makes clear that, in meeting any broader needs for environmentally sound destruction, parties are free to apply technologies, whether on the Montreal Protocol approved list or not, that satisfy national regulatory standards.

In the 2022 MCTOC Assessment Report, this Chapter's scope includes consideration of destruction technologies and is broadened to consider EOL management of controlled substances from the point where they become available for recovery at EOL.

The rationale behind this is the growing interest in and recognition of large banks of controlled substances that continue to accumulate in equipment and products, and that currently only a limited amount is being recovered at EOL for destruction. Effective management of ODS/HFC banks aims to minimise global impacts associated with their potential release, by minimising the amount of virgin refrigerant that is produced, minimising emissions, and by supporting HFC phase-down by making available recovered HFCs for recycling and for reclamation and reuse.

Historically, controlled substances in banks reaching EOL have largely been emitted. This has been the case for EOL CFC refrigerants and foams (except for some long-life applications such as building insulation and chiller refrigerants because of their low leakage rate and/or propensity for recovery).

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[260] UNEP, 2018, *2018 Report of the Medical and Chemical Technical Options Committee, 2018 Assessment Report*, December 2018. https://ozone.unep.org/sites/default/files/2019-04/MCTOC-Assessment-Report-2018.pdf.

This represented a lost opportunity to mitigate significant ozone depletion and climate impacts. HCFCs, and now increasingly HFCs, will be reaching end of life and, if not responsibly recovered, subject to emission. This is anticipated to accelerate over the next several decades as phase-out of HCFCs is completed and phase-down of HFCs under the Kigali Amendment gains momentum. On that basis it is appropriate to consider technically and economically feasible measures that could enhance and maximise the circular economy through life cycle ODS/HFC management, that is, recovery, consolidation, recycling, reclamation, reuse, and, when no longer viable for reuse, destruction of controlled substances in banks at EOL.

This Chapter is structured into five subsequent sections:

- Assessing the current understanding of the quantity of controlled substances available in banks and when those banks might reach their end of life to become potentially available for recovery and eventual destruction.

- Addressing the destruction of controlled substances under the Montreal Protocol in terms of definitions and formal obligations of parties.

- Providing currently available data on the actual recovery and destruction of EOL controlled substances both at a global level based on data reported to the Ozone Secretariat, and for several larger non-Article 5 parties and regions that appear to account for a large portion of available data. This is compared with current bank estimates to provide a general assessment of the estimated proportion of EOL ODS/HFC reaching EOL that is recycled, reclaimed and/or destroyed.

- Discussing the options available for EOL chemicals management, which encompasses the scope of ODS/HFC management, the various barriers and factors that affect developing an effective system, and current initiatives being pursued to promote EOL management globally.

- Assessing destruction technologies, including MCTOC's response to decision XXX/6. This includes criteria and considerations for their assessment, a recommendation for an addition to the list of approved destruction technologies, a recommendation for potential amendment of the existing approved technology classification, global capacity for ODS/HFC destruction, and broader application of ODS/HFC destruction outside that undertaken for compliance with Montreal Protocol obligations.

This Chapter supplements information on EOL management of ODS/HFC and destruction contained in the 2022 Assessment Reports of the respective Technical Options Committees for Flexible and Rigid Foams, Fire Suppression, Methyl Bromide, and Refrigeration, Air Conditioning and Heat Pumps.

8.2 ODS and HFC banks

This section provides background on ODS/HFC banks definitions and research concerning the amount of common ODS and HFC controlled substances estimated to be contained or banked in equipment and products currently in use and in the future. This includes estimates of amounts of these substances reaching end-of-life and thus being available for management to prevent them from being emitted. The section concludes with the outlook for ODS/HFC banks. Options for EOL management are described in section 8.3.

8.2.1 What are banks?

The IPCC/TEAP Report on Safeguarding the Ozone Layer and the Global Climate System 2005[261] (SROC) defines ODS banks as the total amount of substances contained in existing equipment, chemical stockpiles, foams, and other products not yet released to the atmosphere.

A further useful definition is the "reachable" bank, also referred to as "active"[262] bank, being those substances that are contained in equipment or product in use and thus potentially reachable or accessible for management upon entering the waste stream at its end-of-life. In practice, end-of-life can occur at different stages in the lifetime of equipment or for various reasons. For example, in the case of early retirement programs focused on achieving energy savings, recovery might be done earlier than the end of the expected equipment lifetime. In contrast, the "non-reachable" or "inactive" bank denotes substances that were landfilled or illegally dumped within the equipment or product.[263]

ODS/HFC banks management aims to prevent emissions from active banks as far as is technically and economically feasible by monitoring for leaks, installing systems correctly, appropriately maintaining operating systems, and enabling the recovery and management[264] at end-of-life.

8.2.2 History and literature on ODS/HFC banks

Accumulating banks of controlled substances in equipment and products, and the impact of their uncontrolled emissions on ozone depletion and climate, gained increasing attention from approximately 2000 onwards.

The first complete data set on ODS banks was prepared for the SROC in the year 2005.[265] The TEAP supplement[266] to the SROC comprised data sets of ODS banks for 2002 and 2015, providing breakdowns for non-Article 5 and Article 5 parties, substance groups (Halons, CFC, HCFC) and sub-sectors. The data are expressed in metric tonnes, ODP tonnes, and GWP-weighted tonnes (metric tonnes CO_2e). Subsequently published studies focussed on refinements of the underlying model assumptions and the global bank estimates initially presented in the SROC, and which are based on the RIEP model (Refrigerant Inventory and Emission Previsions).[267]

A list of published studies on ODS banks is provided in Table 8.1 and provides a chronology and highlights important definitions and contents.

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[261] IPCC/TEAP, 2005, *Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons*, Authors: Bert Metz, Lambert Kuijpers, Susan Solomon, Stephen O. Andersen, Ogunlade Davidson, José Pons, David de Jager, TahlKestin, Martin Manning, and Leo Meyer (Eds), Cambridge University Press, United Kingdom, pp. 478.

[262] The terms of active and inactive bank are used in the UNEP, 2021, *Report of the Technology and Economic Assessment Panel, Volume 3: Decision XXXI/3 Task Force Report on Unexpected Emissions of Trichlorofluoromethane (CFC-11),* May 2021.

[263] Executive Committee of the Multilateral Fund, Meeting Document: UNEP/OzL.Pro/ExCom/48/42, *Report of the meeting of experts to assess the extent of current and future requirements for the collection and disposition of non-reusable and unwanted ODS in Article 5 countries (follow up to decision 47/52)*, 20 March 2006.

[264] The term management covers actions that would encompasses recovery for recycling, reclamation and reuse, storage pending a management activity, direct destruction, and chemical transformation management options.

[265] Ibid., IPCC/TEAP, 2005.

[266] TEAP, 2005, *Report of the Technology and Economic Assessment Panel, Supplement to the IPCC/TEAP Report*, November 2005.

[267] Clodic, D. and L. Palandre, 2004, *Determination of Comparative HCFC and HFC Emission Profiles for the Foam and Refrigeration Sectors Until 2015, Part 1: Refrigerant Emission Profiles*, Centre d' Energetique (Ecole des Mines de Paris and Armines), Report for U.S. EPA and ADEME, April 2004.

Table 8.1 Overview of studies concerning ODS and HFC banks, modified based on Heubes *et al.*, 2015[268]

Author	Year	Title	Contents
TEAP	2002	Task Force on Destruction Technologies	Material flows of CFC-11, estimated emission of CFC-11 from foams
TEAP	2002	Task Force on Collection, Recovery & Storage	Combined top-down and bottom-up approach to estimate ODS bank in foams and refrigeration equipment for 2002
TEAP	2005	Task Force Report on Foam End-of-Life	CFC-11 bank projection to 2100 (cited from IPCC/TEAP 2005)
IPCC, TEAP	2005	Special Report on Safeguarding the Ozone Layer and TEAP Supplement	First comprehensive data set on ODS banks, split in developed and developing countries for 2002 and 2015
TEAP	2006	Report on Expert Meeting to Assess the Extent of Current and Future Requirements for the Collection and Disposition of Non-Reusable and Unwanted ODS in Article 5 Countries	Definition of "reachable banks" and "accessibility"
TEAP Task Force on HCFC issues	2007	Emissions Reduction Benefits arising from earlier HCFC Phase-out and other Practical Measures	First global prediction of ODS banks until 2050
TEAP XX/7 Task Force	2009	Environmentally Sound Management of Banks of Ozone-Depleting Substances; Interim and Final report	Assessment of effort to manage ODS banks, split in substance groups (CFC and HCFC) and sectors (refrigeration, air conditioning and foam)
TEAP XX/8 Task Force	2009	Assessment of Alternatives to HCFCs and HFCs and Update of the TEAP 2005 Supplement Report Data	Update of the TEAP 2005 data, by including accelerated HCFC phase-out; calculation of ODS banks until 2020
ICF	2010	Identifying and Assessing Policy Options for Promoting the Recovery and Destruction of Ozone Depleting Substances (ODS) and Certain Fluorinated Greenhouse Gases (F-Gases) Banked in Products and Equipment	First bottom-up approach for European Union member states to estimate ODS banks
SKM Enviros	2012	Further Assessment of Policy Options for the Management and Destruction of Banks of ODS and F-Gases in the European Union	Refined bottom-up approach for European Union member states to estimate ODS banks, integrating a floating point of time for EOL rather than a fixed year, taking the annual equipment fleet out of use over several years rather than all at the same time.
SAP	2014	Scientific Assessment of Ozone Depletion: 2014	Global aggregated emissions from ODS banks (2015–2050)

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[268] Heubes, J., Papst, I., Gloel, J., 2015, *Management and destruction of existing ozone depleting substances banks*, G-S03-2015-en-01, GIZ, Eschborn, August 2015. https://www.giz.de/en/downloads/giz2015-en-study-ods-banks-management.pdf. Accessed December 2022.

GIZ Proklima	2015	Management and destruction of existing ozone depleting substances in ODS banks	Overview study
GIZ Proklima	2018	Global banks of ozone depleting substances: A country-level estimate	Top-down estimate per country, using reported consumption data
GIZ Proklima	2020	Banks and Emission of CFC-11 and CFC-12: Country data and possible consequences for global modelling	Investigates country-research data on equipment and product lifetimes and their impact on global modelling
TEAP	2021	Decision XXXI/3 TEAP Task Force Report on Unexpected Emissions of CFC-11	Weibull function for probabilistic distribution of equipment/product lifetime replacing one average lifetime

The GIZ estimate of ODS banks covers CFC-11, CFC-12, HCFC-22, HCFC-141b, HCFC-142b and combines data on HFC banks retrieved from the Green Cooling Initiative Database (country-level RACHP sector data equipment estimates) and was published in 2018 (GIZ 2018).[269] The ODS banks are estimated using a country-based model, taking reported consumption per country up to 2014, attributing the consumption to instant release uses, RACHP, or foam sector. The applied top-down estimates for emission factors and equipment lifetime were informed by earlier work of TEAP.

Studies covering HFC banks are currently rare. The Green Cooling Database[270] (GIZ 2016) calculates RACHP sector HFC banks, which is the major bank-building use of HFCs. In addition, there are some national ODS/HFC banks inventories on Tier 2 level[271] that were carried out within GIZ Proklima projects that cover the RACHP sector.[272] Criteria for a potential funding window were developed for consideration by the Executive Committee (ExCom) of the Multilateral Fund (MLF) "*to provide Article 5 parties with assistance to prepare an inventory of banks of used or unwanted controlled substances and to develop a plan for the collection, transport, and disposal (including consideration of recycling, reclamation, and cost-effective destruction) of such substances*" (ExCom Decision 90/49(c)). Such inventories would support planning, implementation organisations, and the industry stakeholders in directing their efforts.

ExCom document UNEP/OzL.Pro/ExCom/91/66[273] identified that one of the main barriers for the successful implementation of the ODS disposal projects funded by the Multilateral Fund was the absence of a national inventory of the targeted waste substances, resulting in a discrepancy in the amounts of ODS targeted for destruction and the actual amounts destroyed. This demonstrated a lack of understanding on where the waste substances were, and how these could be collected. The paper developed criteria for a funding window to provide Article 5 parties with assistance in the development of inventories of banks of used or unwanted controlled substances and plans for the

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[269] Papst, I., 2018, *Global banks of ozone depleting substances: A country-level estimate*, G-S05-2017-en-01, GIZ, Eschborn, 2018. https://www.green-cooling-initiative.org/fileadmin/Publications/2018_Global_banks_of_ozone_depleting_substances.pdf. Accessed December 2022.

[270] GIZ, 2016, Green Cooling Database, www.green-cooling-initiative.org.

[271] Tier 2 level approach is where banks are calculated by a stock model on appliances in use per application

[272] ODS banks inventories were carried out in Colombia (https://www.international-climate-initiative.com/fileadmin/Dokumente/2018/180820_Bancos_de_SAO_y_HFC.pdf), Dominican Republic, Ghana, Iran (https://www.international-climate-initiative.com/legacy/Dokumente/2019/20190604_IRAN_ODS_Bank_Inventory_-_English_Version.pdf), Tunisia (https://www.international-climate-initiative.com/fileadmin/Dokumente/2018/180820_Results_of_the_national_inventory_of_ozone-depleting_substances_for_the_year_2015.pdf).

[273] Executive Committee of the Multilateral Fund, Meeting Document: UNEP/OzL.Pro/ExCom/91/66, *Criteria for a funding window for an inventory of banks of used or unwanted controlled substances and a plan for the collection, transport and disposal of such substances (Decision 90/49(c))*, 8 November 2022.

collection, transport, and disposal (including consideration of recycling, reclamation, and cost-effective destruction) of such substances (decision 90/49(c)). Decision 91/66 established a funding window for the preparation of national inventories of banks of used or unwanted controlled substances and plans for the collection, transport and disposal of such substances, including consideration of recycling, reclamation and cost-effective destruction; and agreed criteria and funding for the development of those national inventories and plans.[274]

Further guidance material on taking stock of ODS/HFC banks on a national basis and a roadmap for end-of-life banks management was prepared during a GIZ Proklima project that has been ongoing since 2014.[275]

Substantive research has been undertaken on CFC-11 banks in response to the detection of their unexpected emissions. The TEAP Taskforce on Unexpected Emissions of CFC-11 developed banks projection of CFC-11 using a Weibull function for probabilistic distribution of equipment and product lifetimes. This replaces the usual approach of using a single average lifetimes per category and results in a more realistic model of when equipment and products are decommissioned. Bank estimates are continuously refined as part of the on-going work of TEAP and its TOCs.

8.2.3 Estimates of ODS/HFC banks

The data presented below is composed of different data sets applicable to different controlled substances. While TEAP data provide more detail in terms of applications and regional distribution, other available datasets cover more substances. More research and better country data will refine the details of ODS/HFC bank distribution, but is unlikely to change the overall picture, which is described in the following section. An overall summary of presented substances is provided before presenting data per substance.

In total, a combined 6,000 ktonnes of ODS and HFC are contained in the active bank, equalling 16 $GtCO_2e$ (estimate for 2022, combined sources outlined below) (Figure 8.1 and 8.2).

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[274] Executive Committee of the Multilateral Fund, Meeting Document: UNEP/OzL.Pro/ExCom/91/72, Report of the Ninety-First Meeting of the Executive Committee, 9 December 2022.

[275] GIZ, 2017, *Global roadmap on ODS Bank Management*, 2017; *Guideline to conduct an ODS bank inventory*, 2017; *Guideline on policy measures for the management and destruction of ozone depleting substances*, 2017; *Guideline to establish a collection system for equipment containing ODS*, 2017; *Guideline for the transboundary movement of ODS waste*, 2017. Accessible at https://www.giz.de/en/worldwide/30797.html.

Figure 8.1 Total estimated ODS and HFC banks, several sources, 2010–2050 (ktonnes)

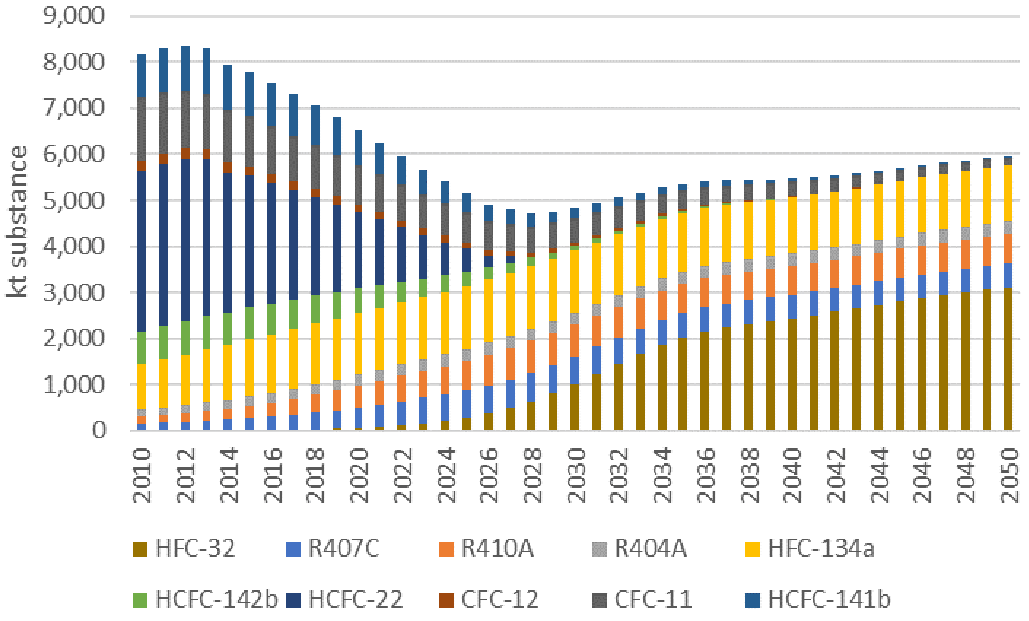
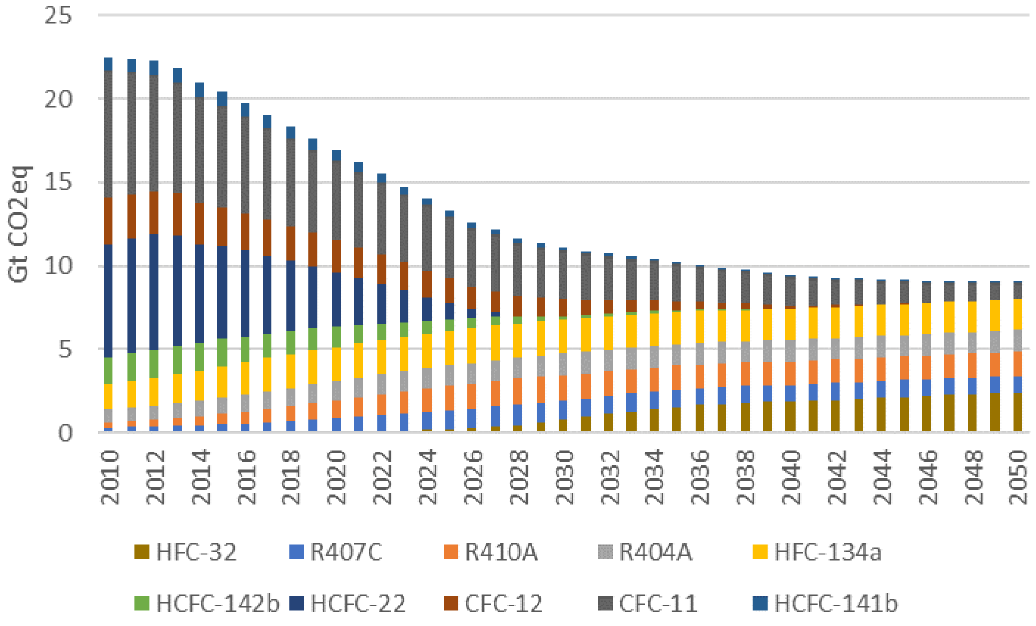


Figure 8.2 Estimated bank of ODS and HFCs, RACHP and foams sector combined, several sources, 2010–2050 in $GtCO_2e$ (GWP as in IPCC AR6)



Annual quantities of between 250 and 400 ktonnes (about 0.5 to 0.8 $GtCO_2e$) of ODS and HFCs are estimated to arise from decommissioning in the RACHP and foams sectors from 2020 to 2050 (Figure 8.3). Combined ODS and HFC annual decommissioning is estimated to start to peak in absolute amounts in the mid-2030s onwards, and peak in amounts by $GtCO_2e$ around 2035 (Figure 8.3 and 8.4).

Figure 8.3 Estimated ODS and HFC amounts being decommissioned, RACHP and foams sectors combined, several sources, 2010–2050 (ktonnes)

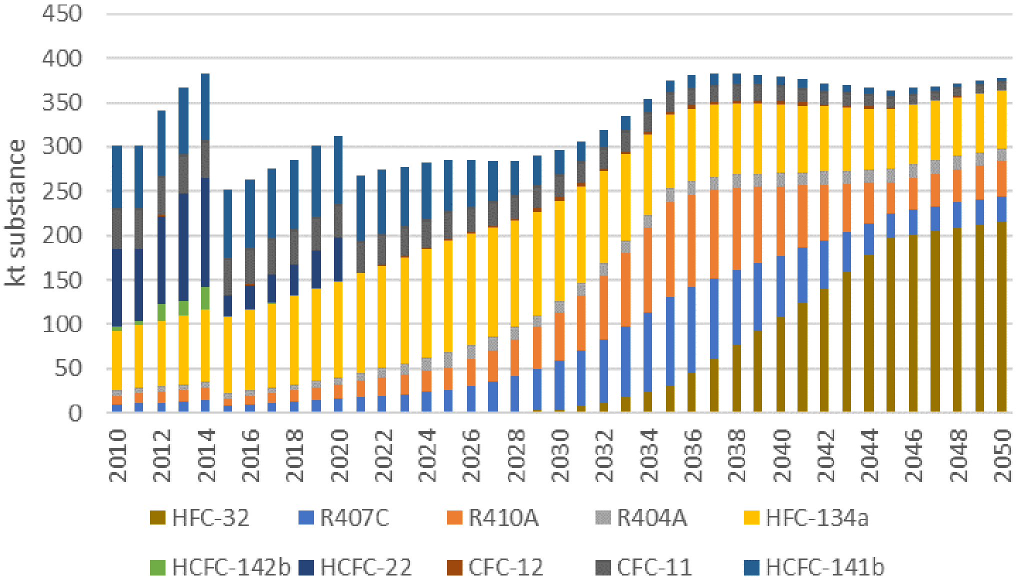
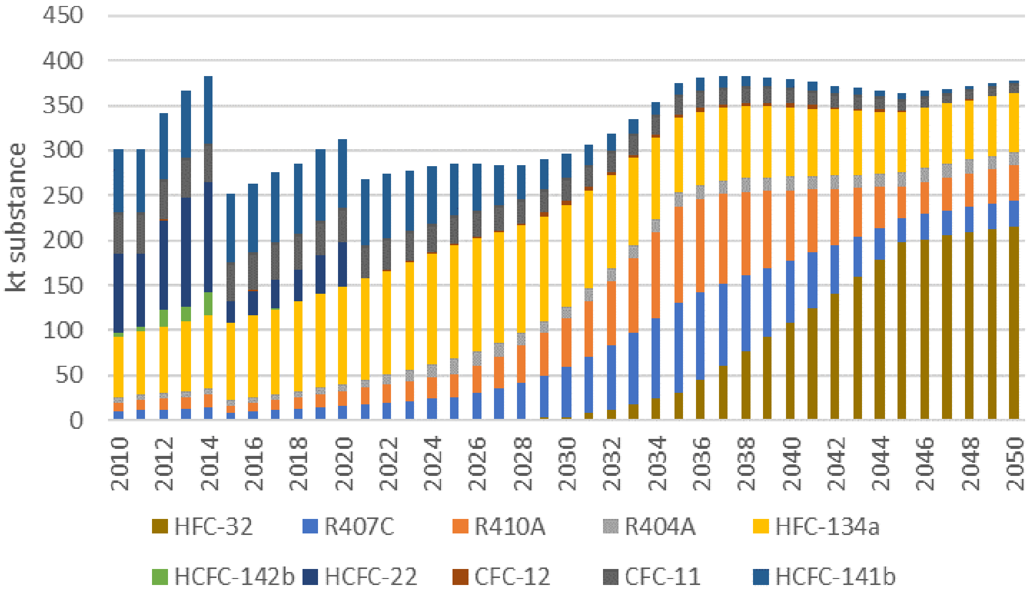


Figure 8.4 Estimated ODS and HFC amounts being decommissioned, RACHP and foams sector combined, several sources, 2010–2050 in $GtCO_2e$ (GWP as in IPCC AR6)



Active global ODS banks of the 5 most common ODS (CFC-11, CFC-12, HCFC-22, HCFC-141b, HCFC-142b) amount to 3,200 ktonnes substance, equivalent to 9.9 $GtCO_2e$ in 2022 (see Figure 8.1 and 8.2). There is a rapid decrease as ODS-containing equipment and products are reaching their end-of-life each year. The 5 most common ODS being decommissioned are estimated at 110 ktonnes (0.27 $GtCO_2e$) in 2022.

Active HFC banks in the RACHP sector, which is the predominant usage of HFCs, are estimated at 2,800 ktonnes (5.5 $GtCO_2e$) in 2022 and 3,900 ktonnes (6.8 $GtCO_2e$) in 2030 (Green Cooling Database, GIZ 2016[270]).

While ODS banks have been more concentrated in non-Article 5 parties, HFC banks are currently more evenly distributed between non-Article and Article 5 parties and are expected to become concentrated in Article 5 parties.

Given the long period since the CFC phase-out in non-Article 5 parties, where most of the CFCs were used, CFC banks are largely emitted except for in-service building insulation foam and unreachable foam waste disposed in landfill. Several countries require by regulation that building foam is removed from the building prior to demolition and is then destroyed, including the blowing agent.[276] The largest current ODS bank in foam is constituted of HCFCs, particularly HCFC-22 (mostly within RACHP equipment), but also HCFC-141b and HCFC-142b mostly contained in foam products.

Sensitivity analysis shows that assumptions on equipment lifetime have a strong impact on the decline rate of banks; if equipment lifetimes are longer – and country-specific studies imply that – the decline rate of banks is lower, resulting in more time until the opportunity to have capacity in place to recover ODS at end-of-life and prevent emissions.[277] On the other hand, as equipment lifetime is a distribution rather than a single value, some equipment will reach EOL earlier, requiring capacity at earlier stages. With HFC banks building up, the challenge of dealing with active banks responsibly persists, even as HCFCs are phased out.

8.2.3.1 CFC-11 banks and amounts reaching end-of-life

The total active and inactive CFC-11 banks (foams, refrigerants, and storage) are estimated to be 1,500 ±100 kilotonnes in 2021. The total active CFC-11 bank is estimated to be 800 ±50 kilotonnes, 3.8 $GtCO_2e$, in 2021.[278] As illustrated in Figure 8.5, the majority of remaining active CFC-11 bank is within construction foam, mostly located in non-Article 5 parties.

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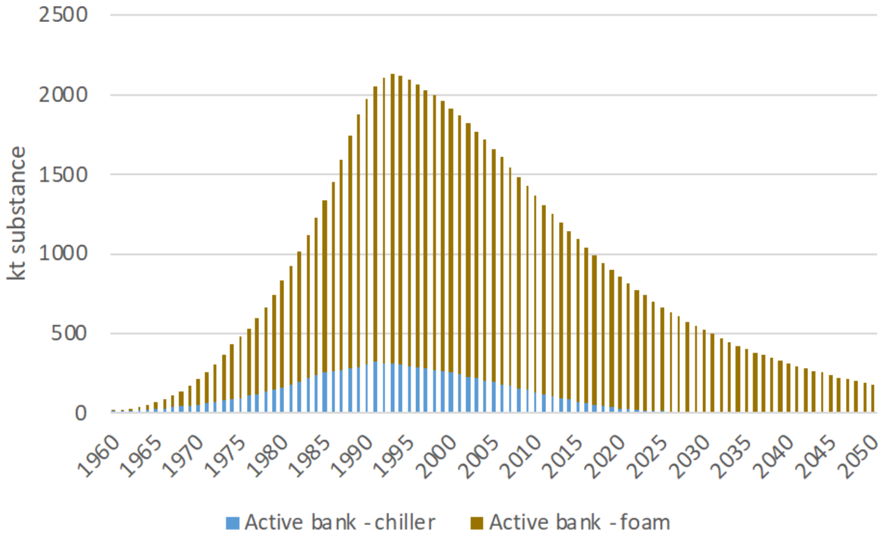
[276] Papst, I., 2020, *Banks and Emissions of CFC-11 and CFC-12: Country data and possible consequences for global modelling*, GIZ, Eschborn, 2020. https://www.green-cooling-initiative.org/fileadmin/Publications/2020_ODS_CFC11_CFC12-banks.pdf. Accessed December 2022.

[277] UNEP, 2021, *Report of the Technology and Economic Assessment Panel, Volume 3: Decision XXXI/3 Task Force Report on Unexpected Emissions of Trichlorofluoromethane (CFC-11),* May 2021.

Papst, I., 2020, *Banks and Emissions of CFC-11 and CFC-12: Country data and possible consequences for global modelling*, GIZ, Eschborn, 2020. https://www.green-cooling-initiative.org/fileadmin/Publications/2020_ODS_CFC11_CFC12-banks.pdf. Accessed December 2022.

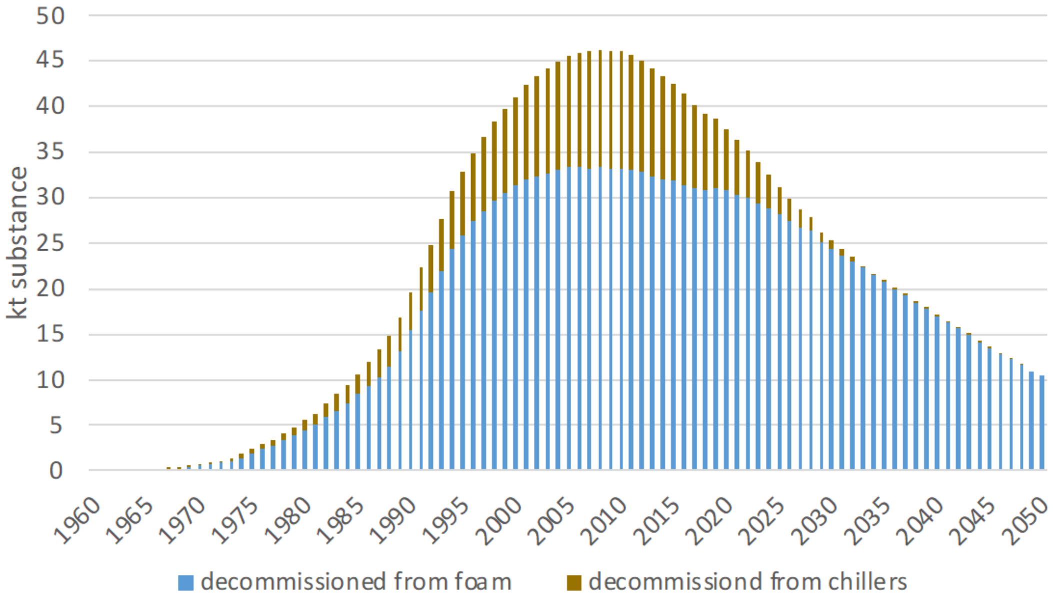
[278] UNEP, 2021, *Report of the Technology and Economic Assessment Panel, Volume 3: Decision XXXI/3 Task Force Report on Unexpected Emissions of Trichlorofluoromethane (CFC-11),* May 2021.

Figure 8.5 Estimated active CFC-11 bank, 1960–2050 (ktonnes) (TEAP 2022[279])



The global peak of the CFC-11 decommissioned from the largest portion of active banks, i.e., all foams in products at end-of-life, is estimated to have occurred around the year 2010, at about 45 ktonnes/year, and then subsequently decreases slowly over time to currently approximately 35 ktonnes/year and projected to reach under 10 ktonnes/year by 2050 (Figure 8.6). These global peaks are dominated by the foam banks, foam products, and decommissioning patterns in the United States and Europe, owing to their overwhelming size.

Figure 8.6 Estimated CFC-11 being decommissioned, 1960–2050 (ktonnes) (TEAP 2022)



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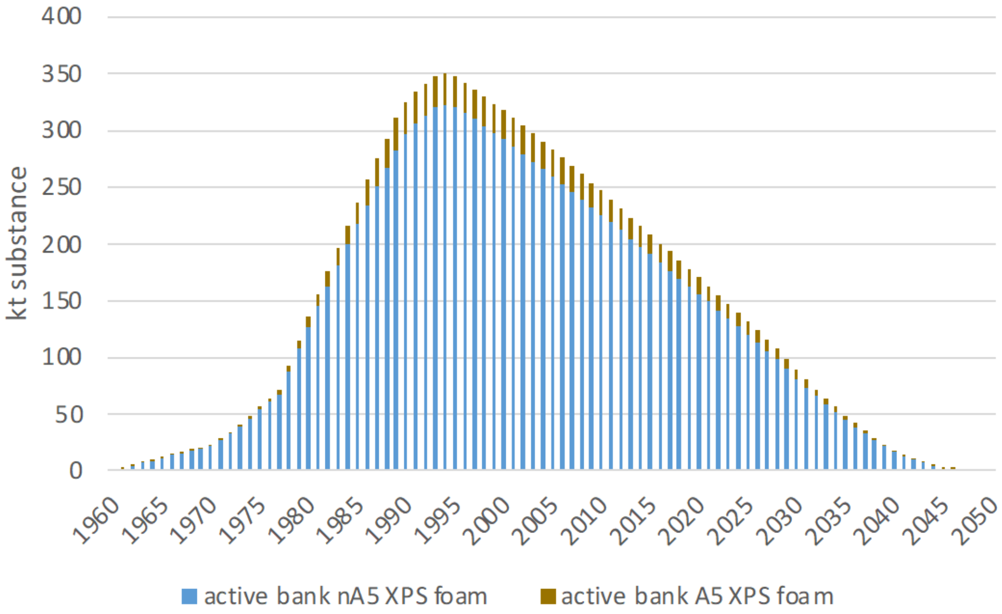
[279] TEAP, 2022, Personal communications with Helen Walter-Terrinoni, FTOC co-chair.

8.2.3.2 *CFC-12 banks and amounts reaching end-of-life*

Historically, CFC-12 banks were composed of refrigerants and foam-blowing agents. While CFC-12 refrigerant banks are believed to have reached their end-of-life, the remaining bank is in foams. The CFC-12 foam bank is much smaller than the CFC-11 foam bank and mainly found in XPS-foams used for construction in non-Article 5 parties.

Figure 8.71 Estimated active CFC-12 bank in XPS Foam, 1960–2050 (ktonnes) (GIZ 2020[280])



Due to the long lifetimes of buildings, the majority of CFC-12 containing foams are expected to be decommissioned in the 2030s (Figure 8.8).

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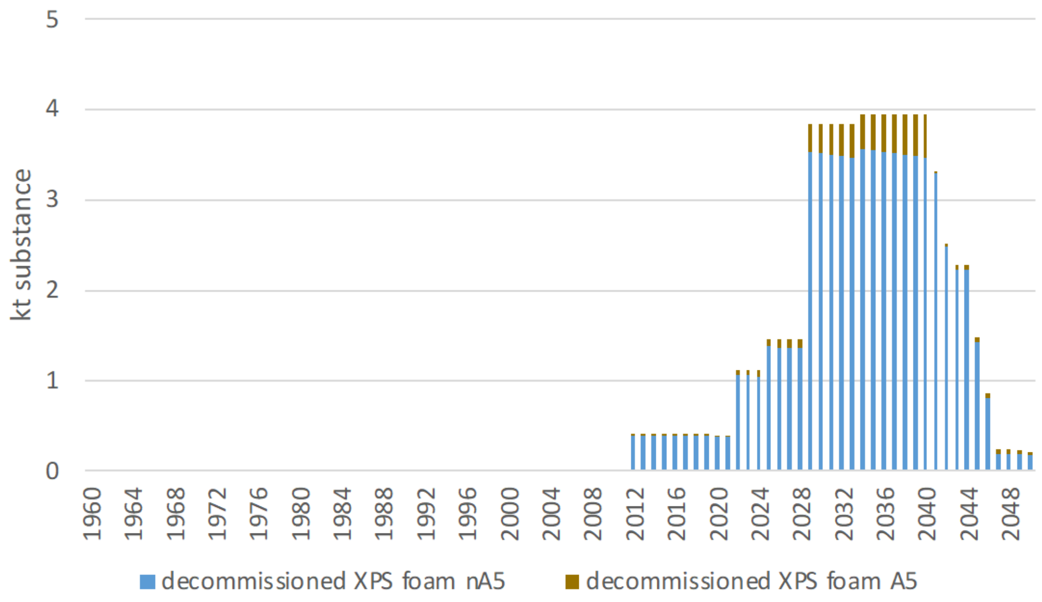
[280] Papst, I., 2020, *Banks and Emissions of CFC-11 and CFC-12: Country data and possible consequences for global modelling*, GIZ, Eschborn, 2020. https://www.green-cooling-initiative.org/fileadmin/Publications/2020_ODS_CFC11_CFC12-banks.pdf. Accessed December 2022.

Figure 8.8 Estimated CFC-12 being decommissioned from XPS foam, 1960–2050 (ktonnes) (GIZ 2020[281])



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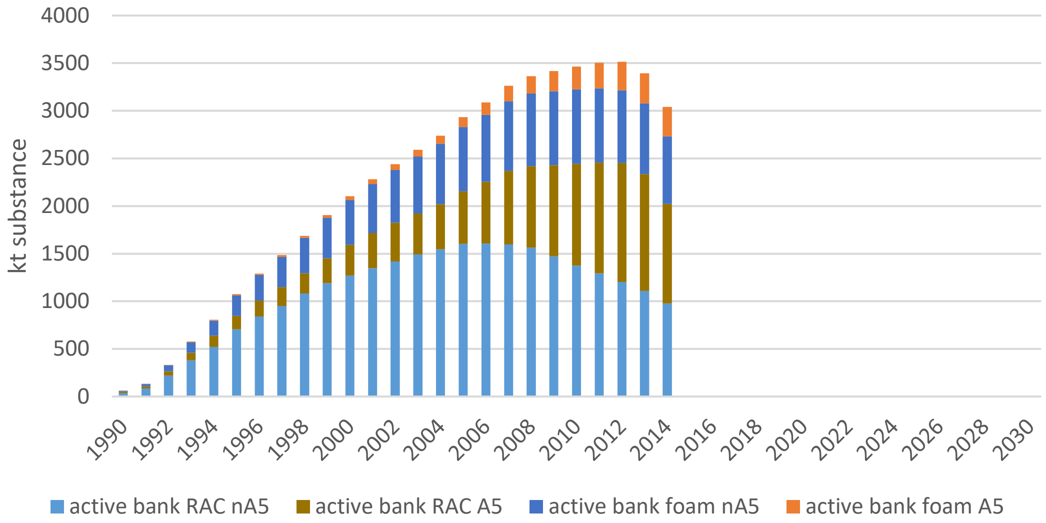
[281] Ibid., Papst, I., 2020. GIZ.

8.2.3.3 HCFC-22 banks and amounts reaching end-of-life

HCFC-22 is mainly used as refrigerant, which constitutes the main bank of HCFC-22. An analysis made in 2018 uses consumption data up to 2014 and shorter equipment lifetimes than were used in more recent models (GIZ 2018[282] and GIZ 2020[283]). The longer equipment lifetimes used in the later study means that the steep downward trend after 2012 that is shown in Figure 8.9 might not be as steep as indicated, resulting in a longer prevalence of active banks after 2030.

Figure 8.9 Estimated active HCFC-22 bank, 1990–2014 (ktonnes) (GIZ 2018)



HCFC-22 being decommissioned was not modelled for a time series after 2020, when amounts in Article 5 parties were estimated to be around 40 ktonnes, with a rising tendency.

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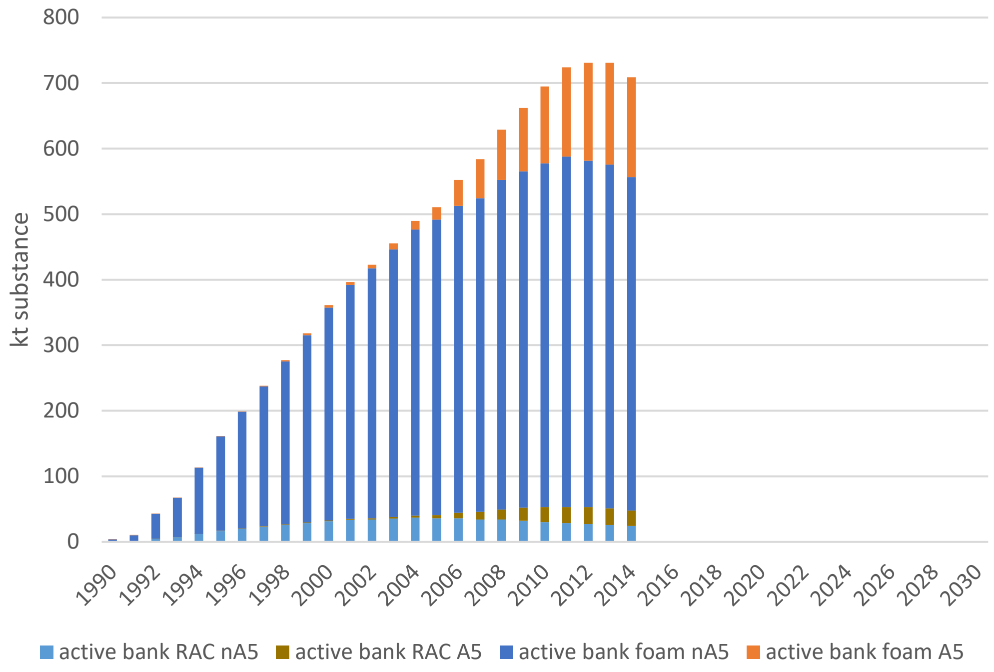
[282] Papst, I., 2018, *Global banks of ozone depleting substances: A country-level estimate*, G-S05-2017-en-01, GIZ, Eschborn, 2018. https://www.green-cooling-initiative.org/fileadmin/Publications/2018_Global_banks_of_ozone_depleting_substances.pdf. Accessed December 2022.

[283] Papst, I., 2020, *Banks and Emissions of CFC-11 and CFC-12: Country data and possible consequences for global modelling*, GIZ, Eschborn, 2020. https://www.green-cooling-initiative.org/fileadmin/Publications/2020_ODS_CFC11_CFC12-banks.pdf. Accessed December 2022.

8.2.3.4 HCFC-142b banks and amounts reaching end-of-life

HCFC-142b is mainly used as a foam blowing agent, which constitutes the main bank of HCFC-142b. Most of the HCFC-142b bank is in non-Article 5 parties. Analysis dates from 2018, using consumption data up to 2014, with a tendency to use shorter product lifetimes than is used in more recent models (GIZ 2018) (Figure 8.10).[284] With longer lifetimes, this means that foams containing HCFC-142b might be expected to reach decommissioning also well after 2050.

Figure 8.10 Estimated active HCFC-142b bank, 1990–2014 (ktonnes) (GIZ, 2018)



HCFC-142b being decommissioned was not modelled for a time series after 2020, when amounts in Article 5 parties were estimated to be around 26 ktonnes, with a rising tendency.

8.2.3.5 HCFC-141b banks and amounts reaching end-of-life

Most of the active bank of HCFC-141b is in construction foams. This has recently shifted, as foams in refrigeration equipment containing HCFC-141b are decommissioned and the blowing agent is either released or added to the inactive bank. The global active bank peak is now estimated to have occurred, with continued decommissioning of appliances and buildings that contain HCFC-141b being greater than new HCFC-141b usage to create new foams (Figure 8.11). The timing of the global peak quantities from decommissioning of foams containing HCFC-141b is estimated to occur over the next 5 years (Figure 8.12).[285]

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[284] Ibid., Papst, I., 2018. GIZ.

[285] UNEP, 2022, *Report of the Technology and Economic Assessment Panel, Volume 1, Progress Report*, May 2022.

Figure 8.11 Estimated active bank of HCFC-141b, 1990–2050 (ktonnes) (TEAP, 2022)

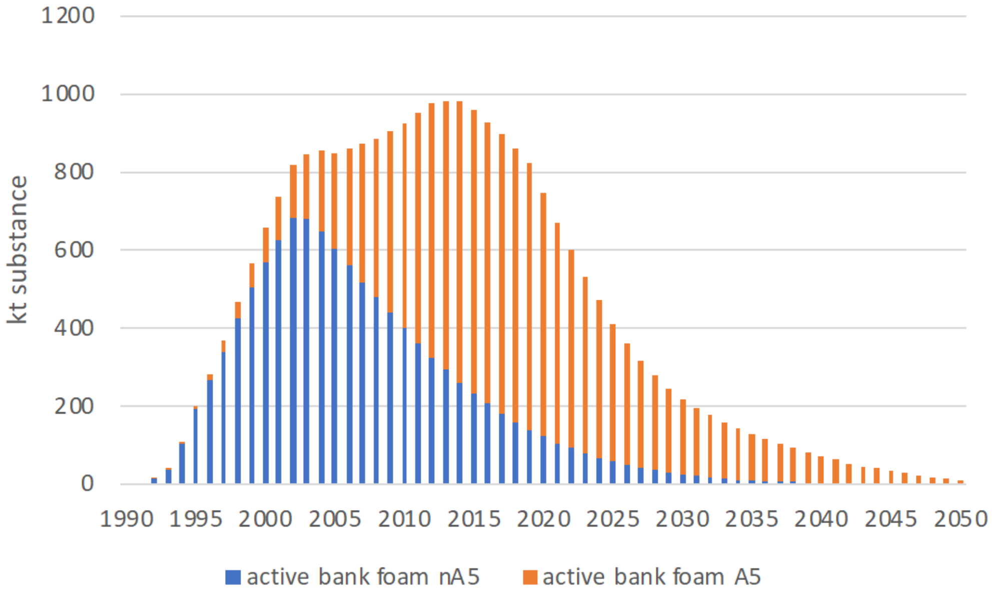
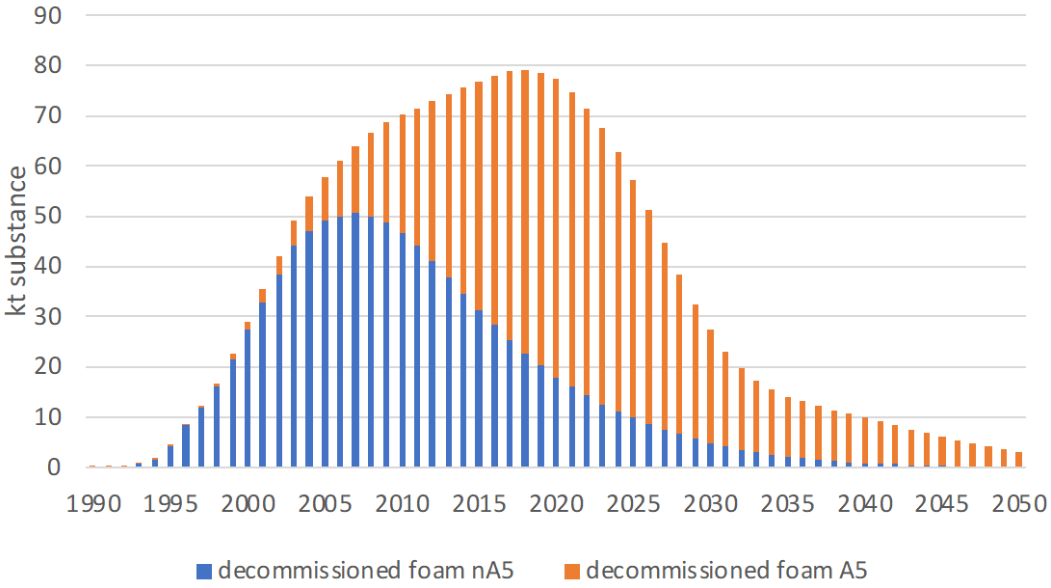


Figure 8.12 Estimated HCFC-141b being decommissioned, 1989–2050 (ktonnes) (TEAP, 2022)



8.2.3.6 HFC bank

Bank estimates for HFC-134a, HFC-32, R-404A, R-407C, and R-410A within the RACHP sector were estimated previously using the database of the Green Cooling Initiative (GIZ 2016); the results of this study are presented in the sections below.[286]

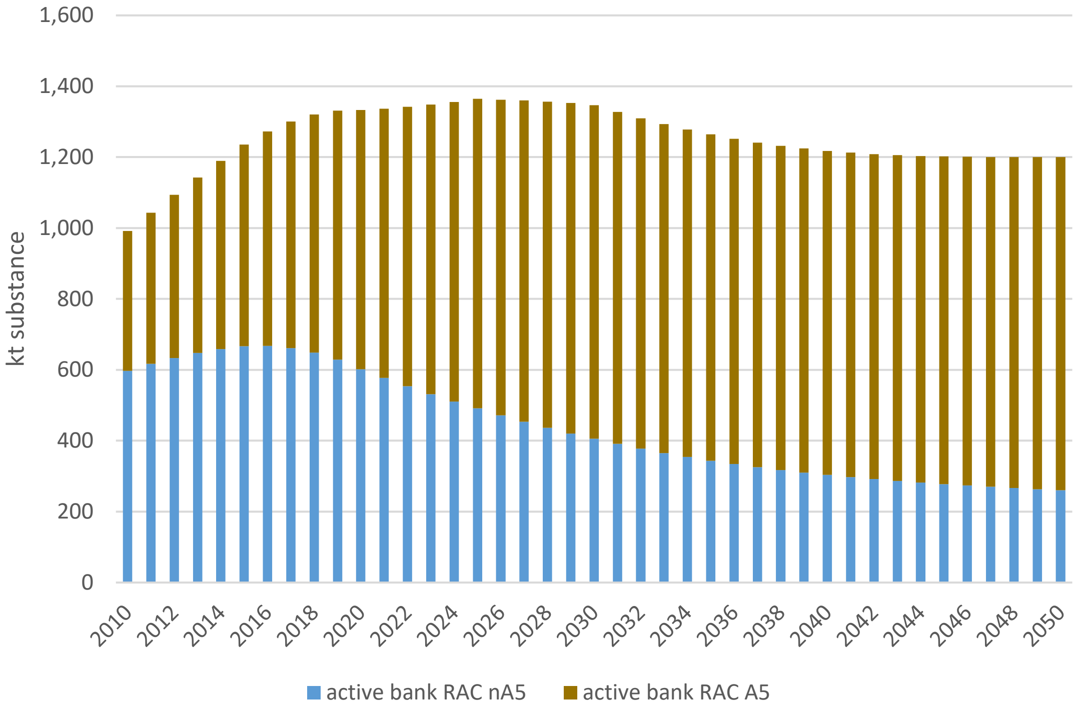
The database employs a top-down Tier 2 approach, where banks are calculated by a stock model on appliances in use per application (19 applications of RACHP equipment in total), projecting RACHP equipment sales and stock up to 2050, deducting banks and emissions using country group specific (non-Article 5 and Article 5) assumptions. As the database and its projections date from 2016, the provisions of the Kigali Amendment were not taken into consideration. However, the effect of the European F-gas Regulation (515/2014) was considered. Nevertheless, the 2016 analysis remains pertinent because the Kigali Amendment is unlikely to significantly change the estimated absolute amounts (in metric tonnes) of refrigerants of any sort that are banked; the Kigali Amendment will have a long-term effect in lowering the GWP (in CO_2e) of the substances that are banked.

Bank estimates of HFCs in foam banks are not currently available.

8.2.3.7 HFC-134a banks and amounts reaching end-of-life

Since HFC-134a is used in several RACHP applications and was introduced during the CFC phase-out, the bank was estimated to be comparably large at approximately 1,300 ktonnes (2 $GtCO_2e$) and almost equally distributed between non-Article 5 and Article 5 parties in 2022 (Figure 8.13).

Figure 8.13 Estimated active bank of HFC-134a, 2010–2050 (ktonnes) (GIZ, 2016)



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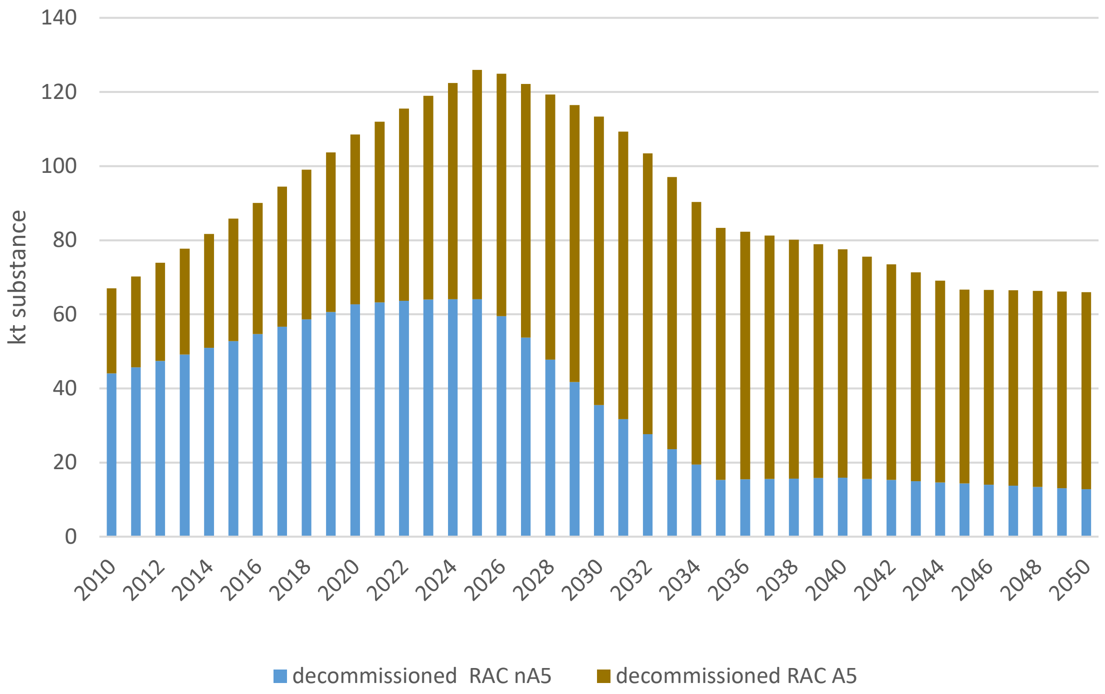
[286] GIZ, 2016, Green Cooling Database, www.green-cooling-initiative.org.

Annual amounts reaching the end-of-life are currently larger in non-Article 5 parties (ca. 64 ktonnes), with Article 5 parties catching up and exceeding the amounts reaching end-of-life in non-Article 5 parties in the coming decade (ca. 78 ktonnes in 2030) (Figure 8.14).

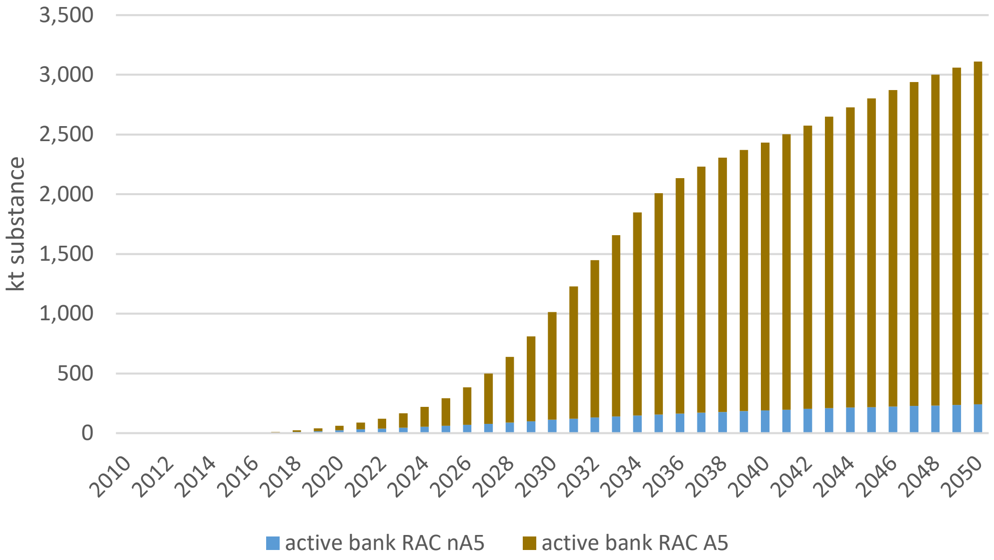
Figure 8.14 Estimated HFC-134a being decommissioned, 2010–2050 (ktonnes) (GIZ, 2016)



8.2.3.8 HFC-32 banks and amounts reaching end-of-life

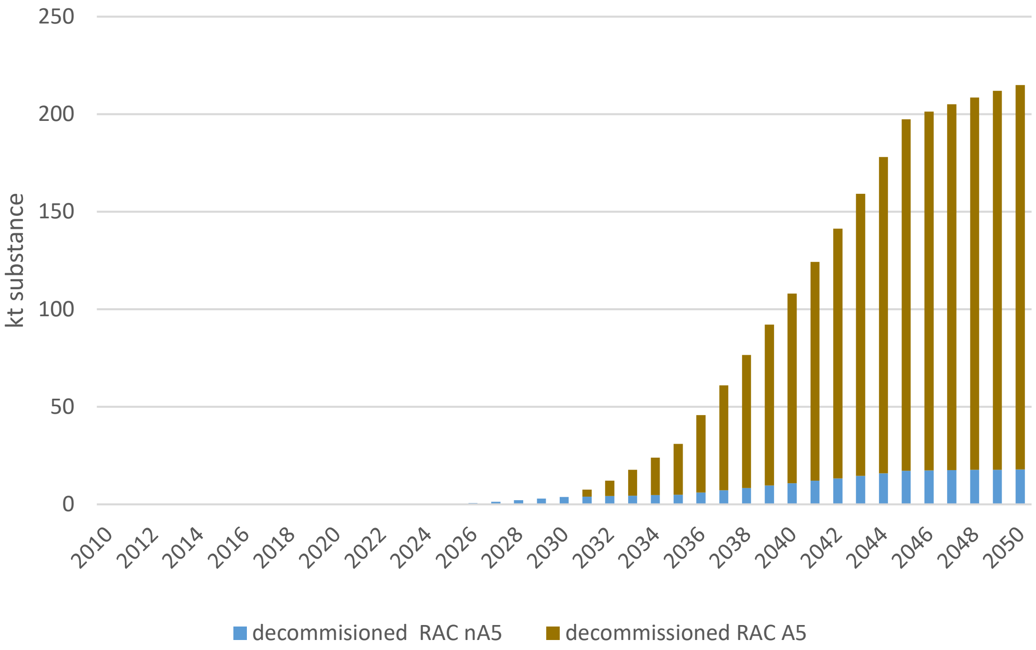
The use of pure HFC-32 as refrigerant is a comparatively recent development, which is reflected in the bank projections, showing a steep increase beyond 2030 in this study, especially in Article 5 parties. The total global active bank of HFC-32 was estimated to be 1,000 ktonnes (780 MMTCO$_2$e) in 2030 (Figure 8.15) (GIZ 2016). With the effect of the Kigali Amendment taken into consideration, trends for HFC-32 are now likely to differ from those projected in this study. Due to the HFC phase-down, HFC-32 is increasingly replacing the R-410A in the same RACHP applications. This trend was not apparent when the original study was undertaken. Nevertheless, the Kigali Amendment is unlikely to significantly change the estimated absolute amounts (in metric tonnes) of banked refrigerants.

Figure 8.15 Estimated active bank of HFC-32, 2010–2050 (ktonnes) (GIZ, 2016)



Tangible amounts of HFC-32 from decommissioned equipment are expected to be available for management from 2030 onwards (Figure 8.16).

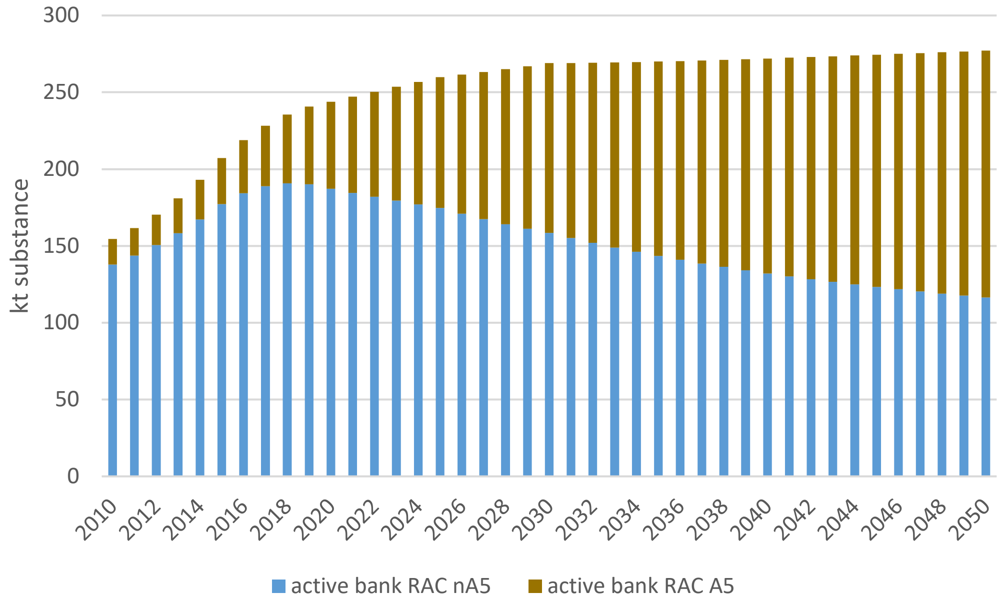
Figure 8.16 Estimated HFC-32 being decommissioned, 2010–2050 (ktonnes) (GIZ, 2016)



8.2.3.9 R-404A (HFC blend) banks and amounts reaching end-of-life

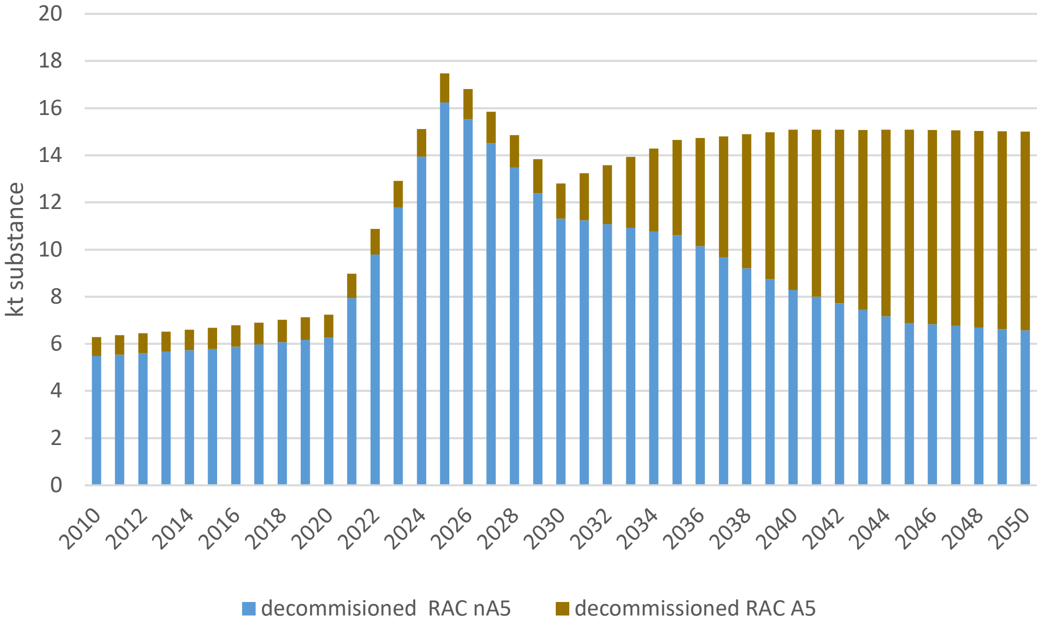
R-404A, an HFC blend of HFC-125, HFC-134a, and HFC-143a, was primarily used to replace R-502 (a blend of HCFC-22 and CFC-115) and HCFC-22 in low and medium temperature refrigeration applications and has been predominantly in banks in non-Article 5 parties, with a trend to increasing banks in Article 5 parties. The total global active bank of R-404A was estimated to be 250 ktonnes (1.2 $GtCO_2e$) in 2022 (Figure 8.17) (GIZ 2016). With the effect of the Kigali Amendment taken into consideration, trends for R-404A are now likely to differ from those projected in this study. Due to the HFC phase-down, R-404A is now being replaced by lower GWP refrigerants. Nevertheless, the Kigali Amendment is unlikely to significantly change the estimated absolute amounts (in metric tonnes) of banked refrigerants.

Figure 8.17 Estimated active bank of R-404A, 2010–2050 (ktonnes) (GIZ, 2016)



The projected amounts available at decommissioning show some dynamic resulting from the transition to other refrigerants in non-Article 5 parties. Due to this transition, available amounts from decommissioning are expected to peak before 2030 (Figure 8.18).

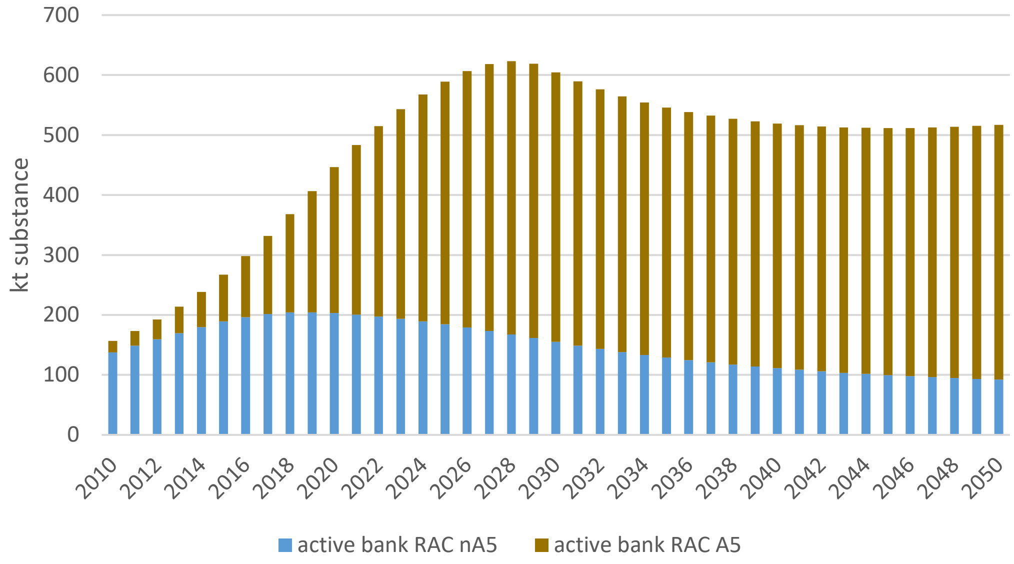
Figure 8.18 Estimated R-404A being decommissioned, 2010–2050 (ktonnes) (GIZ, 2016)



8.2.3.10 R-407C (HFC blend) banks and amounts reaching end-of-life

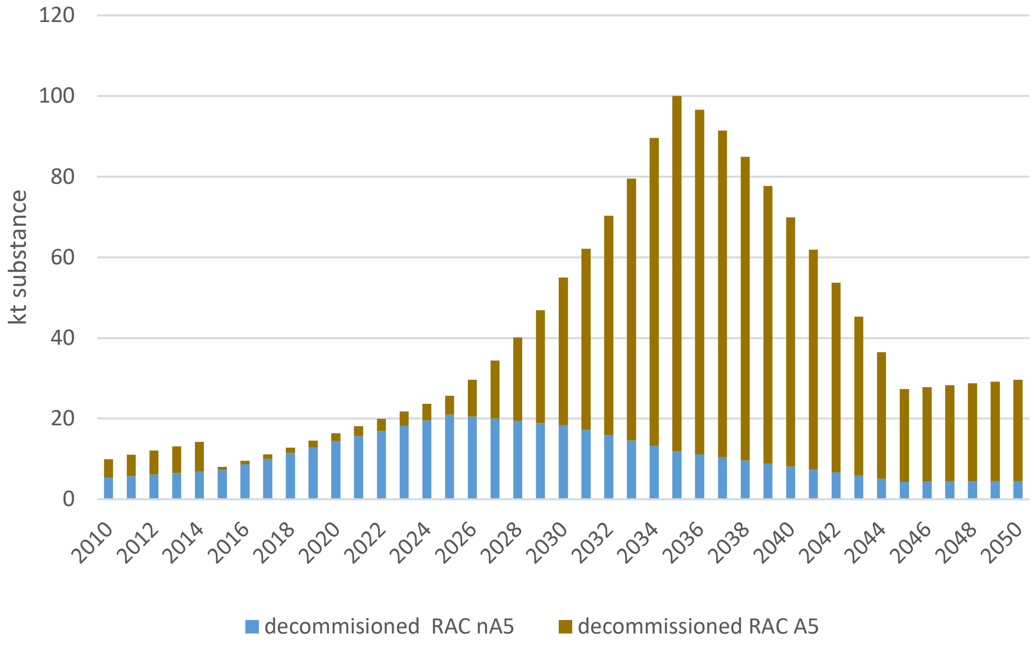
R-407C, an HFC blend of HFC-32, HFC-125 and HFC-134a, is used in air conditioning applications. Similar to R-410A, R-407C banks exhibit a similar trend, with almost equal bank distribution estimated in non-Article 5 and Article 5 parties in 2022, with a trend towards an increasing bank in Article 5 parties. The total global active bank of R-407C was estimated to be 510 ktonnes (980 $MMTCO_2e$) in 2022 (Figure 8.19) (GIZ, 2016). With the effect of the Kigali Amendment taken into consideration, trends for R-407C are now likely to differ from those projected in this study. Due to the HFC phase-down, R-407C is now being replaced by lower GWP refrigerants. Nevertheless, the Kigali Amendment is unlikely to significantly change the estimated absolute amounts (in metric tonnes) of banked refrigerants.

Figure 8.19 Estimated active bank of R-407C, 2010–2050 (ktonnes) (GIZ, 2016)



Expected amounts of substance from decommissioned equipment are projected to increase in the 2030s, predominantly in Article 5 parties (Figure 8.20).

Figure 8.20 Estimated R-407C being decommissioned, 2010–2050 (ktonnes) (GIZ, 2016)

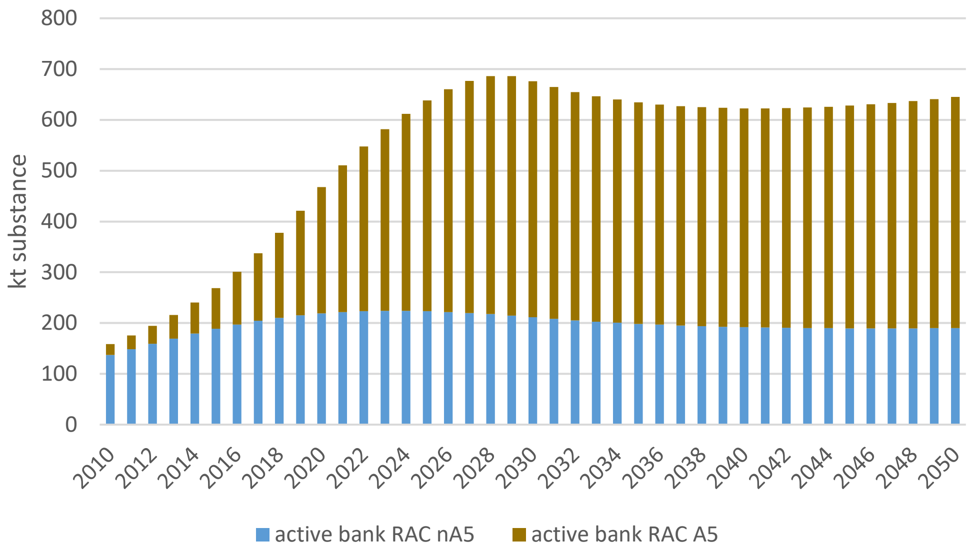


8.2.3.11 R-410A (HFC blend) banks and amounts reaching end-of-life

R-410A, an HFC blend of HFC-32 and HFC-125, is used increasingly in non-Article 5 parties, as air conditioning equipment transitions away from HCFC-22. The total global bank was estimated to be

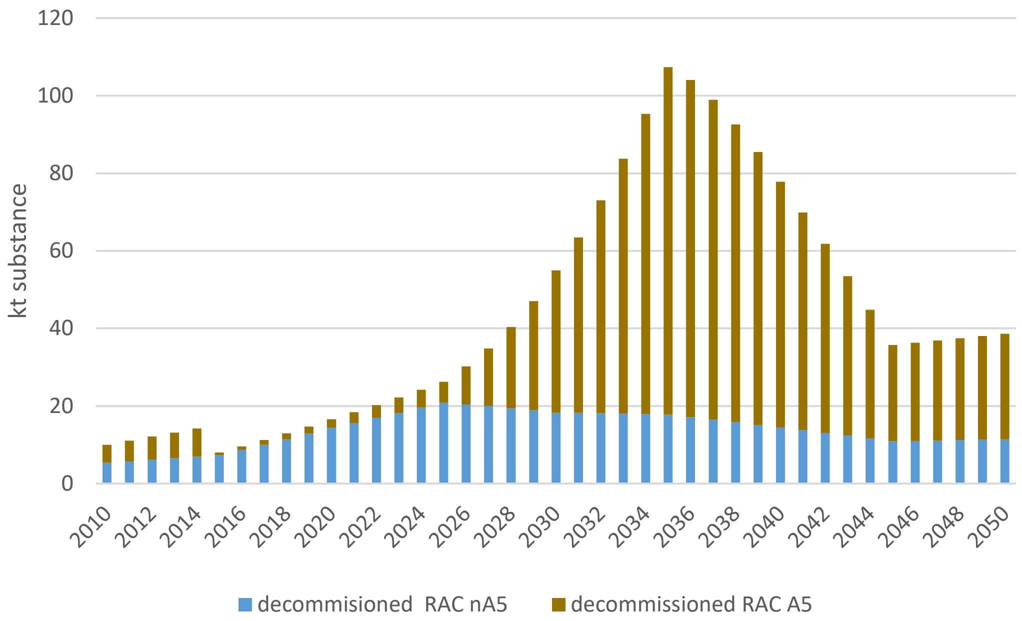
550 ktonnes (1.2 $GtCO_2e$) in 2022 (Figure 8.21) (GIZ, 2016). With the effect of the Kigali Amendment taken into consideration, trends for R-410A are now likely to differ from those projected in this study. Due to the HFC phase-down, R-410A is now being replaced by lower GWP refrigerants, in particular HFC-32. Nevertheless, the Kigali Amendment is unlikely to significantly change the estimated absolute amounts (in metric tonnes) of banked refrigerants.

Figure 8.21 Estimated active bank of R-410A, 2010–2050 (ktonnes) (GIZ, 2016)



The estimated amounts of R-410A from decommissioned equipment follow the increasing trend of the bank, peaking in the 2030s (Figure 8.22).

Figure 8.22 Estimated R-410A being decommissioned, 2010–2050 (ktonnes) (GIZ, 2016)



8.2.4 ODS/HFC banks outlook

With the ongoing transition in Article 5 parties from HCFCs to HFCs and other alternatives, the (refrigerant) amounts of HCFCs available for end-of-life treatment are expected to increase. Non-Article 5 parties are confronted with both HCFCs and HFCs reaching end-of-life. The shift from HCFCs to high GWP HFCs marks a transition from ozone depletion to climate change issues because HFC emissions are reported under national greenhouse gases and are potentially part of nationally determined contributions (NDCs).

The largest banks overall are currently in non-Article 5 parties and will rapidly reach end-of-life in the next decade. If not recovered and responsibly managed as a priority, they will likely be emitted, as happened with CFC banks before them. Accelerated action on the management of EOL ODS/HFCs might increasingly be considered a priority under national greenhouse gas emissions mitigation objectives, especially where there might be currently low rates of recovery and destruction.

Banks in Article 5 parties are currently smaller but growing rapidly and will dominate global banks volumes by the early 2030s. This will be the result of declining banks in non-Article 5 parties and the rapid uptake of HFC-containing equipment in Article 5 parties, occurring with the completion of HCFC phase-out.

Quantities potentially available for recovery and management are expected to increase in Article 5 parties due to the ongoing HCFC phase-out and the later HFC phase-down. Timely efforts to establish effective EOL management capacity to prevent HFC emissions would have a significant impact, given the predicted size and growth of these banks in larger industrialised Article 5 parties.

With improved economies of scale, through the recovery of increased quantities of ODS/HFCs, the anticipated cost per kg of recovered controlled substances for EOL management could be reduced, or minimised, assuming infrastructure is available and investment in EOL management has been made within a supportive policy framework.

Country-specific studies may be needed to investigate and understand local capabilities, organisational arrangements, structures and relationships of refrigerant importers and distributors, and national refrigeration service providers, who usually carry out recovery and collection irrespective of the source of financing.

8.3 Implementation of EOL ODS/HFC management

8.3.1 EOL ODS/HFC banks management

Effective management of accumulated ODS and HFC active banks, by maximising recovery, recycling, reclamation, reuse, and ultimately destruction after all other options have been exhausted, can minimise the global impacts associated with the potential release of emissions at EOL. By maximising recovery, recycling, reclamation and reuse, effective banks management can limit the amounts of controlled substances that would otherwise require destruction and minimise associated costs. Furthermore, for the RACHP sector, effective HFC bank management can also minimise the amounts of controlled substances (virgin refrigerant) that is newly manufactured, minimising overall HFC emissions, and can also aid parties in managing their HFC phase-down targets.

Effective banks management need not be limited to ODS and HFCs. The phase-down of HFCs, and/or the leapfrogging of HFC technologies, will result in increasing banks of other alternative refrigerants and foam blowing agents. HFOs and HCFOs are being used to replace HFCs in some applications, although they are not controlled substances under the Montreal Protocol. Leap-frogging HFC-based equipment into these and other low GWP alternatives contributes to active HFC bank prevention, reducing the quantity of HFCs and the GWP of the bank requiring future EOL management. Nevertheless, resource efficiency and circular economy requirements suggest that effective bank management may also be appropriate for these low GWP alternatives. The breakdown of some HFOs/HCFOs results in the formation of different yields of trifluoroacetic acid (TFA) (see section 2.7.4). In addition, there may be a significant bank of equipment containing hydrocarbons by 2050.

Banks management discussed here is directed towards two main sectors[287], the RACHP and the foams sectors. The RACHP sector deals with refrigerant recovery from concentrated sources. The foams sector deals with recovery of blowing agent from foams, which are dilute sources, where the controlled substance is embedded in the foam product in relatively low mass concentrations relative to the overall product mass. Different approaches to EOL ODS/HFC management are required depending on the concentrated or dilute form in which it appears at end of life, with consequential differences in regulatory requirements, infrastructure, economic factors, and destruction technology requirements.

8.3.2 Management of concentrated EOL ODS/HFC

For the RACHP sector, there are basic measures that can be taken at the source:

1. Promoting on-site recovery and recycling, where technically feasible, meaning, to fill the refrigerant back into the same system after servicing or repairing the system. This can involve a basic cleaning of the refrigerant that can be done on-site to remove water, oil, and particles. On-site recycling is critical to the maintenance and service of RACHP equipment during its lifetime to avoid emissions. The technical skills, equipment, and infrastructure are the same as those required for EOL recovery and recycling.

2. Promoting on-site recovery of controlled substances for subsequent off-site reclamation utilising specialised equipment. Similar to recycling, reclamation allows the reuse of the used controlled substance for servicing existing equipment and in new equipment (where permissible).

3. Transitioning as rapidly as practical away from controlled substances where suitable lower GWP alternatives exist. This could limit the amount of EOL ODS/HFCs requiring management.

From a general resource utilisation efficiency perspective, recycling and/or reclamation are preferable in comparison with destruction, as recycling and/or reclamation reduces the amount of virgin refrigerant required (unless the destruction process can recover basic chemicals such as hydrogen fluoride for further reuse in a beneficial way). However, destruction is the ultimate end-of-life phase for refrigerants, thereby minimising emissions.

Reclamation is the reprocessing and upgrading of recovered controlled substance through such mechanisms as filtering, drying, distillation, and chemical treatment, to restore the substance to a specified standard of performance. It often involves processing “off-site” at a central facility.

Reclamation requires a managed returnable cylinder/container infrastructure to return recovered refrigerant to a central facility. Such a system is typically integrated into refrigerant supply infrastructure and is most effective when returnable containers are mandated, and non-refillable (disposable) containers are prohibited. However, in some settings, such as very low refrigerant use or widely dispersed low density of equipment, the banning of disposable cylinders can be more challenging than in densely populated areas.

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[287] Banks and EOL Halons management is described in detail in the UNEP, 2022, *2022 Report of the Fire Suppression Technical Options Committee, 2022 Assessment Report.*

In some countries, there is developing capability to separate mixtures of refrigerants for reuse, for example by distillation, lower GWP refrigerant components from higher GWP HFCs, with the option of destroying the high GWP HFCs if no longer required.

Where recovered refrigerants are not suitable for reclamation then destruction becomes the only option to avoid emissions. To achieve sufficient quantities for economic destruction, the overall infrastructure for supply and return of refrigerants needs to be readily adaptable and expandable to collect and securely store EOL ODS/HFCs for refrigerant destruction. The 2022 RTOC Assessment Report includes Chapter 13, which discusses servicing and refrigerant conservation.

8.3.3 Management of dilute EOL ODS/HFC

For dilute EOL ODS/HFC, primarily insulating foams from refrigeration appliance and building construction, but also packaging and automotive foam applications, different sets of challenges exist in EOL management. With the transition away from ODS and HFC as blowing agents in many applications, the issue concerns a large existing bank that is reaching its EOL, although this is projected to decline in the future due to effective global transition to low GWP blowing agents.

Historically these foam product waste streams have mostly been part of the general solid waste stream that has utilised land disposal or open burning in some cases. In general, recovery and EOL treatment, largely through some form of thermal destruction, requires several steps starting with separation from the general solid waste stream, either at source or prior to conventional solid waste disposal. This results in a higher solid waste unit cost relative to current land disposal. Given the relatively low proportion of controlled substances within the overall foam product waste volume, low returns are realised in terms of amount recovered for EOL ODS/HFCs per volume handled. The net overall cost/kg of ODS/HFC recovery and destruction is consequently much higher than for concentrated EOL ODS/HFCs. This is compounded by high emission rates of blowing agents during handling and size reduction inherent in the largely manual process required to transport and prepare it for destruction. Alternatively, the extraction of blowing agent can be done in a closed environment but this is also not necessarily cost effective. The net result is poor cost and operational efficiency compared with concentrated ODS/HFC in EOL management in terms of mitigating emissions. This also makes management of dilute waste streams a less attractive target for carbon finance mechanisms.

Refrigeration appliance foam and its treatment can be part of regulations dealing with waste electric and electronic equipment (WEEE), particularly in non-Article 5 parties, often organised under extended producer responsibility (EPR) arrangements. Refrigerators and freezers are collected at source, or segregated from solid waste after collection, as one category of WEEE for which special requirements for recycling apply. In addition to the recovery of refrigerants, the separation of foam and potentially extraction of the blowing agents also occurs after which the foam/blowing agent is destroyed by a qualified technology. Ideally, this is done in a closed environment, where the insulation foam is shredded and, through thermal treatment, the liberated blowing agent is collected in concentrated form for destruction. More commonly, the foam is manually separated from the refrigeration equipment cabinets and doors and then destroyed using available facilities, such as waste to energy facilities, cement kilns, electric arc steel furnaces, or commercial hazardous waste facilities noting that all these options come with considerable losses of blowing agent and inherently poor accuracy of actual quantities destroyed.[288]

To ensure sound treatment of construction insulating foams containing ODS or HFCs, they need to be separated at source from the building prior to its demolition and then destroyed. Some countries have regulations in place making this process mandatory. It is noted that the amounts generated are low

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[288] In the absence of analysis of elements of foam waste, which is not practical, the overall waste stream recovered for management will contain a mixture of controlled substance as well as other blowing agents that will also change over time.

compared to overall national waste streams. Research on additional costs for such a procedure has shown them to be less than 1% of total renovation or demolition costs (Obernosterer *et al.*, 2007[289]). Therefore, separation and destruction of insulating materials containing controlled substances should not substantially impact demolition costs.

A similar regulatory approach to WEEE could potentially be applied to ODS/HFC containing foams in packaging and automotive waste streams, something that would require source or pre-disposal separation from the general solid waste stream, if practical. An additional complication with these foam wastes at EOL, at least in the short-term, may be the potential for them to contain flame retardants now banned under the Stockholm Convention. Options for their destruction are generally currently limited to existing thermal oxidation processes, noting the potential inherent losses involved, although technically similar extraction of blowing agent could be accomplished by shredding and extraction within an enclosed environment with recovered substance being managed as a concentrated EOL ODS/HFC waste stream.

The above approaches for dilute EOL ODS/HFC waste streams are generally implemented within national initiatives for a circular economy approach to the separation of priority solid waste streams. Within a broader policy framework that internalises the associated costs, these policies are anticipated to increasingly break down the barriers and limitations faced by individual waste streams.

8.3.4 Financing EOL ODS/HFC management

Sound and sustainable financing mechanisms for EOL management that cover recovery, collection, recycling, reclamation, destruction and storage (pending any one of the activities mentioned) of controlled substances are required. Several approaches are possible to finance the required infrastructure/capability and to economically incentivise the servicing and waste management sectors.

- Experience shows reclamation can be effective and financially sustainable when an enforced quota system restricts the quantities of new substances available in a market, creating demand for and commodifying reclaimed material.

- Carbon finance mechanisms can be applied within countries or on an international basis. For example, in the United States, the carbon offset registries, like the American Carbon Registry and the Climate Action Reserve Registry, provide carbon credits for the destruction of ODS sourced from United States' territories and other international sources. Verra is another registry promoting and incentivising the creation of offset credits from the destruction of internationally sourced ODS. Regardless of Registry, strict eligibility and additionality criteria apply to the creation of offset credits under the various methodologies. Other "cap and trade" arrangements or applications of carbon taxation can be applied to EOL ODS/HFCs, with appropriate policies and regulatory measures.

- Financing can also be linked to extended producer responsibility schemes, as is done with electrical and electronic appliances including refrigerators and freezers, where importers are expected to cover the cost for recycling of the equipment. This is often organised by an authorised entity that is supported by importers and producers of equipment, depending on their market shares. Such schemes may be mandated or adopted as voluntary initiatives by individual, or groups of, importers and producers.

- Regulatory approaches, such as levy or tax systems, on the import of controlled substances and/or advance disposal charges applied on new equipment purchase, whose revenues are administered by an authorised authority for EOL management. They can be combined with a

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[289] Obernosterer R., Smutny R., Jäger E., 2007, *Nachhaltige FCKW Bewirtschaftung Österreich*, RMA Austria, Villach, November 2007.

refund system for returned substances, providing a financial incentive for recovery, recycling and return for reclamation.

- Early replacement programs, focussed on acquiring new equipment with energy savings, using corporate environmental and sustainability goals, sustainability programs, can also contribute to a sustainable financing scheme.

To date, MLF support for EOL ODS management for Article 5 parties has been limited to a demonstration destruction program completed in 2018.[290] From this, ExCom has followed up with an examination of further action in the area.[291] Furthermore, ExCom decision 90/49[292] allows the inclusion of measures for environmentally sound management of used or unwanted controlled substances in new stages of HPMPs and Stage I Kigali HFC Implementation Plans. This could potentially provide direct grant funding to assist Article 5 parties in expanding refrigeration servicing sector infrastructure to better address EOL ODS/HFC management, as well as capacity strengthening resources to support development of other financing mechanisms.

There has been increasing recognition that management of EOL ODS/HFC and associated banks has yet to be prioritised by either the Montreal Protocol or the Convention on Climate Change. Consequently, collective international action is developing that would raise awareness of this issue and promote independent policy action and financial support for addressing it. An example is the recent establishment of the Climate and Ozone Protection Alliance (COPA)[293], which is an initiative initially funded by Germany and managed by GIZ, with UNDP and UNIDO as implementing partners jointly with GIZ. Its objective is to fill the gap that exists on international action related to EOL ODS/HFC banks management. This would be accomplished through a network of public and private sector partners that would be able to mobilize funding to address the issue both globally and at a country level.

Regardless of the overall financing scheme, recovery needs to be incentivised for the service company/technician who performs the recovery, and logistics need to be integrated into existing structures to optimize handling and transport activities for both concentrated and dilute waste streams. Within regulatory systems, this can mean that the operator is obliged to ensure recovery and thus pay the extra cost for recovery (e.g., in several European countries). Additional incentives can be provided through refunds upon delivery of collected substances. In the case of the RACHP sector, distributors further up the logistics chain would be obliged to take back the recovered refrigerant and either recycle, reclaim, or destroy it. As destruction is expensive and uneconomic, except potentially where a mature carbon finance or other mechanism that creates a viable waste market is operating, it needs to be mandated by regulation.

Collection systems for EOL ODS/HFCs may use the existing infrastructure for refrigerant distribution using the same channels as for new/reclaimed refrigerant in the reverse direction. Some companies have invested in rapid-recovery systems, which are equipped with powerful pumps that speed up and optimise the recovery process, reducing labour cost as well as the downtime of the system and thus improve the economics of the process. Larger refrigerant distributors operating internationally are

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[290] Executive Committee of the Multilateral Fund, Meeting Document: UNEP/OzL.Pro.ExCom/84/11, *Final Report on the Evaluation of Pilot Demonstration Projects on ODS Disposal and Destruction*, November 2019.

[291] Executive Committee of the Multilateral Fund, Meeting Document: UNEP/OzL.Pro/ExCom/89/9, *Synthesis Report Describing Best Practices and Ways for the Executive Committee to Consider Operationalizing Para 24 of Decision XXXVIII/2 (Decision 84/87(b))*, February 2022.

[292] Executive Committee of the Multilateral Fund, Meeting Document: UNEP/OzLPro.ExCom/90/40, *Report of the 90th Meeting of the Executive Committee*, June 2022, p. 43.

[293] https://www.copalliance.org/

increasingly moving toward a business model involving full integration of both the supply of refrigerants and its recovery/reclamation/recycling and EOL management through to destruction.

8.3.5 Transboundary movement barriers to EOL ODS/HFC management

The ability to smoothly undertake the transboundary movement of EOL ODS/HFCs is necessary to achieve global access to environmentally sound destruction of EOL ODS/HFC. In many countries, EOL ODS/HFCs are considered as hazardous wastes, based on their global ozone depleting and climate impacts and their potential for unsuitable disposal. As such their transboundary movement will be subject to the requirements of the Basel Convention on the Control of Transboundary Movements of Hazardous Waste and their Disposal and related international shipping standards. The basis of the Basel Convention is that there must be informed consent by the governments of the exporting country, transit countries, and the importing country, as well as standards for environmentally sound management of environmentally sensitive waste streams. The Convention's objective is to prevent the transfer of hazardous and other waste environmental legacies that originated in developed countries to developing countries, which might not have the capacity or resources to manage such legacies. While generally associated with traditional hazardous chemical wastes, the issue of transferring such environmental liabilities from developed to developing countries has included dilute EOL ODS/HFC wastes contained in exported, used and inoperable refrigeration equipment thereby transferring waste insulation foam for disposal to countries without the capacity to handle it.

While effective in restricting illegal trade in waste, the process of informed consent is inevitably bureaucratic and time consuming given the approvals required by multiple jurisdictions sequentially, resulting in significant transaction costs associated with the process. This is a significant barrier to EOL ODS/HFC management, including reclamation, and/or destruction, particularly for parties that lack national capability for local reclamation and/or destruction, or the resources to undertake export transactions involving the relatively small quantities low-volume consuming countries might generate.

Some of the key complexities relate to:

- Inconsistencies with classification of the material
- Increased administrative efforts
- Increased shipping costs
- Increased time to process Basel paperwork at each port, adding time to the journey
- Difficulties locating a carrier that is prepared to carry material when classified as 'hazardous waste'
- The possibility of venting as a means of responding to challenges of the transboundary movement.

Several approaches, likely in combination, could be adopted to address this issue. These include:

- *Accumulating quantities at source*— An important prerequisite for cost effective EOL management is to accumulate enough controlled substances to be destroyed to make land and/or sea transport viable and justify the individual shipment transaction costs. This requires the collection, consolidation, and secure storage of the controlled substances in appropriately sized and qualified tankage, until a viable quantity is available for shipping. This would typically be an amount that might fill a standard shipping container. For EOL refrigerant, this would involve investment in incremental infrastructure that is developed and operated collectively by refrigeration servicing providers.

- *Development of a regional EOL ODS/HFC management approach*— Recognising the potential for development of smaller scale EOL ODS/HFC destruction facilities (see section 8.6.4) and the potential availability of existing industrial based destruction capacity, such as cement kilns, there could be opportunities for regional cooperation to develop an economically sustainable regional approach using this destruction capacity. A regional approach could serve several countries in reasonable proximity that are willing to cooperate efficiently on Basel Convention approvals.

- *Involvement of refrigerant distribution companies and carbon trading enterprises in facilitating export transactions*— The participation of international refrigerant distribution firms, individually or collectively, could facilitate the consolidation, handling, and export/import transactions of EOL ODS/HFCs requiring destruction. This fits the developing business model of several international companies and is consistent with product stewardship/extended producer responsibility policies. This could also facilitate greater use of carbon trading mechanisms, including participation of entities specialising in brokering such transactions, noting that an equitable distribution of revenues would need to be maintained.

- *International cooperation to facilitate transboundary movement of EOL ODS/HFCs*— International measures might need to be considered to facilitate movement of EOL ODS/HFCs under the Basel Convention, including, e.g., UN Secretariat level dialogue of technical and economic issues relevant to the Montreal Protocol and barriers to the transboundary movement of EOL ODS/HFCs. EOL ODS/HFC management is also relevant to international efforts to curb greenhouse gas emissions, e.g., under the United Nations Framework Convention on Climate Change (UNFCCC). Parties may wish to consider how the Montreal Protocol, the UNFCCC, and the Basel Convention could work together to facilitate transboundary movement of EOL ODS/HFCs to encourage preferential recovery/recycling and environmentally sound destruction of EOL ODS/HFCs, thereby minimising their emissions.

8.4 Destruction of controlled substances under the Montreal Protocol

8.4.1 Montreal Protocol definitions relating to destruction of controlled substances

In the preamble to the Montreal Protocol, parties affirmed that, for the protection of the ozone layer, precautionary measures should be taken to control equitably the total global emissions of substances that deplete it, with the ultimate objective of their elimination based on developments in scientific knowledge. Environmentally sound destruction of surplus or contaminated ODS and HFCs at end-of-life is generally encouraged by the Montreal Protocol because it avoids unnecessary emissions and helps protect the stratospheric ozone layer and/or the climate.

However, the Montreal Protocol does not mandate the destruction of ODS or Annex F Group I HFCs. The exception is HFC-23 (Annex F, Group II) generated in facilities manufacturing Annex C, Group I or Annex F substances, from which emissions must be destroyed to the extent practicable using technologies approved by parties.

The Protocol's definition of 'production' of controlled substances subtracts the amounts destroyed from the amounts produced. The use of destruction technologies approved by parties applies to the amounts of controlled substances destroyed and accounted for within the Protocol's definition of 'production'. In the context of accounting for and subtracting amounts destroyed for the purposes of reporting production, the Montreal Protocol's destruction technology approval process sets a benchmark for technologies to achieve a level of efficiency for destruction of wastes that are controlled substances (destruction and removal efficiency of 99.99% for concentrated sources). This aids in the process of accounting for destroyed amounts.

8.4.2 Destruction of high-volume by-products that are controlled substances

Destruction is also used to minimise and avoid emissions of controlled substance by-products from chemical processes. However, significant by-products can also be potentially valuable feedstocks for other chemical production processes. Carbon tetrachloride (CTC) and HFC-23 are in this category of by-products that can be used as valuable feedstocks. Reported destruction of CTC (previously used to produce CFC-11/-12) peaked in 2007 but has decreased since then, either due to optimised processes minimising its formation, or more recently its increased use as a valuable feedstock.

Emissions of HFC-23 by-product from production of HCFC-22 are a loss of a valuable manufacturing resource, which has resulted in the recent development of chemical processes where HFC-23 generated from production of HCFC-22 can be used as a subsequent feedstock, which would avoid HFC-23 emissions without the need for their destruction.

For HFC-23, Article 2J of the Montreal Protocol requires that:

> ***6***. *Each Party manufacturing Annex C, Group I, or Annex F substances shall ensure that for the twelve-month period commencing on 1 January 2020, and in each twelvemonth period thereafter, its emissions of Annex F, Group II, substances generated in each production facility that manufactures Annex C, Group I, or Annex F substances are destroyed to the extent practicable using technology approved by the Parties in the same twelve-month period.*

> ***7.*** *Each Party shall ensure that any destruction of Annex F, Group II, substances generated by facilities that produce Annex C, Group I, or Annex F substances shall occur only by technologies approved by the Parties.*

The combined effects of paragraphs 6 and 7 are that feedstock uses of HFC-23 appear to be outside the scope of the requirement to apply destruction technology approved by parties. However, this does not avoid the obligation to minimise emissions from HFC-23 feedstock use, as required according to the definition of controlled substances:

> *That insignificant quantities of controlled substances originating from inadvertent or coincidental production during a manufacturing process, from unreacted feedstock, impurities, or that are emitted during product manufacture or handling, shall be considered not to be covered by the definition of a controlled substance contained in paragraph 4 of Article 1 of the Montreal Protocol.*

If the HFC-23 feedstock was used to produce Annex C, Group I, or Annex F substances, then any emissions of HFC-23 from such a process could potentially fall within the scope of Article 2J paragraphs 6 and 7.

In considering how HFC-23 feedstock use might be considered within the Montreal Protocol definitions, and relevant to Article 2J, according to the definition of destruction in the Protocol,

> *"a destruction process is one which, when applied to controlled substances, results in the permanent transformation, or decomposition of all or a significant portion of such substances".*

It is worthwhile noting that the 2018 TEAP Task Force on Destruction Technologies[294] used the term 'conversion' interchangeably with 'transformation', defining "*conversion or non-incineration technologies irreversibly transform halocarbons (including to other saleable products, e.g., acids, vinyl monomers etc.). They primarily rely on chemical transformation to destroy substances.*" The

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[294] UNEP, 2018, *April 2018 Report of the Technology and Economic Assessment Panel, Volume 2, Decision XXIX/4 TEAP Task Force Report on Destruction Technologies for Controlled Substances,* April 2018. See page 2 footnote and section 4.3.2.

TEAP Task Force also determined that one process submitted for consideration as a destruction technology "Chlorination/De-chlorination to Vinylidene Fluoride" is part of a chemical manufacturing process and is therefore not a destruction process. The submitted process uses a controlled substance (HFC-152a) as a feedstock.

In conclusion, feedstock uses of HFC-23 appear to be outside the scope of implementation of Article 2J. However, this does not avoid the obligation to minimise emissions from HFC-23 feedstock use, as required according to the definition of controlled substances. For consistency with the definition of destruction under the Montreal Protocol, forthwith destruction by chemical transformation will be described by TEAP as 'transformation'.

8.4.3 Destruction using Montreal Protocol approved technologies

Parties have taken several decisions to approve technologies that are used for the destruction of controlled substances for the purposes of Montreal Protocol production data reporting requirements under Article 7 and destruction of HFC-23 under Article 2J. Over time, the list of destruction technologies approved by parties has been updated, with the most recent list of approved destruction processes contained in Annex II to the 30th MOP under decision XXX/6 (see section 8.6).

8.4.4 Destruction of controlled substances alongside Montreal Protocol requirements

There can be purposes for destroying and reporting destruction of controlled substances other than those within Montreal Protocol requirements. Many countries that destroy controlled substances might not report that destruction under Article 7, which is for the purposes of calculating production under the Montreal Protocol.

Moreover, some destruction, like the destruction of dilute sources of waste foams, are rarely reported to the Montreal Protocol. These activities are motivated by other factors, ranging from direct regulatory mandates, integration with broader circular economy policies applied to solid waste streams, and a direct need to conserve scarce landfill capacity by targeting high volume waste streams.

These activities can be undertaken outside the reporting and production definition requirements of the Montreal Protocol. The Montreal Protocol requirements to report destruction might not be the primary purpose for these activities.

The destruction of unreported quantities is nevertheless contributing to minimising the total impact of controlled substances on the ozone layer and climate.

8.5 Reported destruction quantities and trends of controlled substances

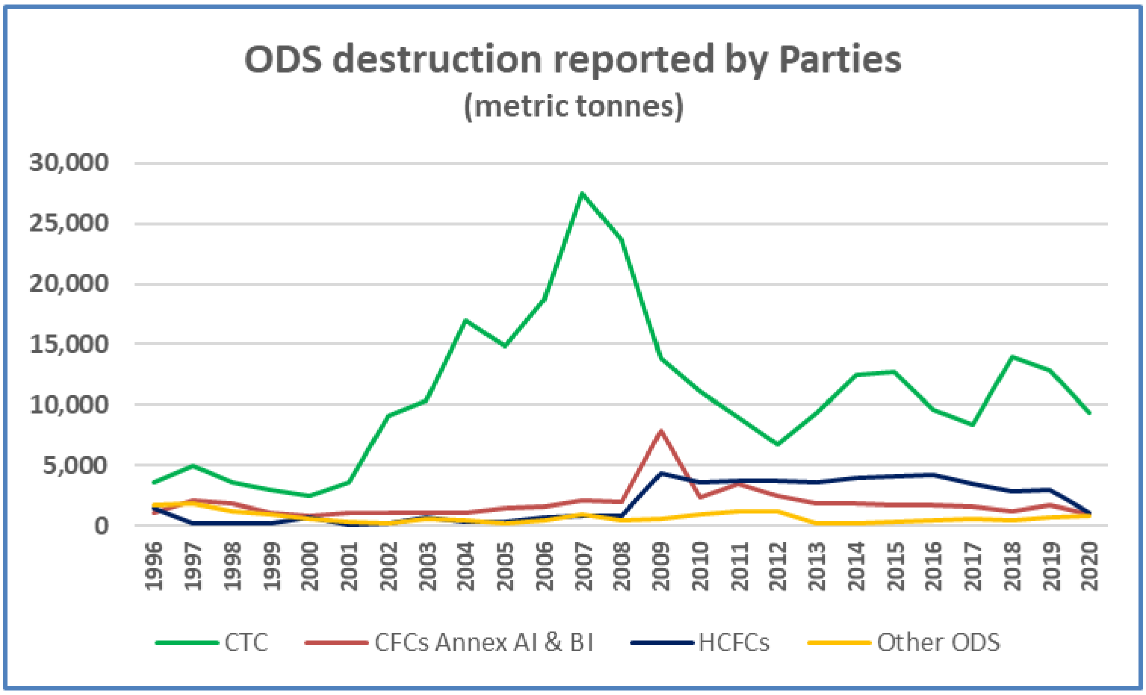
This section presents currently available reported Article 7 data on the amounts of EOL ODS/HFC destroyed by parties as reported to the Ozone Secretariat.

It also presents data available for several high-volume countries and regions, including the European Union. These countries or regions can have mandatory reporting requirements with some form of public disclosure on amounts destroyed and, in some cases, overall amounts recovered for both destruction and reuse. They also currently account for a large portion of the available data on controlled substances recorded as destroyed globally. This cumulatively provides an additional measure of the portion of global banks of ODS and HFCs at EOL that are being destroyed rather than emitted. The final part of this section provides an overall assessment of global performance related to recovery and destruction of global ODS/HFC banks at EOL in terms of trends and potential priorities looking forward.

8.5.1 *Article 7 reported global destruction quantities*

The Ozone Secretariat provides data reported to the Montreal Protocol under Article 7 on the destruction of controlled substances, including for 2020 although this data is not yet complete.[295] The ODS data is summarised in Figure 8.23, which shows the quantities (in metric tonnes) destroyed each year since 1996 for CTC, CFCs (Annex AI and BI), HCFCs and other ODS. Cumulatively, since 1996, 382,574 tonnes of ODS have been reported as destroyed; CTC destruction accounts for 271,575 tonnes, which is 71% of the total reported. Reported destruction of CTC (previously used to produce CFC-11/-12) peaked in 2007 but has decreased since then either due to optimised processes that minimises its formation, or more recently its increasing use as a valuable feedstock.

Figure 8.23 Reported quantities of ODS destroyed, 1996–2020 (tonnes)



Notes: From inspection of the raw data, the 2009 peak in reported CFC destruction appears to be a reporting error, possibly a decimal point in the wrong place. The 2020 data used is not a complete data set, which could account for some, or all, of the apparent decrease in destruction of HCFCs in that year.

Global Article 7 reported destruction of ODS other than CTC indicates that annual destruction has been in the range of 4,475 to 6,355 tonnes and may be trending downward. Total reported destruction of ODS other than CTC in 2019 was 5,272 tonnes (noting that reported 2020 data remains incomplete).

Excluding CTC, non-Article 5 parties have accounted for over 99% of the reported ODS destruction since 1996 and accounted for 94.4% in 2019. In the period 2010 to 2019, which has a complete data set, Japan accounted for 38% of reported ODS destruction excluding CTC, the European Union for 28%, the United States for 31%, and Australia for just under 2%. In 2019, the distribution among major non-Article 5 parties, accounting for the majority of reported ODS destruction other than CTC, was Japan 31.6%, the European Union (including the United Kingdom) 36.6%, the United States 30.5%, and Australia 0.6%, of total reported ODS destroyed excluding CTC.

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[295] UNEP, https://ozone.unep.org/countries/data-table

HFC destruction data reporting for 2019 and 2020 is incomplete due to the timing of reporting, for example, depending on when some parties ratified the Kigali Amendment. From the limited data available, HFC-23 and HFC-134a accounted for most of the reported destruction. In the following section, more data for ODS and HFC destruction, and specific to some countries/regions reporting destruction through other means, is discussed.

8.5.2 EOL ODS/HFC recovery and destruction in exemplar countries or regions

Japan— In Japan, a well-established regulatory system operates for the management of EOL ODS and HFCs. This is regulated under the "Act on Rational Use and Proper Management of Fluorocarbons", most recently updated in 2018, and supported for domestic appliances through the "Home Appliance Recycling Act". This legislation collectively requires measures throughout the lifecycle of fluorocarbons to minimise emissions, including recovery of ODS and HFCs from home appliances, vehicles, and commercial/industrial equipment at their end of useful life. Recovered ODS/HFCs must be recycled or destroyed. Under the authority of the Ministry of Environment and Ministry of Economy, Trade and Industry, the operation of recovery and EOL ODS/HFCs management is administered through members of the national refrigeration servicing association (Japan Association of Refrigeration and Air Conditioning Contractors[296] (JARAC)) and the electrical appliance recycling industry. The operational system involves a nation-wide network of 25 licenced recycling operators and 60 licenced destruction locations. An overview of this system, as operated by JARAC, was provided at a MOP-31 side event with presentations available on-line.[297]

Dating from the enactment of the fluorocarbon legislation in 2001, annual recovery has grown progressively from approximately 2,000 tonnes to 3,000 tonnes in 2014, and 3,900 tonnes in 2017. However, the percentage recovered compared with the estimated total available at EOL remained relatively constant, between 30% and under 40%, indicating that it was not matching growth in what was becoming available from the bank of fluorocarbons. In 2018, this resulted in setting specific targets on elimination of what should be available in large commercial and industrial systems, specifically 50% recovery in 2020 and 70% recovery in 2030.

Data available through the Ministry of Environment[298,299,300] indicates that in 2020 recovery was 5,425 tonnes out of an estimated 9,642 tonnes available, which should exceed the 2020 50% recovery target applied to large commercial and industrial systems. This data also shows that of the current recovery amounts, a high proportion of what is recovered was destroyed as opposed to recycled (4,099 tonnes or 76%, including automotive air conditioners). Additional quantities of EOL ODS/HFCs are recovered, recycled, and destroyed under separate legislative requirements for domestic appliances. In 2021, a total of 2,562 tonnes of refrigerant was recovered, of which 2,270 tonnes was recycled and 261 tonnes was destroyed. Additionally, 240 tonnes of blowing agent from insulation was recovered and destroyed.

Figure 8.24 provides an overall graphical illustration of the recovery and disposition of fluorocarbons from industrial refrigerators and air conditioners and automobile air conditioners, and domestic refrigerators and air conditioners. Using composite data available for 2020 and 2021, the disposition

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[296] Japan Association of Refrigeration Air-Conditioning Contractors, https://www.jarac.or.jp.

[297] Japan Refrigeration and Air Conditioning Industry Association (JRAIA), 2019, JRAIA's Side Event at MOP-31, November 5, 2019. https://www.jraia.or.jp/english/relations/unep2019_mop31.html.

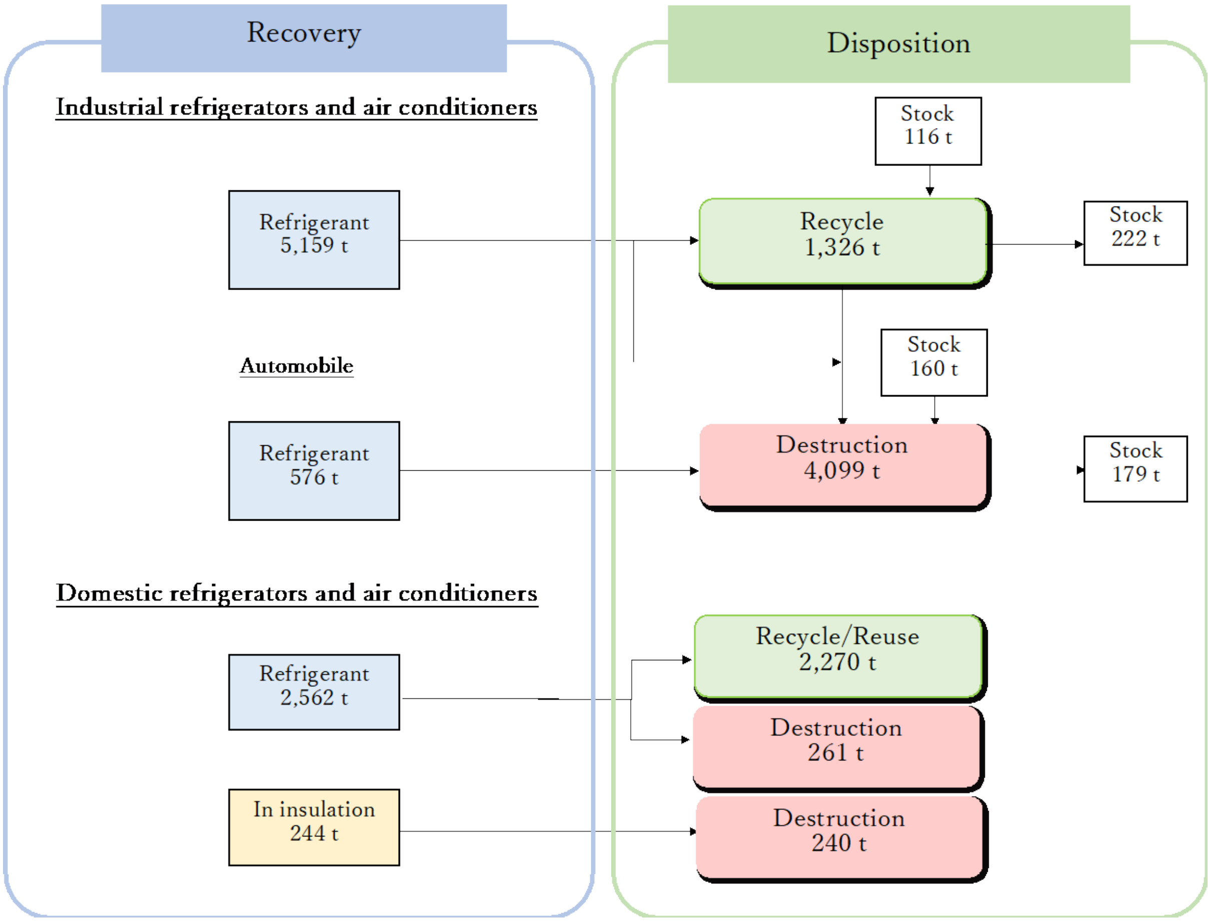
[298] Ministry of the Environment, Japan. https://www.env.go.jp/press/109865.html.

[299] Ministry of the Environment, Japan. https://www.env.go.jp/content/000074636.pdf.

[300] Ministry of Economy, Trade and Industry, Japan. https://www.meti.go.jp/press/2021/12/20211224004/20211224004-3.pdf

of recovered fluorocarbons, including refrigerant and blowing agent, indicates a nominal annual average of 8,196 tonnes, of which 3,596 tonnes was recycled and 4,600 tonnes was destroyed.

Figure 8.24 Graphical illustration of the recovery and disposition of fluorocarbons from industrial refrigerators and air conditioners and automobile air conditioners (2020) and domestic refrigerators and air conditioners (2021) in Japan



Australia— In Australia, Refrigerant Reclaim Australia (RRA) is an industry-run not-for-profit organisation that manages a refrigerant product stewardship program supported through a government-backed co-regulatory approach. Under Australian Government requirements, technicians are legally obligated to recover and return refrigerant for safe disposal; and licensed importers of bulk refrigerant and pre-charged equipment above a certain threshold are required to participate in a product stewardship program as a condition of their import licences. RRA is established as the only approved product stewardship organisation for the Australian refrigerants industry that provides destruction services. The industry stewardship program is funded through an industry levy charged per kg on all HCFC, HFC and HFO/HFC blends, both in bulk and equipment, that is imported into Australia. The levy on imported refrigerant is collected and administered by a trust on behalf of RRA.

The industry-run program provides a rebate to technicians for returned unwanted and contaminated refrigerant, providing an economic incentive that avoids illegal venting. When the technician/contractor returns unwanted refrigerant to the wholesaler, the wholesaler pays a contractor rebate. When the wholesaler returns unwanted refrigerant to RRA, RRA re-imburses the wholesaler. The rebate helps offset the costs of administration and assets required to support the program.

Through accumulated remaining funds, RRA operates a national collection service that transports recovered refrigerants to a central storage facility where they are destroyed using environmentally safe technology. For ODS, this system has operated since the 1993. In 2003, it became mandatory for the refrigeration and air conditioning industry also to recover, return, and safely dispose of HFCs and PFCs under the Ozone Protection and Synthetic Greenhouse Gas Management Act, with RRA extending its stewardship program include HFCs and to safely process or dispose these refrigerants.

RRA[301] data for 2020/2021 on the system's performance provides quantities of refrigerant recovered, reclaimed for reuse, used for feedstock, and directed to destruction. In 2020/2021, 493 tonnes (CFCs 4.96 tonnes, HCFCs 40.23 tonnes, HFCs 431.23 tonnes, other including hydrocarbons 16.85 tonnes) was recovered and destroyed and 87.03 tonnes was reclaimed for re-sale. Data for 2020/2021 indicate nominal recovery rates of between 50–65%, based on a comparison of total refrigerant recovered in 2021 against the estimated total quantity of refrigerant expected to be available at end-of-life in that year in Australia.[302] There has been a significant increase in the proportion of HCFC sent back for destruction as well as a noticeable decline in product reclaimed for re-sale, which historically was predominantly HCFC-22.

RRA[303] notes that refrigerant recovery has followed the country's consumption phase-out schedules, with CFCs now declining to very low levels. HCFCs dominated recovery until 2012, after which it rapidly declined to a currently relatively low level that is now sustaining demand for reclaimed servicing refrigerant. HFC recovery continued to rise with an overall growth of recovery and destruction until reaching a relatively stable level in 2018. RRA anticipates significant growth in demand for recovery services is anticipated through to 2030 and beyond as Australia completes its HCFC phase-out and HFC phase-down and equipment replacement with low GWP refrigerants accelerates. As these banks reach their end-of-life, increased investment in infrastructure will be required to sustain the program. RRA has undertaken projections of volumes of HCFC and HFC that could be recovered between 2020 and 2030, indicating that recovery could roughly double in this period from the current levels to over about 1,000 tonnes annually, with 75% HFCs and 25% HCFCs. While banks of legacy refrigerant continue to grow and require end-of-life management, levies on imported refrigerant will inevitably decline with the HFC phase-down. The financial requirement to manage the estimated national ODS/HFC Bank at end of life under its product stewardship program is presented as a financial contingent liability to be managed through the accumulated funds held under trust for years to come.

European Union— The European Union has two regulations that require recovery of ODS and HFCs from a wide range of refrigeration, air-conditioning and other equipment, for recycle, reclaim or destruction and the reporting of quantities destroyed as part of wider reporting requirements. These are Regulation 1005/2009 on substances that deplete the ozone layer and Regulation 517/2014 on fluorinated greenhouse gases (F-gas Regulation). The European Environmental Agency (EEA) issues annual reports of the collated reported data for ODS[304] and F-gases.[305] The most recent reports have data through 2020.

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[301] Refrigerant Reclaim Australia, 2022, Potential Recovery. https://refrigerantreclaim.com.au/program-performance/potential-recovery/. Accessed December 2022.

[302] Personal communications, Kylie Farrelley, General Manager, Refrigerant Reclaim Australia, November 2022.

[303] Refrigerant Reclaim Australia, *Refrigerant Reclaim Australia: 2019–2020 Annual Report*. https://refrigerantreclaim.com.au/wp-content/uploads/2021/08/RRA-2019-20-Annual-Report.pdf.

[304] European Environment Agency, 2021, *Ozone-depleting substances 2021*. https://www.eea.europa.eu/themes/climate/ozone-depleting-substances-and-climate-change-1/ozone-depleting-substances-2021. Accessed December 2022.

[305] European Environment Agency, 2021, *Fluorinated greenhouse gases 2021: Annex to public briefing*, https://www.eea.europa.eu/publications/fluorinated-greenhouse-gases-2021/fluorinated-greenhouse-gases-2021-annex/view.

In 2020, 5,943 tonnes of controlled substances (ODS) were destroyed in total, a 28% decrease compared with 2019. This was the largest decrease observed since 2012 and the lowest recorded value since 2013. The largest quantities destroyed were of CTC, CFCs and HCFCs (73%, 11% and 9% of the total destroyed, respectively). Expressed in ODP tonnes, of the 6,083 ODP tonnes, the largest quantities destroyed were of CTC, CFCs and Halons (79%, 10% and 10% of the total destroyed, respectively).

In 2020, total reported destruction of HFCs was approximately 1,250 tonnes down from a 2019 peak of 1,645 tonnes. From destruction data reported to the Ozone Secretariat, HFC-23 is less than 50% of the total HFC destroyed. F-Gas destruction was effectively all HFCs. In 2020, 1,590 tonnes of HFCs were reported as reclaimed accounting for 11% of European Union production of virgin HFCs, or 3% of total European Union HFC supply (as metric tonnes). However, the quantities of HFCs reclaimed may be higher as reporting requirements may not capture all reclamation activity.

Combining the ODS and HFC data, and excluding CTC from ODS and HFC-23, the total amount of remaining ODS and HFCs destroyed from banks at EOL (primarily recovered refrigerant) in 2020 is estimated to be approximately 2,300 tonnes.

United States— In the United States, the Clean Air Act (CAA) prohibits knowingly venting or releasing ozone-depleting and substitute refrigerants while maintaining, servicing, repairing, or disposing of appliances or industrial process refrigeration equipment. There is also an EPA requirement for reporting quarterly and annually in the Ozone Depleting Substance Tracking System of Class I or Class II ODS.[306,307] Reporting of HFCs was added to destruction data totals in 2021. This ODSTS data forms the basis for reporting of ODS/HFC destruction as part of the United States' annual reporting under Article 7 of the Montreal Protocol. A paper published by EPA in 2021[308] provided an overview of this data for between 2010 and 2018, which indicated that the destruction of Class I and II[309] ODS steadily declined from approximately 4,500 tonnes/year to 2,500 tonnes in 2018, a trend followed by CFCs that declined from approximately 1,400 tonnes to 400 tonnes during the same period. Destruction of HCFCs remained relatively constant during this period, with approximately 500 tonnes destroyed in 2018. The total amount of destruction reported under with Article 7 was 2,744 tonnes for 2020.

Canada— In Canada, management of recovered and EOL ODS/HFCs is based on a now mandatory system supported through a levy on imported refrigerants either in bulk or large stationary equipment governed by national pollution prevention plan regulations[310],[311] and harmonized provincial regulations. Operationally, this system is largely administered through a national industry association (Heating, Refrigeration and Air Conditioning Institute) and specifically Refrigerant Management Canada although several larger firms operate and report independently under the regulations. The system, specifically the levy, funds the cylinder handling, testing, storage transportation and

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See also European Environment Agency, 2020, *Fluorinated greenhouse gases 2020*, for HFC destruction quantities in 2019. https://www.eea.europa.eu/publications/fluorinated-greenhouse-gases-2020.

[306] U.S. EPA, Ozone-Depleting Substances (ODS) Recordkeeping and Reporting. https://www.epa.gov/ods-phaseout/ozone-depleting-substances-ods-recordkeeping-and-reporting.

[307] U.S. EPA, https://www.epa.gov/system/files/documents/2021-12/ozone-depleting-substance-tracking-system-odsts-pia-npp-final-2021.pdf.

[308] U.S. EPA, 2021, *ODS Destruction in the United States and Abroad*, EPA 430-R-21-006, April 2021.

[309] U.S. EPA, Phaseout of Ozone-Depleting Substances (ODS). https://www.epa.gov/ods-phaseout.

[310] Government of Canada, 2016. Canada Gazette, Part I, Volume 150, Number 21: Supplement, *Notice requiring the preparation and implementation of pollution prevention plans in respect of halocarbons used as a refrigerant*, May 21, 2016.

[311] Government of Canada, *Halocarbons: pollution prevention planning notice*. https://www.canada.ca/en/environment-climate-change/services/pollution-prevention/planning-notices/performance-results/halocarbons-overview.html.

destruction of waste ODS and HFC refrigerants, noting that domestic appliances and small and automotive air conditioners are not financially supported. Environment and Climate Change Canada reports the cumulative prevention of 585 tonnes of ODS/HFC emissions through 2019 under the above regulations. In terms of actual destruction, Canada provided MCTOC with data by controlled substance destroyed, based on export to facilities in the United States. Reported destruction was 192 tonnes in 2018, 184 tonnes in 2019, 172 tonnes 2020, and 111 tonnes in 2021. Destruction amounts had an increasing trend up to 2018. In terms of types of controlled substance, HFCs are the predominant controlled substance being destroyed.

8.5.3 Assessment of actual EOL ODS/HFC destruction achieved

The trends for global, regional, and national destruction of EOL ODS/HFCs are more clearly understood by separating the destruction of unwanted by-product from chemicals production from controlled substances recovered from equipment and products (the bank, which may also include unwanted stockpiles from commercially distributed controlled substances). The unwanted by-product is primarily excess CTC not used as feedstock and HFC-23 by-product from HCFC-22 production, which is substantively destroyed in the originating chemical production facilities or at commercial destruction facilities, as it is produced within a short timescale. These are not considered as part of the banks that result in emissions, either during equipment use or released at end-of-life. This bank is predominately refrigerants and blowing agents and their recovery at end of life for reuse or destruction that minimizes emissions.

CTC production, demand, use as feedstock, and destruction are discussed in detail in Chapter 2. CTC is an inevitable co-product of chloromethanes production and can be minimised to 5% or less of the total output of the chloromethanes or increased depending on requirements. Excess CTC, including distillation residues, are destroyed. Reported destruction of CTC peaked in 2007 but has decreased since then either due to optimised processes minimising its formation, or more recently its increasing use as a valuable feedstock. CTC destruction was 9,320 tonnes in 2020, as reported by the European Union, the United States, and the Republic of Korea, compared with reported total CTC production for feedstock use of 288,935 tonnes.

HFC-23 is an inevitable by-product of HCFC-22 manufacture, the rate of which has reduced over time from as high as 4% to nearer 2% by weight or less. Although HFC-23 not used as feedstock is required to be destroyed to the extent practicable under Article 2J of the Montreal Protocol, there is at present incomplete reporting, for example, depending on when some parties have ratified the Kigali Amendment. The countries/regions that reported HCFC-22 production in 2020 are Argentina, China, Democratic People's Republic of Korea, the European Union, India, Japan, Mexico, the Republic of Korea, the Russian Federation, and the United States. However, according to a 2020 paper[312], global HFC-23 emissions derived from atmospheric measurements were historically at their highest level in 2018, in contrast to expected emissions of HFC-23 as by-product, primarily from reported HCFC-22 production, that were estimated to be much lower. The paper concludes that the discrepancy between expected emissions and observation-inferred emissions makes it possible that planned reductions in HFC-23 emissions may not have been fully realised or there may be substantial unreported production of HCFC-22, both or either of which would result in unaccounted for HFC-23 by-product emissions. In addition, the timing of projects to implement abatement technologies may contribute to emissions.[313] Other potential sources of HFC-23 are discussed in Chapter 2.

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[312] Stanley, K.M., Say, D., Mühle, J. *et al*., Increase in global emissions of HFC-23 despite near-total expected reductions, *Nat Commun*, 2020, **11**, 397. https://doi.org/10.1038/s41467-019-13899-4.

[313] See, for example, UNEP/OzL.Pro/ExCom/90/40, 23 June 2022, and Chemours press release, Chemours Announces Project to Reduce HFC-23 Emissions, March 8, 2021. https://www.chemours.com/en/news-media-center/all-news/press-releases/2021/chemours-announces-project-to-reduce-hfc-23-emissions.

As for the 2018 MCTOC Assessment Report, an estimate of the current global EOL ODS destruction rate has been repeated in this 2022 assessment using two available time series projections for reachable banks of ODS, namely the 2009 TEAP Task Force Decision XX/7 Report: Phase 2 (Figure 3.3, page 20) and the GIZ data presented in Figure 8.3 above for the last year for which global reported Article 7 data for destroyed quantities is available (2019 in this case). The 2009 TEAP Report projection for ODS available at EOL is 175,000 tonnes in 2019, and the GIZ report is 220,000 tonnes ODS available at EOL in 2019. The reported Article 7 data for destroyed quantities for 2019 was 5,272 tonnes of ODS, excluding CTC. Recognising that the reported Article 7 data does not account for actual total quantities of ODS destroyed globally, the resulting global destruction rates are 3% and 2.4% based on the TEAP and GIZ 2019 projections respectively and corresponding reported Article 7 data.

As noted in Section 8.2, the banks of EOL ODS/HFCs currently remain predominately in non-Article 5 parties and are projected to remain so for the next decade, after which rapid growth in banks in Article 5 parties will overtake the then declining banks in non-Article 5 parties. Given that a substantial part of banks in non-Article 5 parties will reach EOL in the next decade, prioritising their effective management would avoid EOL emissions that might otherwise occur. Otherwise, the experience of allowing substantial emissions of readily reachable CFC banks will be repeated for the banks of HCFCs and HFCs.

Non-Article 5 parties account for most of the available data reporting on ODS/HFC recovery and destruction and likely account for a large proportion of active bank management globally.

Based on available information, there are only a few countries that have reported effective recovery and destruction programs. For example, Australia achieved nominal recovery rates of between 50–65% in 2020/2021, based on a comparison of the actual refrigerant recovered for reclamation or destruction against the estimated total quantity of refrigerant expected to be available at end-of-life in that year. Of the refrigerant amounts recovered, 85% was destroyed and 15% was reclaimed in 2020/2021. As another example, Japan has achieved average recovery rates at disposal of between 30–40% (the amount recovered at disposal/estimated amount available). Of the refrigerant amounts recovered at disposal, a high proportion is destroyed, e.g., average 53% based on composite data available for 2020 and 2021.

As an overall conclusion, despite a few reported examples, global recovery and destruction rates of EOL ODS/HFCs from decommissioned equipment and products are likely to fall well below a level where a significant impact is being achieved in mitigating ozone depletion or greenhouse gas emissions. This is likely true on a country level in all but a few non-Article 5 parties. With substantial improvements in EOL management in non-Article 5 parties in the near-term, the opportunity to mitigate emissions of ODS and greenhouse gases though recovery of HCFCs and HFCs would be realised. For Article 5 parties, as increasing amounts of HFCs and HFCs reach EOL, accelerated capacity building is a priority so that capacity would be available to manage EOL ODS/HFC in the longer term.

8.6 Destruction technologies and their application

This section addresses destruction technologies and their application, including through the list of destruction technologies approved by Montreal Protocol parties as well as their application more broadly in managing EOL ODS/HFCs outside the obligations of the Montreal Protocol.

It responds to decision XXX/6 on destruction technologies for controlled substances, which requests TEAP to assess destruction technologies listed (in annex II to the report of the Thirtieth Meeting of the Parties) as not approved or not determined, as well as any other technologies, and to report to parties. It clarifies definitions of categories of approved destruction technologies. Several related issues are raised, including a recommendation to add one technology, already approved for one application category, for another application category. A review is provided in response to an inquiry made to MCTOC regarding the application of a listed technologies proposed in smaller scale configurations. Finally, global destruction technology capacity is reviewed relevant to destruction of EOL ODS/HFCs.

8.6.1 Montreal Protocol list of approved destruction technologies

Environmentally sound destruction of surplus or contaminated ODS and HFCs at end-of-life is encouraged by the Montreal Protocol because it avoids unnecessary emissions and helps protect the stratospheric ozone layer and/or the climate.

The Montreal Protocol does not mandate the destruction of ODS or Annex F Group I HFCs. The exception is HFC-23 (Annex F, Group II) generated in manufacturing facilities, from which emissions must be destroyed to the extent practicable using technologies approved by parties.

As mentioned earlier in this chapter, the Protocol's definition of 'production' of controlled substances subtracts the amounts destroyed from the amounts produced. The use of destruction technologies approved by parties applies to the amounts of controlled substances destroyed and accounted for within the Protocol's definition of 'production'. Article 7 data reporting requires production data to be reported by parties, including the amounts of controlled substances destroyed by technologies approved by parties. The Protocol also allows parties to manufacture an amount of controlled substance almost equivalent to the quantity destroyed with technology listed as approved, within the same year as destruction, and within the same group of substances.

Parties have taken several decisions to approve destruction technologies that are used for the destruction of controlled substances for the purposes of Montreal Protocol production data reporting requirements. Over time, the list of destruction technologies approved by parties has been updated, with the most recent list of approved destruction processes contained in Annex II to the 30th MOP under decision XXX/6.

Destruction technologies approved by the Montreal Protocol can be grouped into three general categories: thermal oxidation, plasma technologies, and chemical transformation technologies. Approved destruction technologies are those that are proven to result in the permanent transformation or decomposition of all or a significant portion of the substance being destroyed.

As a general category, chemical transformation (or non-incineration) technologies are those that primarily rely on chemical transformation to convert halocarbons, sometimes to potentially useful chemicals (e.g., acids, vinyl monomers etc.). Chemical transformation as a destruction process differs from the conversion processes involving feedstock uses because, generally, a feedstock is specifically produced to manufacture a desired chemical and is not considered a waste. A waste by-product or substance at end-of-life may be destroyed by thermal oxidation or plasma technologies, without producing useful chemicals.[314]

8.6.2 Response to decision XXX/6 on destruction technologies

Decision XXX/6 on destruction technologies for controlled substances requests TEAP to assess destruction technologies listed (in annex II to the report of the Thirtieth Meeting of the Parties) as not approved or not determined, as well as any other technologies, and to report to parties.

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[314] Chemical transformation applies to non-incineration technologies, which may or may not produce useful products in the process of destruction of controlled substances. Incineration technologies can produce useful products in the process of destruction of controlled substances, for example reactor cracking produces technical-grade quality HF and HCl.

In consultation with the Ozone Secretariat, TEAP and its MCTOC reported in the 2021 and 2022 TEAP Progress Reports that an assessment in response to decision XXX/6 would be included in this 2022 Assessment Report based on available information.

MCTOC outlined preparations for its assessment of destruction technologies under this decision in the 2020 and 2021 TEAP Progress Reports, including suggested guidance on the type of relevant information needed for assessment. The 2020 and 2021 TEAP Progress Reports invited parties to submit this type of information in response to decision XXX/6 paragraph 3. Information from parties was requested to be submitted no later than January 2022 to allow time for assessment. No information was submitted by parties.

MCTOC is not currently aware of new test data relating to already approved destruction technologies (Table 8.2, based on Annex II, MOP-30 list of technologies subject to review that are either not approved, not determined), or new technologies that would allow an assessment. MCTOC notes that several mainstream destruction technologies continue to lack specific data on demonstration of DRE for Annex F HFCs. MCTOC is aware of some developments, including in the scale and application of existing approved destruction technologies and emerging interest in chemical transformation, that are noteworthy in this 2022 Assessment Report and in response to this decision. MCTOC also raises issues regarding already approved technologies for the consideration of parties.

Table 8.2 Based on Annex II, MOP-30 list of technologies subject to this review that are either not approved or not determined*

Technology	Applicability										
	Concentrated Sources									Dilute Sources	
	Annex A		Annex B			Annex C	Annex E	Annex F			Annex F
	Group 1	Group 2	Group 1	Group 2	Group 3	Group 1	Group 1	Group 1	Group 2		Group 1
	Primary CFCs	Halons	Other CFCs	Carbon Tetrachloride	Methyl Chloroform	HCFCs	Methyl Bromide	HFCs	HFC-23	ODS	HFCs
DRE	99.99%	99.99%	99.99%	99.99%	99.99%	99.99%	99.99%	99.99%	99.99%	95%	95%
Cement Kilns	Approved	Not Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Not Determined		
Gaseous/Fume Oxidation	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Liquid Injection Incineration	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Municipal Solid Waste Incineration										Approved	Approved
Porous Thermal Reactor	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Not Determined		
Reactor Cracking	Approved	Not Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Rotary Kiln Incineration	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved	Approved	Approved
Thermal Decay of Methyl Bromide	Not Determined	Not Determined	Not Determined	Not Determined	Not Determined	Not Determined	Approved	Not Determined	Not Determined		
Argon Plasma Arc	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Inductively coupled radio frequency plasma	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Not Determined	Not Determined		
Microwave Plasma	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Not Determined	Not Determined		
Nitrogen Plasma Arc	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Portable Plasma Arc	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Not Determined		
Chemical Reaction with H_2 and CO_2	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		

Gas Phase Catalytic De-halogenation	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Not Determined		
Superheated steam reactor	Approved	Not Determined	Approved	Approved	Approved	Approved	Not Determined	Approved	Approved		
Thermal Reaction with Methane	Approved	Approved	Approved	Approved	Approved	Approved	Not Determined	Not Determined	Not Determined		

*Orange shaded cells indicated those destruction technologies subject to review under decision XXX/6, excluding any new technology for which information might become available.

8.6.3 Background to TEAP assessment of destruction technologies

In the preamble to decision XXX/6, parties:

- Noted that Destruction and Removal Efficiency (DRE) is the criterion considered in their approval of destruction technologies, and

- Suggested that parties also consider TEAP's other technical advice on emissions of substances other than controlled substances in the development and implementation of their domestic regulations.

For its assessment under decision XXX/6 or future assessments, TEAP will assess destruction technologies for their destruction and removal efficiency and make recommendations to parties for potential approval for inclusion on the list of approved technologies.

TEAP will also provide technical advice about emissions of other pollutants and the technical capability of destruction technologies as part of its assessment. In addition to providing parties with technical guidance, this will also ensure internal consistency with previous assessments.

The TEAP assessment will consider the following parameters:

1. Destruction and Removal Efficiency (DRE)[315], which is a minimum of 99.99% for concentrated sources and 95% for dilute sources (e.g., foams)

2. Emissions of halogenated dioxins and furans[316]

3. Emissions of other pollutants: acid gases (HCl, HF, HBr/Br_2), particulate matter (total suspended particles, TSP), and carbon monoxide (CO)

4. Technical capability, where the technology has demonstrated destruction on at least a pilot scale or demonstration scale, and for which the processing capacity is no less than 1.0 kg/hr of the substance to be destroyed, whether ODS or a suitable surrogate.

The DRE is a measure of the efficiency of destruction and is the basis of TEAP's recommendations to parties. The 99.99% DRE minimum for concentrated sources of controlled substances is considered protective for minimising ozone depletion and climate impact. In the case of controlled substances contained in products such as closed cell foams and considered dilute sources, a DRE of 95% minimum is adopted for assessment purposes.

The technical performance advisory criteria for other pollutant emissions are measures of potential impacts of the technology on human health and the environment. The destruction technologies are assessed against advisory criteria, which is consistent with previous assessments, and technical advice provided in relation to destruction technologies recommended based on DRE.

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[315] Destruction and Removal Efficiency (DRE) is determined by subtracting from the mass of a chemical fed into a destruction system during a specific period of time the mass of that chemical alone that is released in stack gases and expressing that difference as a percentage of the mass of that chemical fed into the system. If interconversion to other controlled species is possible, it is recommended that analysis is used to measure emissions and that any controlled species is taken into account when determining DRE.

[316] Depending on the waste stream, polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polybrominated dibenzodioxins (PBDDs), polybrominated dibenzofurans (PBDFs), polyfluorinated dibenzodioxins (PFDDs), polyfluorinated dibenzofurans (PFDFs). For mixed substance destruction, mixed halogenated dioxins and furans can be formed.

The technical capability advisory criterion considers the extent to which the technology has been demonstrated to destroy ODS/HFCs (or a comparable recalcitrant halogenated organic substance such as polychlorinated biphenyl (PCB)) effectively and is technically capable of commercial-scale destruction.

To undertake its assessment and provide its technical advice, and to provide advice that the technology has the *minimum* level of technical capability to destroy ODS/HFCs efficiently and safely, TEAP considers information for all these parameters.

The following technical performance assessment and advisory criteria is used for TEAP assessments of destruction technologies. These represent a minimum DRE for destroying ODS/HFCs and maximum advisory levels of emissions of pollutants to the atmosphere that would be considered as an acceptable *minimum* level of technical capability.

Table 8.3 Technical performance assessment and advisory criteria

Performance Qualification	**Units**	**Concentrated Sources**	**Diluted Sources (e.g., foams)**
DRE	%	99.99	95
Dioxins/furans	ng-ITEQ/Nm^3	0.2	0.5
HCl/Cl_2	mg/Nm^3	100	100
HF	mg/Nm^3	5	5
HBr/Br_2	mg/Nm^3	5	5
Particulates (TSP)	mg/Nm^3	50	50
CO	mg/Nm^3	100	100

Notes to the table:
All concentrations of pollutants in stack gases and stack gas flow rates are expressed based on dry gas at normal conditions of 0°C and 101.3 kPa, and with the stack gas corrected to 11% O_2 (as referred to by normal cubic metre, Nm^3). NB. Different stack gas conditions may apply in different countries for different technologies.
ITEQ: International Toxic Equivalents[317]
Acid gases will be assessed based on the specific halogen species present in the waste stream.
TSP – total suspended particles

The technical performance assessment (DRE) and advisory criteria (for pollutants other than controlled substances) serve as a benchmark used by TEAP for comparison purposes. They do not constitute standards, nor do they necessarily meet internationally accepted emissions guidance for pollutants, such as those adopted by the Basel Convention.[318] They were developed only for the purposes of the Montreal Protocol for screening and recommending generic technologies that might be considered technically capable of meeting basic acceptable limits of pollutant emissions.

Operators of destruction technologies are required to meet local DRE requirements and pollutant emissions controls. In addition, the performance of technologies are plant and operation specific. Emissions management is a matter for operators and government agencies within national regulatory

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[317] The International Toxic Equivalents (ITEQ) scheme was established by NATO in 1988. More recently the TEFs were re-evaluated by the World Health Organisation and the revised TEQ scheme is generally universally accepted, with the updated TEFs used in the TEQ calculation. Some of the data reviewed by the 2018 TFDT quotes TEQ values. A detailed discussion of ITEQ and TEQ is in UNEP, 2018, *April 2018 Report of the Technology and Economic Assessment Panel, Volume 2, Decision XXIX/4 TEAP Task Force Report on Destruction Technologies for Controlled Substances,* April 2018, p. 13.

[318] UNEP, 2019, UNEP/CHW.14/7/Add.1/Rev.1, *General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants*, May 2019, Paragraph 161. http://www.basel.int/Implementation/TechnicalMatters/DevelopmentofTechnicalGuidelines/TechnicalGuidelines/tabid/8025/Default.aspx. Accessed December 2022.

frameworks. A recommendation by TEAP or an approval by parties of a destruction technology under the Montreal Protocol does not guarantee that local emissions requirements can or will be met on a specific facility employing an approved technology. There may be other concerns or emissions of interest to governments at their national or local levels.

Waste ODS/HFCs may be classified as hazardous wastes, with additional requirements imposed through relevant legislation, nationally, or regionally (European Union). Waste ODS/HFCs may also be subject to international reference guidance (such as adopted by the Basel Convention) in terms of emissions performance, including more comprehensive measures of destruction efficiency, other potential emissions, and sources of emissions and monitoring.

8.6.4 Application of reduced scale destruction technologies

MCTOC has been aware of increasing interest in development of smaller scale variants of currently approved technologies. One proponent made preliminary enquiries about the status of a smaller scale variant of the Argon Plasma Arc technology for refrigerant destruction. This technology is approved by the Montreal Protocol and has been operated at commercial scale in several locations worldwide since the 1990s. Although several power ratings for the argon plasma arc were implemented during the development of the technology, to date all the commercially operating plants have been built with a 150kW plasma torch power rating.

According to the proponent of this technology, over the last few years, there has been an increasing call for a smaller capacity unit to meet two market requirements:

- Countries where the ongoing end-of-life (EOL) refrigerant quantity is not large enough to warrant a plant capable of processing several hundreds of tonnes per annum, but where the cost of shipping the recovered refrigerant to a location with existing destruction capacity is high. In this instance, a plant of suitable capacity can be permanently located in the country in question, reducing shipping costs of the refrigerant including transaction and approval costs associated with the Basel Convention. Additionally, it eliminates the need to transfer the refrigerant to vessels (approved for international transhipment, thereby eliminating the associated fugitive emissions of refrigerant during the transfer process).

- Countries where the national and international regulatory hurdles of shipping an existing stockpile of recovered refrigerant to a location with existing destruction capacity are difficult to surmount. Under this scenario, a relocatable plant can be bought into the country in question, where the refrigerant can be processed locally.

To meet these two requirements, the proponent is planning to offer a smaller configuration of the argon plasma arc technology, with 20% of the capacity of existing commercially operating plants. The smaller configuration is expected to have a 30kW torch. This smaller unit will utilise the identical type of technology as the existing facilities. The proponent is leveraging the experience gained from the operation of other smaller capacity plants during the original technology development. While specific performance data is not yet available for the smaller unit, it is expected to provide the same degree of high-reliability, safe and complete destruction of refrigerants as its larger cousin.

The advantages of the smaller unit are that it utilises the same argon plasma arc technology, with its demonstrable, auditable, high-performance destruction of EOL refrigerants, which has been proven to meet international standards for DRE, including TEAP's recommended minimum 99.99% DRE and technical performance advisory criteria for other pollutant emissions, while processing any refrigerant or mixture of refrigerants. The unit will provide a smaller capacity package for quick mobilisation and is designed for markets aiming to overcome the challenges relating to small stockpiles and transboundary waste movement.

MCTOC has reviewed the available information. The type of technology, Argon Plasma Arc, is already approved for the destruction of a range of controlled substances for the purposes of the Montreal Protocol. There is no reason to consider the down-sized version of this technology to be any different on a technical basis and in terms of performance to the higher capacity, higher powered torch version already approved by parties. As a general category these technologies (large and small) are ostensibly the same. As such, MCTOC does not consider there to be a need for parties to approve this as a separate category of technology. Of course, national and/or local governments require their own performance standards to meet emissions limits, and it is expected that this technology, once commercialised and during operation, would be required to meet local emissions standards on an installation specific basis.

This review raises a potential housekeeping issue regarding the approved list of destruction technologies. Several years ago, a technology classed as Portable Plasma Arc that employed a small-scale nitrogen plasma arc process and was added to the list as a separate approved technology from Nitrogen Plasma Arc, which is listed as a separate class. The commercial version of the Portable Plasma Arc technology was marketed for a few years but proved to be unsustainable economically. Given the assessment here, that the Argon Plasma Arc technology could be scaled down and remain approved, it raises the question as to the need to have the differentiation related to scale for the Nitrogen Plasma Arc technology.

Parties may wish to consider removing the category, Portable Plasma Arc, as a separate approved technology to rationalise and consolidate the list of approved destruction technologies.

8.6.5 Approved destruction technologies recommended for dilute EOL ODS/HFC destruction

The approved list of destruction technologies applicable to dilute EOL ODS/HFC is currently limited to municipal solid waste and rotary kiln incineration, noting that municipal solid waste incineration is unique to the destruction of dilute waste. Cement kilns are not an approved technology for the destruction of dilute waste, even though it is an approved technology for the destruction of concentrated EOL ODS/HFCs, except for Halons, methyl bromide and HFC-23.

In terms of DRE and the technical performance advisory criteria for other pollutants, cement kilns have already demonstrated that they meet DRE for concentrated sources (99.99% versus 95% for dilute sources), which would qualify them for destruction of dilute sources. Cement kilns are utilised successfully for other halogenated waste streams, such as PCBs. As such, this technology can be recommended for inclusion on the list of approved destruction technologies for dilute EOL ODS/HFCs. As with all technologies, specific facilities would need to be qualified under national regulatory requirements to be permitted to receive the dilute EOL ODS/HFCs solid waste.

It seems improbable that parties would choose to deduct the calculated amounts of controlled substances destroyed from dilute sources for the purpose of reporting production under the Montreal Protocol, as is the original intended purpose of the list of approved technologies. However, the approved list of technologies appears to have taken on an unintended de facto function, giving validation to approved destruction technologies that goes beyond the narrower production reporting requirements intended by parties through their decisions. As such, a destruction technology that is not approved can be wrongly overlooked and misunderstood as being unsuitable. Industry sources indicate that if a destruction technology is not on the approved list, a party, or a commercial operator (e.g., in the carbon markets), can be reluctant to apply those technologies for ODS/HFC destruction, despite them being capable of destruction to an acceptable level of efficiency.

As discussed in section 8.6.5 below, a general review of available global EOL ODS/HFC destruction capacity includes cement kilns as an important contributor. This technology is widely available in countries that would otherwise not have economically accessible facilities with other approved technologies and may enhance destruction capability in Article 5 parties. This option for foam waste streams is being utilized in some countries, such as Colombia, largely because of foam waste streams restrictions being placed on conventional disposal. Recognising the significant contribution of foam blowing agents to banks of remaining CFCs and HCFCs, and the long service life involved in building insulation applications, expanded available destruction options should be considered, especially when considering the broader opportunities to mitigate the climate impacts of greenhouse gases.

Parties may wish to consider inclusion of cement kilns as an approved destruction technology for dilute sources of ODS and Annex F, Group 1, HFCs, for which there is already approval for concentrated sources.

8.6.6 Global capacity for ODS/HFC destruction

MCTOC notes that the destruction of controlled substances is not fundamentally limited by the technologies themselves. Among the range of technologies that have already been approved for use for purposes of meeting obligations under Article 7 of the Montreal Protocol, many are installed and operational globally on a commercial basis.

The scope of available destruction facilities covered by this menu of technologies includes:

- Commercial hazardous waste facilities destroying a wide range of halogenated chemical waste streams
- Destruction facilities with similar capabilities integrated into chemical production plants
- Speciality facilities intended specifically for controlled substances
- Industrial facilities, such as cement kilns, mineral (ore) processing, electric arc furnace steelmaking etc., capable of accepting waste streams for destruction in production processes, and
- Energy from waste facilities processing solid waste containing controlled substances.

Furthermore, this range of technology options and the facilities employing them provides substantial global capacity capable of destroying the amounts of EOL ODS/HFCs projected to becoming available from recoverable banks as reflected in Section 8.2 above. A recent review by U.S. EPA[319] provides an estimate of available capacity both for the United States and globally. In the United States, over 70 facilities were identified as destroying controlled substances, of which 27 (operated by 19 companies) are commercial hazardous waste management facilities and the remainder are employed internally or in association with chemical production plants. While data on what is received by these facilities generally applies to ODS, it is noted that most facilities would be equally qualified to destroy HFCs. Overall, the current amounts of controlled substances destroyed represents 0.1% of hazardous waste managed in the country, indicating no current capacity limitations. It also notes that this capacity could be significant increased if co-disposal in cement kilns meeting regulatory requirements were utilized. The report also estimates globally there are 169 or more facilities destroying ODS globally, of which 80 are in Japan, 49 are in the European Union, and 11 are in the United States. Twenty or more facilities are identified in Article 5 parties (Algeria, Argentina, Brazil, China, Colombia, Cuba, Indonesia, Mexico, Nigeria, Venezuela) that should have the capability to destroy ODS in Article 5 parties.

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[319] U.S. EPA, 2021, *ODS Destruction in the United States and Abroad*, EPA 430-R-21-006, April 2021.

As a general conclusion, the ability to substantially increase the amount of EOL ODS/HFCs destroyed is not inherently limited by global capacity but rather is limited by the ability to recover meaningful amounts, which requires a combination of:

- Regulatory action
- Increased infrastructure for collection and storage to accumulate economic quantities
- Development of new better scaled destruction capacity closer to source
- Utilisation of existing local destruction capability if available
- Regulated but efficient transborder access to facilities available elsewhere
- Sustainable financial mechanisms supporting each part of the EOL management process.

9 Aerosols

9.1 Aerosol products and market profile

Aerosols are used in a wide range of different applications. The term aerosol product describes a product *pressurised* with a propellant that expels its contents from a canister through a nozzle. Aerosols incorporate propellants and solvents with the appropriate technical properties and characteristics in formulations designed to deliver a product for its intended purpose.

Propellants include compressed gases (nitrogen, nitrous oxide, carbon dioxide) or liquefied gases, which are liquid inside the pressurized container. These liquefied gas propellants include hydrochlorofluorocarbons (HCFCs e.g., HCFC-22), hydrofluorocarbons (HFCs) (e.g., HFC-134a, HFC-152a), hydrofluoroolefins (HFOs, e.g., HFO-1234ze(E)), hydrocarbons (HCs), and dimethyl ether (DME).

Some aerosol products contain solvents, including HCFCs, HFCs, hydrofluoroethers (HFEs), aliphatic and aromatic solvents, chlorinated solvents, water, esters, ethers, alcohols, ketones, and hydrochlorofluoroolefins (HCFO, e.g., HCFO-1233zd(E)). HCFCs, including HCFC-141b, are still currently used in some countries and are being replaced by HFCs, HFEs and HCFOs, which are further discussed in Chapter 4, Solvents. If solvents are included in an aerosol product using a liquified gas propellant, the solvent constitutes up to 50–90% of the contents; and with a compressed gas propellant (e.g., carbon dioxide), the solvent constitutes up to 95% of the contents.

Aerosols can be divided into categories:

- Consumer aerosols, including personal care products like deodorants and hair sprays, cleaning products, air fresheners, furniture and textile care, household pesticides, food, veterinary, convenience products.

- Technical aerosols, including automotive and industrial, paints, lubricant sprays, dusters, contact cleaners, safety horns, degreasers, mould release agents.

- Medical aerosols, including aerosols that deliver medical treatment through nasal and topical aerosol sprays. These medical aerosols are used to deliver topical medication mostly onto the skin, but also to the mouth, and other body cavities. Pressurised metered dose inhalers (pMDIs) are the major application for medical aerosol products, which are described separately in the next chapter.

This chapter addresses, specifically, consumer, technical and non-pMDI medical aerosols, referring to them generically as aerosols. pMDIs are described in Chapter 10 and treated separately from the assessment of aerosols that follows (unless otherwise specified).

Ozone-depleting propellants and solvents (CFCs and HCFCs) have been replaced with technically and economically feasible alternatives in aerosol products. Small uses of HCFCs remain in 2022 in a few countries (including China and the Russian Federation) for specific medical aerosol products.

A significant proportion of aerosol propellants have migrated to hydrocarbons and DME, which dominate in the consumer aerosol market. Hydrocarbons and DME are highly flammable propellants. They are also used in technical aerosols where flammable propellants can be used safely. Hydrocarbons and oxygenated hydrocarbons (such as DME) are volatile organic compounds (VOCs) that contribute to photochemical smog generation. In some jurisdictions, strict VOC controls (e.g., in California) can have an impact on the choice of propellant, where hydrocarbons are avoided. The use of compressed gases (nitrogen, nitrous oxide, carbon dioxide) as propellants has increased because of these regulations and the availability of better cans.

There are also not-in-kind (NIK) technologies that compete with pressurised aerosol products to perform the same or similar functions, including trigger sprays, finger pumps, squeeze bottles, roll-on liquid products (e.g., for deodorants), and non-sprayed products (e.g., for polishes and lubricating oils). NIK alternatives are sometimes not as easy to use or achieve lower performance for some applications.

Alternative propellants and solvents are suitable for certain product types depending on the properties of the alternative and/or the intended product purpose or local VOC regulations. Some alternatives will not be technically suitable for some formulations. Like CFCs before them, non-flammable and non-toxic HFCs have been used in aerosols when flammability, toxicity, safety in use, and/or VOC content are considerations, e.g., personal defence sprays. HFCs, including HFC-152a, are often used where emissions of VOCs are controlled. However, HFCs and HFO-1234ze(E) are more expensive than hydrocarbons and are therefore mostly used when their properties are needed for the aerosol product and the advantages outweigh the costs. Fluorinated chemicals can also have lower solvency and are sometimes blended with more flammable chemicals with higher solvency to improve the performance of the aerosol product.

As an overall result of these factors, a smaller proportion of aerosols migrated to using HFCs where:

- Emissions of VOCs, such as hydrocarbons and DME, are controlled
- A non-flammable propellant is needed, and/or
- A propellant is necessary that is safe to inhale, such as HFC-134a.[320]

HFC-134a (100-year GWP 3,500) is used more commonly as a propellant in technical and medical aerosols, where its non-flammable and inhalation safety properties have advantages. Extensive respiratory toxicological studies were conducted that proved its safety as a propellant in respiratory use (e.g., for use in pMDIs).

HFC-152a (100-year GWP 124) is used more commonly as a propellant in consumer aerosols. HFC-152a has moderate flammability, with a lower explosive limit (LEL) of 3.9% by volume in air at room temperature. It is used alone as a propellant, or in blends with hydrocarbons, to meet VOC regulations.

HFO-1234ze(E) (100-year GWP <1) is classified as non-flammable, with a flammable range of 8.0–8.5 volume percent in air (at one atmosphere and temperatures >30°C). HFO-1234ze(E) is becoming increasingly available as a low-GWP alternative for aerosol applications that would otherwise use HFCs, such as technical and consumer aerosols where non-flammable and low-GWP properties are needed. HFO-1234ze(E) is also used in jurisdictions that have VOC emission controls. HFO-1234ze(E) is used in the United States for technical and some consumer aerosol applications. Duster products that were previously manufactured in the United States with HFC-134a propellant are now manufactured with HFO-1234ze(E).

HFC-152a and HFO-1234ze(E) are also blended with HFC-134a to produce propellants with lower GWP (than HFC-134a) and lower flammability (than HFC-152a or HFO-1234ze(E)).

HFC-152a and HFO-1234ze(E) are produced in the United States and China.

Propellants with flammability risks require special equipment, training and handling during production, and the more flammable propellants also require special precautions in use. Hence, replacement of HFC-134a propellant with HFC-152a or HFO-1234ze(E) does not depend solely on

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[320] In China, HCFC-22 is also used for some non-MDI medical aerosols.

cost but also on the performance of the final product and manufacturing capabilities to manage flammability risks.

Traditional aerosol propellants are widely available worldwide. There are some differences in price depending on whether they are locally produced or imported. Their prices are also affected by the transportation costs from the supplier to the filling plant. In most cases compressed gases and LPG mixtures are relatively inexpensive, except in some Article 5 Parties that consequently do not have significant aerosol production.

HFCs and DME are more expensive propellants than hydrocarbons as they are chemically synthesised, and their transportation costs can be significant when they are exported, particularly in Article 5 Parties where movement of pressurized vessels in and out of customs can be complicated. HFO-1234ze(E) is more expensive than HFCs; nevertheless, it is finding use in high-end applications and in markets that do not accept the HFCs that they replace, e.g., Europe.

Ozone-depleting substances (ODS) (CFC-113, methyl chloroform, HCFC-141b) used in aerosols as solvents have been migrated to hydrofluorocarbons (HFC-43-10mee, -365mfc, -245fa), hydrofluoroethers (HFEs), aliphatic and aromatic solvents, chlorinated solvents, oxygenated organic chemicals, and low-GWP chemicals, such as hydrofluoroolefins and hydrochlorofluoroolefins, including methoxytridecafluoroheptene (MPHE) and HCFO-1233zd(E). HCFO-1233zd(E) and MPHE can be used as solvents for technical aerosols.[321]

An assessment of the technical and economic feasibility of alternatives to aerosols containing Annex F HFCs is outlined under section 9.3, including the availability and accessibility of in-kind and not-in-kind aerosol products.

9.1.1 Developments in not-in-kind technologies

There is ongoing work to improve the delivery of aerosols that work with air (compressed gas) and even to develop propellant-free alternatives for aerosol products. These patented technologies seek to provide continuous dispensing, deliver pure product (which might not be a benefit as this can result in coarser sprays, where it is the vaporization of the liquid propellant that creates the fine mist consumers want in some products), and work at any angle. It is likely that these technologies will capture some market segments depending on price and characteristics of the final product.

9.1.2 Global aerosol market profile

Global aerosol demand was estimated at more than 16 billion units (cans) in 2021.[322] Europe is the largest regional aerosol producer and market, with estimated production of over 5 billion units, accounting for about 33% of global production. North America is the second largest regional market, accounting for about 23%, and China and Latin America each account for about 17% of global unit production. In terms of revenue, Asia Pacific is one of the fastest growing regions. Governments, like those of China and India, are promoting investments and increasing consumer spending. This results in increased demand for aerosol products.

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[321] ICF International, 2016, *Preliminary Assessment of Global HFC Consumption in Aerosols*, September 2016. Draft report prepared for U.S. EPA, made available through personal communications.

[322] Aerosol Committee of China Packaging Federation, 2022, *Global Aerosol Production Data Release*, 9 September 2022. http://www.aerosolchina.com/newsinfo/4379539.html. Accessed October 2022.

Personal care aerosol products account for the largest global aerosol market share (by volume), accounting for more than 40% in 2021.[323] Household aerosols account for another major sector of the global aerosol market, followed by automotive and industrial, food, paints sectors, with medical and other sectors accounting for the smallest share.

While the European Union's aerosol market is the largest overall globally, its HFC consumption for aerosols has been phased out. This compares with the United States, with the largest HFC consumption in aerosols. This reflects market variations in aerosol propellant and solvent choices based on the different industry and regulatory environments for HFCs and VOCs. For example, the European Aerosol Federation (FEA) agreed to a voluntary industry production and import ban of HFC-152a, facilitated by the absence of HFC-152a production plants in Europe.

Forecasts for global growth of the aerosol market estimate compound annual growth rate of 6.6% from 2022 to 2030.[324] Some of the factors behind this growth include:

- Increasing demand for personal care aerosols, such as deodorants, shaving creams, hair and body sprays, which rarely if ever use HFCs.
- Rising popularity of aerosol products in the food industry, which rarely if ever contain HFCs.
- Emerging economies of Asia Pacific driving demand for aerosols in paints and household products.
- Technological developments, including airless dispensers and bi-compartmental technology.

9.1.3 Aerosols in different regions

In the sections below, the current situation in a variety of significant aerosol manufacturing regions and markets is described, including North America, given this market represents a large portion of HFC propellant use in aerosols today, and a selection of other significant regions, including Europe, Asia, and Latin America.

Regulatory controls are increasingly limiting and/or prohibiting HFC use for aerosol propellants and solvents where other suitable alternatives are available. The regulatory status in different countries that are relevant to HFC use in aerosol products is also summarised below under each region.

North America

North America is the second largest regional producer of aerosols in the world with about 3.75 billion cans in 2021, or 23% of global aerosol volume.[325]

By volume, HFC use (HFC-134a and HFC-152a) in aerosols in North America accounts for the majority of global HFC usage for this application.

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[323] Grand View Research, 2022, *Aerosol Market Size, Share & Trends Analysis Report By Material (Steel, Aluminium), By Type (Bag-In-Valve, Standard), By Application (Personal Care, Household), By Region (EU, APAC), And Segment Forecasts, 2022 – 2030*, 2022. https://www.grandviewresearch.com/industry-analysis/aerosol-market#. Accessed August 2022.

[324] Grand View Research, 2022, *Aerosol Market Size, Share & Trends Analysis Report By Material (Steel, Aluminium), By Type (Bag-In-Valve, Standard), By Application (Personal Care, Household), By Region (EU, APAC), And Segment Forecasts, 2022 – 2030*, 2022. https://www.grandviewresearch.com/industry-analysis/aerosol-market#. Accessed August 2022.

[325] Aerosol Committee of China Packaging Federation, 2022, *Global Aerosol Production Data Release*, 9 September 2022. http://www.aerosolchina.com/newsinfo/4379539.html. Accessed October 2022.

HFC-134a use has significantly declined as technical aerosols convert from HFC-134a to HFO-1234ze(E). From an estimated 11,100 tonnes in 2015[326], HFC-134a use in aerosols has reduced by 90% to about 1,100 tonnes in North America and is expected to decline further in 2023.

HFC-152a, with its much lower GWP than HFC-134a, continues to be widely used as a propellant, often blended with hydrocarbons in personal care products. In addition to GWP, regulations to reduce VOCs are the primary challenge for consumer product formulators in the U.S. HFC-152a currently remains a critical component in achieving ever lower VOC levels.

From an estimated 29,100 tonnes in 2015[327], estimated HFC-152a consumption (including imports) in aerosols in North America has increased slightly to about 34,000 tonnes in 2021. Consumption has remained relatively constant over the last few years and is expected to grow in the short to medium term due to strengthening VOC requirements. Industry anticipates possible downward pressure on HFC-152a consumption in aerosols towards the end of the 2020s.

In August 2022, the California Air Resources Board (CARB) enacted amendments to its Regulations for Reducing VOC Emissions from Consumer Products that impose lower VOC limits on aerosol products sold in California. For major aerosol manufacturers, this has the broader practical effect of reducing VOC content for all aerosol products sold within the United States, due to state cross-border trade in products that can meet the California benchmarks. These new requirements will come into effect on 1 January 2023 with a reduction of up to 50–55% in VOC content in consumer aerosol products. These reductions are expected to trigger an associated increase in use of HFC-152a in aerosols, and to a lesser extent HFO-1234ze(E) as it builds market share. Additional VOC content reductions will come into effect in 2029 and 2033. More jurisdictions are expected to follow California's lead in reducing VOC levels to curb photochemical smog generation.

HFO-1234ze(E) continues to gain traction as an alternative to HFC-152a propellant, particularly in products that can command higher prices, such as haircare and tyre inflator aerosol products. North America produces HFC-152a locally and imports from China. With supply chain pressures in the last two years, and competition with other sectors using HFC-152a, HFO-1234ze(E) is building market share as a more competitively priced propellant option for some products.

About 10% of aerosol products in North America use compressed gases as propellants.[328] Usage of compressed gases as propellants is increasing in those products where these are suitable, such as air-care products. However, increases are generally due to their replacement for products using hydrocarbon propellants, to meet VOC requirements, not as replacements for HFC propellants.

Under its Significant New Alternatives Program (SNAP), U.S. EPA listed HFC-125, HFC-134a, and HFC-227ea as unacceptable alternatives to ozone-depleting substances from 2016 onwards, except for certain technical and medical uses (pMDIs) for HFC-134a and HFC-227ea.[329]

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[326] ICF International, 2016, *Preliminary Assessment of Global HFC Consumption in Aerosols*, September 2016. Draft report prepared for U.S. EPA, made available through personal communications.

[327] Ibid., ICF International, 2016.

[328] The National Aerosol Association, https://www.nationalaerosol.com/history-of-aerosol/. Accessed September 2021.

[329] U.S. EPA, 2015, *Protection of Stratospheric Ozone: Change of Listing Status for Certain Substitutes Under the Significant New Alternatives Policy Program*, Federal Register/Vol. 80, No. 138, Monday, July 20, 2015, Rules and Regulations. Cleaning products for removal of grease, flux and other soils from electrical equipment or electronics; refrigerant flushes; products for sensitivity testing of smoke detectors; lubricants and freeze sprays for electrical equipment or electronics; sprays for aircraft maintenance; sprays containing corrosion preventive compounds used in the maintenance of aircraft, electrical equipment or electronics, or military equipment; pesticides for use near electrical wires, in aircraft, in total release insecticide foggers, or in certified organic use pesticides for which U.S. EPA has specifically disallowed all other lower GWP propellants; mould release agents and mould cleaners; lubricants and cleaners for spinnerettes for synthetic

In the United States, the American Innovation and Manufacturing (AIM) Act 2020 establishes a phase-down for HFC production and consumption and facilitates the transition to next generation technologies. A rulemaking provides for the distribution of allowances and a trading system for HFC production and consumption consistent with the Act. Application-specific allowances are also listed in the Act, which includes personal defence sprays (and pMDIs). Authority is given to U.S. EPA to restrict HFC use on a sector or subsector basis to support transition to next generation technologies, which is initiated through stakeholder petitions. A petition[330] from the Household and Commercial Products Association and the National Aerosol Association was granted in October 2021, which starts a 2-year rule-making process by U.S. EPA to consider restricting the use of HFCs in a sector or sub-sector by October 2023. The industry association petition requested prohibition of the use of HFCs as aerosol propellants as was previously deemed "unacceptable" under the SNAP Program in 2015 and 2016 (SNAP Rules 20 and 21). The petition outlined reasons, which include state differences in the promulgation of regulations to implement the SNAP Rules.

In April 2018, the government of Canada launched an HFC phase-down plan to limit HFC consumption by 85% by 2030, in line with the Kigali Amendment to the Montreal Protocol. Much of the regulation focuses on imports. There are product-specific controls. Since 2019, aerosols should use propellants with a GWP lower than 150, with exceptions such as certain cleaning products for electronics. With the approval of the Minister of Environment, exceptions can be granted, if:

- The product is necessary for health and safety or is critical for the good functioning of society; and
- There are no alternatives that are technically and economically feasible.
- The Amendments will not prevent the use and sale of products manufactured or imported before the date of prohibition.

Central and South America

Latin America is the equal third largest regional aerosol producer in the world, with 17% of global aerosol volume. [331] Of Latin American countries, Brazil is the largest producer of aerosols with around 1.0 billion cans (38%) in 2021, followed by Argentina (31%) and Mexico (26%). Personal care aerosol products predominate (57%), followed by insecticides (18%) and home care (14%) aerosols. Environmental impact and recycling of post-consumer aerosols are important issues on the industry's agenda. In 2015, estimated production of non-pMDI aerosols containing HFC propellants in Latin America was about 3% of the global total HFC aerosol volume.[332] In 2015, HFC consumption in aerosols was estimated to be 400 tonnes HFC-134a and 1000 tonnes HFC-152a. Aerosols containing HFC propellants currently makes up an unknown portion of production, including for those companies exporting aerosols to meet VOC requirements in North America.

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fabrics; duster sprays specifically for use on removal of dust from photographic negatives, semiconductor chips, specimens under electron microscopes, and energized electrical equipment; adhesives and sealants in large canisters; document preservation sprays; MDIs approved by U.S. FDA for medical purposes, wound care sprays; topical coolant sprays for pain relief; and products for removing bandage adhesives from skin.

[330] Household & Commercial Products Association and National Aerosol Association, 2021, *HCPA and NAA Petition to Reinstate HFC Prohibitions for Aerosol Propellant from SNAP Rules 20 and 21 under AIM Act*, July 6, 2021. https://www.regulations.gov/document/EPA-HQ-OAR-2021-0289-0037.

[331] Angel Rasgido and Geno Nardini, 2021, *Latin American Aerosol Industry, 2021 Volume and Current Situation*, presentation to Federación Latinoamericana del Aerosol. Provided through personal communications, September 2022.

[332] ICF International, 2016, *Preliminary Assessment of Global HFC Consumption in Aerosols*, September 2016. Draft report prepared for U.S. EPA, made available through personal communications.

China

China is the equal third largest regional aerosol producer in the world with about 2.7 billion cans in 2021, or 17% of global aerosol volume. The main aerosol products in the China market are automotive, technical, and industrial (including construction) aerosols (21%), paint aerosols (17%), and insecticide aerosols (15%), using mainly LPG, DME or their mixtures; and personal care products (17%), medical and animal care aerosols (15%), recreational (ribbons) and dust removing aerosols, using mainly compressed gases (CO_2), HFC-134a and HFC-152a.

Around 1,000–1,100 tonnes HFC-134a is currently used in medical aerosols (excluding pMDIs) in China, and around 120 tonnes HFC-134a is used for technical and novelty aerosols (dusters and aerosol Christmas snow). An estimated 5000 tonnes HFC-152a is used in China for the manufacture of technical and novelty aerosols (e.g., dusters, Christmas snow, chalk sprays) mostly intended for export. Domestic consumption of HFC-152a aerosols is minor due to its relatively higher price compared with hydrocarbons.

Financial considerations are a key factor in the choice of propellant. Due to their higher cost, HFCs are currently less commonly used as propellants. However, with development of the economy in China, and improving living standards, environmental considerations are also now key factors in the choice of propellant.

Other than for pMDIs, China banned the use of CFCs as aerosol propellants in 1997. Around the year 2000, China's state environmental protection administration established national standards for technical requirements for aerosols to protect the environment, with requirements for VOC content tightening the uses of LPG and DME as propellants. While personal care aerosol products currently hold a relatively smaller share on the domestic market (17%), their popularity is increasing.

Since 2020, HCFC use in China for medical aerosols, including for Traditional Chinese Medicines, are estimated to be about 100 tonnes (HCFC-22 and HCFC-141b), a reduction of over 95% from 2018. Flammability safety concerns with some economically feasible alternatives, such as DME or LPG, are currently a barrier to their use as replacements in this application.

The industry is anticipating increasing use of HFCs in the short term. In the long term, compressed gases and HFOs are seen in China as the likely best candidates to replace HFCs, LPG and DME. There are their own challenges with these replacements. HFOs, such as HFO-1234ze(E) and HFO-1234yf, are currently expensive in China, although the use of HFO-1234ze(E) is emerging in some aerosols, including for novelty aerosols, duster products, and pet training aerosols. There can be technical challenges in formulating aerosol products to use compressed gases. Despite these challenges, "safe and green" propellants are seen as the future trend.[333]

Europe

Europe is the largest regional producer of aerosols in the world, constituting around 33% of global volume with around 5.2 billion cans in 2021 (including the United Kingdom).[334] Its large share is mainly attributable to personal care aerosols.

The breakdown of propellant use by aerosol volume is 55% hydrocarbons, 20% DME, 15% nitrogen or compressed air, and the balance HFO-1234ze(E).

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[333] You, Y. and Shao, Q., (eds.), 2018, *The Chinese Aerosol Industry, Products and Market*, Aerosol Europe Pub., Germany, 2018. Print.

[334] Aerosol Committee of China Packaging Federation, 2022, *Global Aerosol Production Data Release*, 9 September 2022. http://www.aerosolchina.com/newsinfo/4379539.html. Accessed October 2022.

Of the continental European region countries, Germany (1 billion cans) and France (0.65 billion cans) are the largest aerosol producers. [335]

The United Kingdom is the largest producer of aerosol products in the broader European region, producing 1.44 billion cans in 2021. [336] In 2016, it was estimated that HFC-containing aerosols accounted for 5% of F-gas emissions in the United Kingdom (with HFC pMDIs accounting for a further 6%). As part of the broader European region, it is understood that HFC-134a propellants have now been phased out in aerosol manufacture.

The European aerosol industry voluntarily began transitioning away from HFCs under a Code of Practice adopted in 2002. European Union F-gas regulations specifically prohibit the sale of technical aerosols containing HFCs with a GWP of above 150, from 2018 onwards, except where the aerosol is needed to meet national safety standards or for medical applications. An earlier European Union F-gas regulation prohibited the sale of aerosols containing HFCs with a GWP above 150 in novelty aerosols and signal horns from 4 July 2009 onwards. European Union aerosol producers have been converting products to HFOs and hydrocarbon-based products. Technical aerosols containing HFCs are subject to a ban under Swiss legislation. HFCs are currently only allowed in aerosols where there are no other safe, practical, economic, or environmentally acceptable alternatives available. It is understood that aerosols manufactured in Europe using HFC-134a (e.g., technical and automotive) and HFC-152a have been phased out and replaced with propellant alternatives, such as HFO-1234ze(E).

India

Up to 90% of aerosol production are estimated to use hydrocarbon propellants in India. Spray paint aerosols for the automotive industries make up the major portion of the aerosol market in India, which are manufactured using hydrocarbon propellants.[337] Healthy growth in the aerosol industry is expected in the next decade, with rising demand for aerosols in automotive industries and the aftermarket and expanding Indian manufacturing industry. HFCs are used for the manufacture of medical aerosols and pharmaceutical inhaler (pMDI), using between 3000–4000 tonnes HFCs in 2021, mainly HFC-134a. Consumption of HFC propellants is understood to be mostly for pharmaceutical inhaler (pMDI) manufacture. HFC-152a is currently not produced in India and consumption estimates, if any, are not available. HCFC propellants are likely soon to be phased out or no longer used in aerosol manufacture in India; the HCFC phase-out management plan requires phase-out by the end of 2024.

Japan

Japan implemented voluntary measures to reduce the use of HFCs in aerosols as early as the year 2000. In 2013, Japan enacted a law updating their existing fluorocarbon regulation. The objective of the new legislation is to reduce HFC emissions through measures that cover the total life cycle of fluorocarbons from manufacture through disposal. In 2007 there was a limitation of HFC-134a use to applications without safe, practical, environmentally acceptable alternatives.

9.2 Use of controlled substances in aerosols

9.2.1 Consumption and Availability of HCFCs for medical aerosols

HCFC production and consumption (as defined) in non-Article 5 parties was required to be phased out by 1 January 2020, with allowance for essential use exemptions if authorised by the Montreal

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[335] Ibid., Aerosol Committee of China Packaging Federation, 2022.

[336] Ibid., Aerosol Committee of China Packaging Federation, 2022.

[337] Prescient and Strategic Intelligence, 2021, *India Industrial Aerosol Market Research Report: By Application (Spray Paints, Cleaning, Maintenance) – Industry Analysis and Growth Forecast to 2030*, January 2021. https://www.psmarketresearch.com/market-analysis/india-industrial-aerosol-market. Accessed October 2022.

Protocol. Between 1 January 2020 and 1 January 2030, for any non-Article 5 party, Article 2F, paragraph 6, allows HCFC consumption and production in any year up to 0.5% of the baseline consumption allowance, for restricted applications including topical medical aerosol applications for the specialised treatment of burns. Otherwise, aerosol use of HCFCs can continue in non-Article 5 parties from recycled or stockpiled sources, for as long as those sources remain.

HCFC production and consumption (as defined) in Article 5 parties will be phased out by 1 January 2030, with allowance for essential use exemptions if authorised by the Montreal Protocol. Between 1 January 2030 and 1 January 2040, for any Article 5 party, Article 5, paragraph 8 *ter*, allows HCFC consumption and production in any year up to 2.5% of the baseline consumption allowance, for restricted applications including topical medical aerosol applications for the specialised treatment of burns. Otherwise, aerosol use of HCFCs would be allowed to continue in Article 5 parties from recycled or stockpiled sources, for as long as those sources remain.

The following section describes aerosols using HCFCs in non-Article 5 parties, where recycling and use from existing stockpile may be on-going in small quantities, and in Article 5 parties.

In the Russian Federation, topical medical aerosol applications use HCFC-22 (as a propellant) and HCFC-141b (as a solvent), which are now being sourced from stockpiles. The products are aerosol foams used for the treatment of radiation burns, to provide local anti-inflammatory and antiseptic action and to stimulate healing. One company, located in Siberia, produces oil of sea-buckthorn (hipopheae oleum) from local plantations and uses it in the production of two very popular foam medical aerosol products, using around 20 tonnes annually of HCFC-22 and HCFC-141b in 2018. The indications for use of one product are for wounds, rehabilitation after skin transplantation, dermatitis, trophic ulcer, burns (including solar and thermal), skin infections, discomfort, itching etc.

Indications for use of the other product are for colpitis (nonspecific, trichomoniasis), vulvitis, erosion or condition after cervical diathermocoagulation, condition after removal of the uterus body; proctitis (erosive and radial), proctosigmoiditis, anal fissures, ulcerative colitis (distal and limited forms), Crohn's disease, rectal and perineal wounds, intraoperative diagnostics and prevention of intestinal anastomosis insufficiency in operations on the large intestine, inflammatory processes in the disconnected rectum in preparation for recovery operations, erosive and ulcerative lesions of the mucous membrane of the oral cavity and periodontal (acute, chronic), burns (II–III degree), in wounds (after radical excision of purulent focus).

HCFC-22 and HCFC-141b are used in China for aerosols, including for Traditional Chinese Medicines, by several large pharmaceutical companies and some smaller companies. HCFC-22 is used as propellant, and HCFC-141b is used for its solvent properties. After 2020, use has been estimated to be small, around 100 tonnes per year. Flammability safety concerns with some economically feasible alternatives, such as DME or LPG, have been a barrier to their use in this application. Other potential technical alternatives, such as HFC-134a, present an economic impediment in this application. After 2020, no quota in China will be issued for the use of HCFCs by pharmaceutical companies for aerosols. Due to the large market supply of HCFC-22, it is speculated that small amounts may flow into small aerosol users.

Relevant to the use of HCFC-141b in topical medical aerosols, the National Institute for Occupational Safety and Health (NIOSH) have presented the immediately dangerous to life or health (IDLH) air concentration value for HCFC-141b to be 1,700 ppm (8,245 mg/m^3). Cardiac sensitization is the most sensitive indicator of toxicity and of a potentially lethal and irreversible health endpoint that serves as the basis for the IDLH value for HCFC-141b).[338] HCFC-141b is also classified as a grade 1 health

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[338] U.S. National Institute for Occupational Safety and Health (NIOSH), 2016, *Immediately dangerous to life or health (IDLH) value profile: 1,1-di-chloro-1-fluoroethane (HCFC-141b)*, Dotson GS, Maier A, Parker A, Haber L. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for

hazard by the U.S. Hazardous Materials Identification System (HMIS). HMIS is a voluntary hazard rating scheme developed by American Coatings Association (ACA) to help employers comply with workplace labelling requirements of the U.S. Occupational Safety and Health Administration's (OSHA) revised Hazard Communication Standard. The National Fire Protection Association (NFPA) also lists HCFC-141b as a grade 2 health hazard, as an irritant particularly to eyes.

9.2.1 Consumption of Annex F HFCs

A preliminary assessment of global HFC consumption (manufacture and import less export) in aerosols made by ICF for U.S. EPA[339] characterised global and regional market consumption of aerosols containing HFCs for the year 2015. Global HFC demand[340] in aerosols was estimated to be around 45,000 tonnes (~15,000 tonnes HFC-134a; ~30,000 tonnes HFC-152a) in 2015, corresponding to direct emissions with a climate impact of about 25 MMTCO_2e. In 2015, HFC propellant consumption for aerosol manufacture corresponded to direct emissions that were estimated to be about 3% of global total GWP-weighted emissions of HFCs.[341]

Estimating global HFC consumption in aerosols is difficult due to the confounding impact of imports and exports in the reported figures, leading to potential double counting. Nevertheless, an addition of the regional data outlined earlier, with some assumptions made to fill regional data gaps, can provide a rough global estimate. For 2021, global HFC demand is estimated to be around 44,000 tonnes (~3,000 tonnes HFC-134a; ~41,000 tonnes HFC-152a), corresponding to direct emissions with a climate impact of about 9.4 MMTCO_2e. This represents an overall reduction in the global warming impact of HFC-containing aerosols of more than 50% since 2015. These reductions are due to the decrease in global consumption of HFC-134a in aerosols, especially in North America. Meanwhile, there has been an increase in the global consumption of HFC-152a in aerosols since 2015.

HFC demand in aerosols continues to be dominated by the North American market, which, according to the ICF estimates, in 2015 consumed about 85% of the global total of HFC aerosols (in metric tonnes), with the Asia and Asia-Pacific region consuming around 10%. This ratio is likely to have changed by 2021, with probable growth in HFC aerosol consumption in the Asia and Asia-Pacific region.

SAP 2022[342] reports estimated global emissions of HFC-152a of 51,000 ±8,000 tonnes. One OECD study[343] has estimated aerosol consumption of HFC-152a to be around 80% of all applications. Other applications of HFC-152a (including as a foam blowing agent and in refrigeration) contribute to

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Occupational Safety and Health, DHHS (NIOSH) Publication 2016–168. DHHS (NIOSH) Publication No. 2016–168, September 2016.

[339] ICF International, 2016, *Preliminary Assessment of Global HFC Consumption in Aerosols*, September 2016. Draft report prepared for U.S. EPA, made available through personal communications.

[340] HFC demand is equivalent to HFCs used for aerosol production, adjusted for imports and exports of HFC aerosol products, where that information was available. Specific data on imports and exports of HFC-containing consumer aerosol products for the United States was not readily available, so consumption for these products is assumed to be equivalent to production, based on data from the then Consumer Specialty Products Association (CSPA), now known as the Household & Commercial Products Association (HCPA), the United States' industry trade association for chemical products companies.

[341] As derived from atmospheric observations, total emissions of HFCs summed to 0.88 (± 0.07) GtCO_2e/year in 2016, as taken from: World Meteorological Organization (WMO), 2018, *Executive Summary: Scientific Assessment of Ozone Depletion: 2018*, World Meteorological Organization, Global Ozone Research and Monitoring Project – Report No. 58, 67 pp., Geneva, Switzerland, 2018.

[342] World Meteorological Organization (WMO), 2022, *Scientific Assessment of Ozone Depletion: 2022*, GAW Report No. 278; WMO: Geneva, 2022.

[343] OECD, 2016, Screening Information Dataset (SIDS) Initial Assessment Report, 1,1-DIFLUOROETHANE (HFC-152a) CAS N°: 75–37–6, Paris, France, 18–21 April 2006. https://hpvchemicals.oecd.org/ui/handler.axd?id=6415a8cf-4a7b-4c8e-b943-f61ed5304b0d. Accessed October 2022.

banks, with their resulting emissions occurring over a longer period after initial consumption. Nevertheless, these global HFC-152a emissions estimated from atmospheric measurements, taking into account longer term emissions from applications with banks, provide a range that is generally consistent with the estimated level of global HFC-152a consumption in aerosols in 2021, and their associated more immediate emissions, of ~40,000 tonnes.[344]

9.3 Technical and economic assessment of aerosols containing controlled substances and their alternatives

An assessment follows of the technical and economic feasibility of alternatives to Annex F HFCs in aerosol uses. The assessment criteria referenced in decision XXVIII/2 have been slightly modified to remain relevant to this application, using the following criteria:

i. Commercially available
ii. Technically proven
iii. Environmentally sound
iv. Economically viable and cost effective
v. Safety in production and use, considering flammability and toxicity issues
vi. Easy to use

"Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization" has been adjusted to *safety in production and use, considering flammability and toxicity issues*. "Easy to service and maintain" has been adjusted to *easy to use*. Technically proven is interpreted to mean the technology has been proven to work for that application, or an aspect of it.

Aerosol production has developed differently in each country due to regulations for flammability and occupational safety, VOC controls, and the availability from suppliers of HCFCs, HFCs, or their alternatives for aerosol production. The availability and number of different aerosol products varies within parties and regions and is closely related to the development of the local aerosol industries. Hence, alternatives are not necessarily interchangeable because of regional or local differences. The aerosol product type can also determine the propellant used, which could be related to performance requirements for the end use or the higher market value of the product, e.g., allowing a more expensive propellant.

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[344] Modelling generally assumes HFC emissions from aerosols to occur within a 2-year period from initial HFC consumption.

Table 9.1 Technical and economic assessment of aerosol uses of controlled substances and their alternatives (excluding pMDIs)

Controlled substances and alternatives	Aerosol products	Commercially available	Technically proven	Environmentally sound	Economically viable	Safety in production and use	Easy to use
Propellants							
HCFC-22 HCFC-141b	Medical aerosols, including topical coolants to numb pain, burns treatment. HCFC-141b is a solvent in the product formulation.	🟩[1]	🟩	🟥[1]	🟩	🟧	🟩
HFC-134a	Technical aerosols, including dusters, electronic contact cleaners, flux removers, wasp and hornet sprays, aircraft insecticides. Medical aerosols, including metered dose corticosteroid spray, throat/mouth topical sprays (disinfectants, anti-inflammatories, anaesthetics), anaesthetic, analgesic, calamine sprays for minor blunt injuries or itches, nitro-glycerine sublingual sprays.	🟩[1]	🟩	🟥[1]	🟧[2]	🟩	🟩
HFC-152a	Consumer and medical aerosols, including tyre inflators, safety horns, personal care products (e.g., hairspray, cosmetics, deodorants), food, novelty aerosols, household cleaning, room fresheners, for diaper rash for babies, nitro-glycerine sublingual sprays, sunscreen sprays.	🟩[1]	🟩	🟧[1]	🟩	🟧[3]	🟩

Controlled substances and alternatives	**Aerosol products**	**Commercially available**	**Technically proven**	**Environmentally sound**	**Economically viable**	**Safe to use in production and use**	**Easy to use**
Propellant Alternatives							
HFO-1234ze(E)	Aerosols like those using HFC-134a and HFC-152a. Replacing HFC propellants in higher priced aerosol products. Electronic cleaners, dust removers, novelty, and cleaning/disinfection products used on board aircraft.	◆	◆	◆	🔶[2]	🔶[3]	◆
Blends of: Propane *n*-Butane Isobutane	Consumer and medical aerosols, including personal care products (e.g., hairspray, cosmetics, deodorants), food, room fresheners, anaesthetic, analgesic, calamine sprays for minor blunt injuries or itches; cut or wound sprays; sprays to prevent bedsores; foot sprays and other anti-fungal products; vaginal hygiene sprays, rectal foams for treatment of colitis; foams for scalp hair loss; sunscreen sprays.	◆	◆	🔶[4]	◆	🔶[3]	◆
Dimethyl ether (DME)	Consumer aerosols including cosmetics, especially hairsprays and styling foams, sunscreen sprays. Medical aerosols including, anaesthetic, analgesic, calamine sprays for minor blunt injuries or itches; anti-fungal products.	◆	◆	🔶[4]	◆	🔶[3]	◆
Carbon dioxide	Technical and medical aerosols including dust cleaners, anaesthetic, analgesic, calamine sprays for minor blunt injuries or itches.	◆	◆[5]	◆	◆	◆	◆
Nitrogen	Consumer and medical aerosols including shaving cream, sunscreen sprays, food, cosmetics, air fresheners, deodorants, throat/mouth topical sprays (disinfectants, anti-inflammatories, anaesthetics), sterile saline solutions.	◆	◆[5]	◆	◆	◆	◆

Controlled substances and alternatives	**Aerosol products**	**Commercially available**	**Technically proven**	**Environmentally sound**	**Economically viable**	**Safety in production and use**	**Easy to use**
			"Not-in-kind" Alternatives				
Pump sprays	Variety of consumer and medical applications	🟩	🟩	🟩	🟩	🟩	🟧[6]
Drops		🟩	🟩	🟩	🟩	🟩	🟧[6]
Creams		🟩	🟩	🟩	🟩	🟩	🟧[6]

🟩 Yes or More acceptable; 🟧 Not always or Less acceptable; 🟥 No or Unacceptable.

1. HCFCs and high-GWP HFCs to produce aerosols (excluding pMDIs) are either phased out (HCFCs in non-Article 5 parties) or restricted by regulation or actively discouraged by suppliers in many parties. HCFCs and HFC-134a are non-flammable propellants. HFC-134a is used when flammability and/or toxicity are a consideration. HFC-152a, while another Annex F HFC, has a lower GWP and is becoming more commercially available than HFC-134a, with its higher GWP, for those regions starting their HFC phase-downs.

2. HFC-134a and HFO-1234ze(E) are expensive compared with hydrocarbons and therefore only used when their safety properties are necessary for the specific product (non-flammable, low toxicity), and the benefits outweigh the increased cost.

3. Hydrocarbons and DME are highly flammable propellants. HFC-152a has low to moderate flammability and is often used alone or in blends with hydrocarbons to lower their flammability. HFC-152a can also be blended with HFC-134a propellant to produce a propellant with lower GWP and lower flammability. HFO-1234ze(E) is classified as non-flammable, with a flammable range of 8.0–8.5 volume percent in air (at one atmosphere and temperatures >30°C). Flammable propellants require special equipment, training and handling during production, and the more flammable propellants require special precautions in use.

4. Hydrocarbons and oxygenated hydrocarbons are volatile organic compounds (VOCs) that contribute to photochemical smog generation in areas of high urban density. In some jurisdictions, strict VOC controls (e.g., in California) can have an impact on the choice of propellant, where hydrocarbons are avoided, although medical aerosols have been largely exempted from these requirements.

5. Carbon dioxide and nitrogen are gaseous propellants, not liquefied propellants, and as such are technically suitable for some but not all aerosol product applications.

6. Aqueous sprays and drops are well-established as "not-in-kind" alternatives for many consumer and medical aerosol products, including nasal sprays. Aqueous formulations in general and other "not-in-kind" alternatives, such as creams, are used in many consumer and medical aerosol applications. "Not-in-kind" alternatives can sometimes be less convenient to use. Aerosols can be favoured due to their ease of use.

Table 9.2 Characteristics of controlled substances and their alternatives used as propellants and solvents in aerosols

Controlled substances and alternatives	ODP	100-year GWP[1]	Flammability	Comments
Propellants				
HCFC-22	0.055	1810	Non-flammable at atmospheric temperature and pressure	Recommendations for workplace exposure limits.
HFC-125	0	3500	Non-flammable	-
HFC-134a	0	1430	Non-flammable	Approved for use in metered dose inhalers (pMDIs). Very low acute inhalation toxicity.
HFC-152a	0	124	Flammable, less so than HCs (LEL 3.9% volume in air)	Low acute inhalation toxicity. Recommendations for workplace exposure limits.
HFC-227ea	0	3220	Non-flammable	Approved for use in pMDIs. Very low acute inhalation toxicity. Due to cost and high GWP, probably used exclusively in pMDIs.
Propellant Alternatives				
HFO-1234ze(E)	0	<1	Non-flammable. A flammable range of 8.0–8.5 volume percent in air (at one atmosphere and temperatures >30°C). Exhibits flame limits at elevated temperatures.	Used as replacement for aerosols previously using higher GWP HFC propellants (e.g., novelty). Recommendations for workplace exposure limits.
Hydrocarbons and blends (propane, *n*-butane, isobutane)	0	≤4	High flammability (Isobutane, LEL 1.8% volume in air)	Recommendations for workplace exposure limits.
Dimethyl ether (DME)	0	1	Highly flammable	-
Compressed gases • CO_2 • N_2 • Air • N_2O	 0 0 0 0.017	 1 0 - 298	Non-flammable	 Recommendations for workplace exposure limits. - - Recommendations for workplace exposure limits.
"Not-in-kind", e.g., - Pump sprays - Liquids - Roll-on liquids/sticks	 0 0 0	 0 0 0	Non-flammable where liquid dispensed is non-flammable	Indirect life cycle climate impacts

Controlled substances and alternatives	**ODP**	**100-year GWP**[1]	**Flammability**	**Comments**
Solvents				
HCFC-141b	0.11	725	Non-flammable	Recommendations for workplace exposure limits.
Blends of HCFC-225ca/ HCFC-225cb	0.025 0.033	122 595	Non-flammable	Recommendations for workplace exposure limits.
HFC-43-10mee	0	1640	Non-flammable	Recommendations for workplace exposure limits.
HFC-365mfc	0	794	Flammable	Recommendations for workplace exposure limits.
HFC-245fa	0	1030	Non-flammable	Recommendations for workplace exposure limits.
Solvent Alternatives				
HFO-1336mzz(Z)	0	2.08[2]	Non-flammable	Recommendations for workplace exposure limits.
HCFO-1233zd(E)	<0.0004	3.88[2]	Non-flammable	Recommendations for workplace exposure limits.
HCFO-1233yd(Z)	0.00003	<1	Non-flammable	Recommendations for workplace exposure limits.
Hydrofluoroethers HFE-449s1 HFE-569sf2	 0 0	 297 59	 Non-flammable Non-flammable	 None. Recommendations for workplace exposure limits.
Aliphatic and aromatic solvents (e.g., Hexane, Heptane)	0	≤3	Highly flammable	Recommendations for workplace exposure limits.
Halogenated solvents e.g. Trichloroethylene Perchloroethylene Dichloromethane *n*-Propyl bromide	 ~0 ~0 ~0 ~0.011[3]	 140 Low 9 	 Non-flammable Non-flammable Non-flammable (combustible at high temperature) Highly flammable	Recommendations for workplace exposure limits.
Oxygenated organic compounds (e.g., Esters, Ethers, Alcohols, Ketones)	0	<20	Flammable	Check recommendations for workplace exposure limits.
Water-based formulations	0	0	Non-flammable	Indirect life cycle climate impacts
"Not-in-kind" (see above)	0	0	Non-flammable where liquid dispensed is non-flammable	Indirect life cycle climate impacts

1. AR4 2. AR6 3. Latitude dependent.

Commercially available— Technically and economically feasible alternatives to HCFCs and HFCs are commercially available for all aerosols, although not all alternatives might be suitable or commercially available across all aerosol applications in all locations.

Aerosol products were reformulated to use CFC-free propellants, mainly hydrocarbons (butane, propane, isobutane, DME), although HCFCs and HFCs have been used in specific applications.

NIK alternatives, including hand-pumped aqueous sprays, drops and creams, are also used where CFC-containing aerosols might have been used previously.

Many factors affect the selection of a given propellant or alternative, including regulatory approval of products, industry codes of conduct, VOC controls, supplier, regulatory controls on HCFCs and HFCs, ease of use, and propellant properties, such as flammability or safety for certain uses.

Regulatory controls for HFCs used as aerosol propellants and solvents are increasingly limiting and/or prohibiting high-GWP HFC use where other suitable alternatives are available. For example, HFC-134a is no longer used as a propellant in technical aerosols in Europe. In some instances, HFC-152a, with a GWP of 124, can be considered relatively more acceptable within these regulatory controls than HFC-125 and HFC-134a, with their significantly higher GWPs of 3500 and 1430.

Technically proven— Aerosols incorporate propellants and solvents with the appropriate technical properties and characteristics in formulations designed to deliver a product for its intended purpose. The alternatives listed in Table 9.2 are technically proven for use in aerosols, although sometimes only for certain product types depending on the properties of the alternatives and/or the intended product purpose. Some alternatives will not be technically suitable for some formulations.

Hydrocarbons and DME are highly flammable chemicals that are also VOCs that contribute to photochemical smog generation. Like CFCs before them, non-flammable and non-toxic HFC-134a is often used in aerosols when flammability or toxicity is a consideration. HFCs are also used where emissions of VOC are controlled. However, HFCs are more expensive than hydrocarbons and are therefore mostly used when their properties are necessary for the aerosol product and the advantages outweigh the costs.

HFC-134a is used more commonly as a propellant in technical aerosols where its non-flammable properties have advantages. HFC-134a is also used in medical aerosols. Extensive respiratory toxicological studies were conducted for HFC-134a (IPACT-1) and HFC-227ea (IPACT-2), which proved their safety as propellants in respiratory use (e.g., pMDIs). Any propellant intended for inhaled medications requires toxicological tests.

Propane or isobutane (and their blends) tend to cause an "oily" or slightly stinging taste, and so are not favoured for nasal or oral use. Most other pressurised medical aerosol products tend to use propane/butane mixtures or DME and compressed gases to a lesser extent. Medical aerosol products for use on or near the nose or mouth, and on babies, where flammability and safety are of importance, tend to use HFCs or nitrogen. For treatments where there is a significant risk of inhalation into the respiratory tract, HFCs are preferred, where safety has been proven for HFC-134a and HFC-227ea.

HFC-152a is used more commonly as a propellant in consumer aerosols. HFC-152a is also being used in medical aerosols. HFC-152a has low to moderate flammability, and is used alone, or in blends with hydrocarbons to lower their flammability. HFC-152a is also blended with HFC-134a to produce a propellant with lower GWP and lower flammability. It is also used in jurisdictions that have VOC emission controls.

HFO-1234ze(E) is emerging as an in-kind alternative for all HFC aerosol propellant uses, although currently mainly in high value products due to its higher cost than HFCs.

NIK alternatives are sometimes not as easy to use or achieve lower performance for some applications.

In most parties, there are no regulatory requirements for the use of *specific* propellants for medical aerosols. However, a change in propellant for products approved for a medical use (like the nasal pMDIs) would necessitate a new development programme and regulatory approval. In the United

States, some regulated products may not require prior approval following the over-the-counter monograph system (also known as “grandfather clause” for products with a long time of use), provided they do not change propellant. In Japan, the Japanese pharmacopoeia codex for additives, and other official compendia limit propellants for medical aerosols. If a pharmaceutical company uses a new propellant in an aerosol product, necessary toxicity data on both propellant and the aerosol product are required for registration. All aerosols in the European Union are regulated, especially relating to flammability, under the Aerosol Dispensers Directive 75/324/EEC and subsequent amendments.

Environmentally sound— Aerosols are a totally emissive use, and so the propellant and solvent can have a direct environmental impact. In some parties, HCFCs and some HFCs are prohibited for use in the manufacture of aerosol products. In some non-Article 5 parties that have phased out HCFC production, stockpiles continue to be used for some specific aerosol products. HCFCs are gradually being phased out in Article 5 parties in aerosol manufacturing. Some parties have prohibited the introduction to market of some new aerosol products containing HFCs. Other parties are implementing the Kigali Amendment phase-downs into regulations that will gradually limit the supply of HFCs to end uses.

HFC-125, HFC-134a, HFC-227ea, and HFC-43-10mee, have high GWPs. In some applications, HFC-152a is used because it has a lower GWP than HFC-134a and lower flammability than hydrocarbons. HFC-152a are currently a preferred propellant choice where VOC controls limit the use of hydrocarbon propellants, although there is also increasing use of HFO-1234ze(E) as an in-kind alternative to HFC-152a. HFC-152a can also be blended with HFC-134a propellant to produce a propellant with lower GWP and lower flammability.

In Article 5 parties, HFC-134a can be preferred to HFC-152a due to aerosol manufacturing concerns about the flammability of HFC-152a. HFO-1234ze(E) is a small use in Article 5 parties, where it is generally used to manufacture aerosols (e.g., novelty aerosols) for export.

When considering direct climate impacts, the more climate-friendly alternative propellants include hydrocarbons and their blends, DME, HFO-1234ze(E), carbon dioxide and nitrogen, and NIK alternatives. The more climate-friendly alternative solvents include hydrofluoroethers, oxygenated organic compounds, aliphatic and aromatic solvents, chlorinated chemicals, low-GWP fluorinated chemicals, and NIK alternatives.

In areas with high urban densities, photochemical smog generation can be a major environmental and health problem. Hydrocarbons and oxygenated hydrocarbons, such as DME, are VOCs that contribute to photochemical smog generation. In some jurisdictions, strict VOC controls (e.g., in California) can have an impact on the choice of propellant, where hydrocarbons are avoided.

Economically viable and cost effective— Hydrocarbons and their blends are the most affordable propellant for aerosol products. HFCs and HFO-1234ze(E) are more expensive and are therefore used by manufacturers for specific applications where a propellant with low flammability and proven safety is needed, and often for high value products.

Safety in production and use— The flammability of hydrocarbons, DME, HFC-152a, and their flammable blends, makes safety a priority in the production and use of aerosols containing these ingredients. Flammable propellants and solvents require special equipment, training and handling in aerosol production, and special precautions in aerosol use.

HFO-1234ze(E) is classified as non-flammable although possesses a flammable range of 8.0–8.5 volume percent in air at one atmosphere under certain conditions, which needs to be considered in manufacturing, storage, and handling.

Easy to use— Pressurised aerosols, using propellants, are sometimes considered more convenient products to use than NIK alternatives, such as aqueous sprays, drops and creams. Flammable propellants and solvents require safety precautions in the use of aerosol products.

9.4 Minimising high-GWP aerosols

HFC use is limited in aerosols, owing to cost, safety, or regulatory reasons, or to applications where VOC controls might limit hydrocarbon use, or where a propellant with low flammability and/or proven safety is needed. HFC consumption in this sector has been estimated as the third largest after the refrigeration and air conditioning and foams sectors, where aerosols are a totally emissive use. There would be environment benefits in promoting low-GWP and climate-friendly alternatives and by avoiding high-GWP propellants and solvents. In many cases, HFC propellants and solvents can be substituted with low-GWP options, and NIK alternatives are commercially available where they are suited for the intended purpose.

The reformulation of aerosols to use alternative low-GWP propellants and solvents, or the development of NIK technologies as replacements, incurs costs to industry. It is technically feasible to replace HFC-134a and HFC-152a used in consumer aerosols with alternatives. HFOs may be suitable as replacements for HFC-134a and HFC-152a, although feasibility needs to be considered on a case-by-case basis. The higher cost of HFOs can be an economic barrier to transition.

It is difficult to quantify the costs of conversion of high-GWP HFC-containing aerosol products to low-GWP and NIK alternatives. Costs may include reformulation, redesign, production re-engineering, safety, training and education, product testing, and consumer information, and will depend on the application, the market, and its regulatory environment.

Parties may wish to consider the advantages of reducing the use of HFCs in the aerosol sector, where that is technically and economically feasible. Given that aerosols are totally emissive, any action taken in this area would provide rapid HFC consumption and emission reduction. Accounting by a country, including their aerosol production and their import of finished aerosols containing HFCs, might help it determine the implications of any phase-down policies, including financial implications.

10 Pressurised Metered Dose Inhalers

Medical Acronyms and Glossary

Bronchodilator	Short-acting or long-acting medication, which acts to dilate the airways: a short-acting bronchodilator helps to relieve symptoms associated with muscular spasms of the airways, also known as a *reliever*; a long-acting bronchodilator helps to control and prevent symptoms, including for COPD, also known as *preventer* or controller.
COPD	Chronic obstructive pulmonary disease
DPI	Dry powder inhaler
mDPI	Multi-dose dry powder inhaler
ICS	Inhaled corticosteroid, which is an anti-inflammatory inhaled medication
LABA	Long-acting beta-agonist, which is a bronchodilator
LAMA	Long-acting muscarinic antagonist, a *bronchodilator* used to treat COPD in a person who has persistent symptoms, sometimes also used in asthma, also known as anticholinergic
MART	Maintenance and reliever therapy
pMDI	Pressurised metered dose inhaler
Preventer	Anti-inflammatory inhaled medication, which is also known as controller medication or maintenance therapy
Reliever	*Bronchodilator* inhaled medication, also known as rescue medication
SABA	Short-acting beta-agonist, which is a *bronchodilator,* and also known as *reliever* medication
Salbutamol	A short-acting *reliever* medication
SAMA	Short-acting muscarinic antagonist, a *bronchodilator* used to treat COPD in a person who has intermittent symptoms, also known as anticholinergic
SMI	Soft mist inhaler

10.1 Conditions treated with pMDIs: prevalence, treatment, and medical trends

Asthma and chronic obstructive pulmonary disease (COPD) are the most common chronic diseases of the respiratory tract. Both illnesses account for high healthcare expenditure, and COPD in particular is responsible for premature death.

In 2019, the World Health Organization (WHO) estimated the global prevalence of asthma at 262 million, with 455,000 deaths per annum. Asthma is included in the WHO Global Action Plan for the Prevention and Control of Non-communicable Diseases and the United Nations 2030 Agenda for Sustainable Development.[345]

In 2019, the global prevalence of COPD was estimated at 391.9 million cases among people aged 30–79 years. The prevalence continues to rise with increasing tobacco consumption in developing countries. COPD is the third leading cause of death worldwide, causing 3.23 million deaths in 2019.

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[345] WHO, 2022, *Global Health Estimates: Life expectancy and leading causes of death and disability.* https://www.who.int/data/gho/data/themes/mortality-and-global-health-estimates. Accessed November 2022.

Nearly 90% of COPD deaths in those under 70 years of age occur in low- and middle- income countries.[346]

Inhalation therapy is the mainstay of treatment for asthma and COPD. Inhaled medication can reduce symptoms, exacerbations, and mortality, allowing people with asthma to lead a normal, active life and provide COPD patients with an improved quality of life. Inhaled drugs are targeted to the airways, where they have maximal benefit with least side effects. This is achieved by modulating particle size through inhaler design.

Other diseases treated by the inhaled route include cystic fibrosis, bronchiectasis, pulmonary arterial hypertension, and respiratory tract infections. These diseases require treatment with relatively high doses of drugs, which are often delivered by nebuliser rather than a portable inhaler. Delivery of drugs via the respiratory tract for systemic diseases (e.g., insulin for diabetes) remains an area of interest.

10.1.1 Asthma

Asthma is a chronic inflammatory condition of the airways.[347] Its prevalence increased and then stabilised in developed countries in the late 20th century, but its prevalence continues to increase in developing countries, to some extent because of air pollution. In some regions of Africa, especially in urban areas, the prevalence has been doubling every decade and now approaches that of developed countries.[348] There remains a wide difference in reported prevalence between some countries, such as Indonesia where prevalence is about 1%, to the United Kingdom and New Zealand where it is approaching 20%. Some of these trends may relate to the proportion of patients that are accurately diagnosed.

Asthma can vary in severity from mild asthma with intermittent symptoms through to severe and/or chronic asthma requiring specialist support, frequent hospital admissions with extensive medication, and despite this, in some cases, death. WHO estimates that 80% of global asthma deaths occur in low- and middle- income countries.

Asthma has two primary features, airway inflammation and bronchoconstriction, in which there is a muscular spasm of the airways. Controlling airway inflammation using inhaled corticosteroids is the mainstay of asthma treatment and is associated with reduced exacerbations and death. Globally, inhaled bronchodilators, which relieve the symptoms associated with bronchoconstriction, are still the most widely used drug in asthma, even though there is evidence that they increase the risk of exacerbations and death unless used alongside inhaled steroids.

10.1.2 COPD

Chronic obstructive pulmonary disease is a condition of narrowing and inflammation of the airways in conjunction with damage to the lung tissue (emphysema), often accompanied by mucus

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[346] Adeloye, D., Song, P., Zhu, Y., Campbell, H., Sheikh, A., Rudan, I., on behalf of NIHR RESPIRE Global Respiratory Health Unit, Global, regional, and national prevalence of, and risk factors for, chronic obstructive pulmonary disease (COPD) in 2019: a systematic review and modelling analysis, *Lancet Respir. Med.*, 2022, **10**, 447–458. https://doi.org/10.1016/S2213-2600(21)00511-7.

[347] Global Initiative for Asthma, 2022, *Global Strategy for Asthma Management and Prevention (2022 Update)*, 2022. https://ginasthma.org/wp-content/uploads/2022/07/GINA-Main-Report-2022-FINAL-22-07-01-WMS.pdf. Accessed November 2022.

[348] GBD Chronic Respiratory Disease Collaborators, Prevalence and attributable health burden of chronic respiratory diseases, 1990–2017: a systematic analysis for the Global Burden of Disease Study 2017, *Lancet Respir. Med.*, 2020, **8**, 586–595. https://doi.org/10.1016/S2213-2600(20)30105-3.

hypersecretion (chronic bronchitis).[349] The relative severity of these two features may vary from patient to patient, but they both contribute to progressive obstruction of the airways. The commonest cause of COPD is cigarette smoking, although exposure to biomass fuel smoke may also play an important role in developing countries. In some patients, occupational dusts, or environmental pollution (including household air pollution) may cause COPD in susceptible individuals. There is increasing evidence for factors early in life having an impact on maximally achieved lung function and thus of risk of COPD subsequently. COPD is a main component of multimorbidity in the elderly and it is one of the main drivers of social inequality in health.

It varies in severity from slight breathlessness on exertion to disabling breathlessness and chronic respiratory failure. A proportion of patients suffer from frequent exacerbations with a significant impact on the individual's quality of life and a large impact on health resources, with COPD exacerbations being responsible for many health systems' "winter bed crisis". Patients become progressively and irreversibly disabled if they continue to smoke, and smoking cessation is a major individual, as well as a general, public health issue.

In addition to the treatments listed below, COPD patients benefit from pulmonary rehabilitation and physical activity in general, and for those who still smoke, smoking cessation support, including pharmacological treatment, is essential. However, in most health systems smoking cessation clinics are not available and treatment of nicotine addiction is under-prioritised.

10.1.3 Treatment of asthma and COPD

Prevention of asthma remains impossible for the majority, until it is clearer what has driven the increased prevalence. This seems to be a cohort effect, with increased levels of asthma in children now leading to increased levels in adults. The pathology of asthma usually arises in early life, and even if a form of prevention were to be developed today, it seems likely that this would not impact significantly on the prevalence of asthma for many decades.

Prevention of COPD requires public health leadership so that rates of tobacco smoking decline. Controls on advertising and bans on smoking in public places together with increasing the legal age for buying cigarettes, and high taxes on tobacco products have been associated with significant declines in tobacco consumption in developed countries, assisted in some countries by nicotine replacement therapies. However, increasing affordability of tobacco and lack of advertising controls are driving the increasing prevalence of COPD in developing countries. The global increase in air pollution is also a risk factor for COPD and poor lung health in general. Reducing indoor pollution from cooking and heating sources inside homes is an important measure for preventing COPD, particularly in developing countries. With global trends for increased longevity, increasing numbers of elderly will develop COPD in later life.

Inhaled therapy remains the mainstay of treatment for established asthma and COPD. Inhalers offer effective symptomatic benefit and control of disease, by delivering drugs directly to the airways, whilst minimising systemic side effects. The particle size is a factor in targeting the drug to the lungs. If the particles are too large, then the drug is deposited in the mouth and throat and is ineffective. If the particles are too small, they are simply exhaled and wasted.

Consensus treatment is being promoted through the GINA (Global Initiative for Asthma) recommendations for asthma[350] and the GOLD (Global initiative for chronic Obstructive Lung

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[349] Global Initiative for Chronic Obstructive Lung Disease, 2022, *Global Strategy for Prevention, Diagnosis and Management of COPD: 2022 Report*, 2022. https://goldcopd.org/2022-gold-reports-2/. Accessed November 2022.

[350] Global Initiative for Asthma, 2022, *Global Strategy for Asthma Management and Prevention (2022 Update)*, 2022. https://ginasthma.org/wp-content/uploads/2022/07/GINA-Main-Report-2022-FINAL-22-07-01-WMS.pdf. Accessed November 2022.

Disease) recommendations for COPD[351]. For both asthma and COPD, there have been two main categories of inhaled treatment, bronchodilators (“relievers”) and anti-inflammatory medications (“preventers/controllers”). Inhaled salbutamol (a short-acting reliever) remains by far the most used treatment worldwide, mainly as inexpensive HFC pressurised metered dose inhalers (pMDIs), and with an increasing amount of multi-dose dry powder inhalers (mDPIs) used in developed countries and single capsule dry powder inhalers (DPIs) used in parts of the developing world (e.g., South Asia). The pivotal role of inhaled steroids is now recognised in improving asthma control, reducing acute attacks, and is associated with reduced asthma mortality.

In the last decades, a new trend has been the introduction of combinations of long-acting bronchodilators and inhaled corticosteroids (LABA/ICS) in a single inhaler to improve asthma control. These combinations are given once or twice daily, with twice-daily treatments being adjusted by additional dosing according to symptoms (MART therapy). They are mainly used in developed countries, but their use is expanding to developing countries.

Once-daily mDPI-delivered combination LABA/ICS treatments have been introduced which are clinically effective in real-world studies. They both improve asthma control and can simultaneously substantially reduce carbon footprint.

Combination inhalers combining two different bronchodilators (long-acting bronchodilators and long-acting anti-muscarinic agents, LABA/LAMA) and triple therapies with an ICS (LABA/LAMA/ICS) are now on the market. These have been initially focused on personalising treatment for COPD patients. Most COPD patients will benefit from a LABA/LAMA combination over a single bronchodilator and for those who benefit from ICS, sometimes from a convenient single triple inhaler. Consensus treatment of COPD is being achieved through the GOLD guidelines.

Treatment regimens will continue to evolve, with regional and country variations. In some countries, there are already requests from patients for sustainable treatments with a low carbon footprint. It can be anticipated that this trend will become stronger and more widespread, and there is likely a knowledge gap for health professionals that needs to be addressed.

Oral drugs are also prescribed for asthma and COPD. In developing countries, inexpensive methylxanthines (theophylline) are widely available, but some of these can have serious side effects (excess dosage can be fatal). Similarly, low-dose prednisolone is used as an alternative to inhaled corticosteroid, with all the resulting well-known side effects to corticosteroids. In developed countries, and especially the United States, oral montelukast occupies a significant proportion of the asthma market for preventive drugs although it is generally less effective than inhaled steroids. In developing countries, it is also a significant treatment; for example, oral montelukast is one of the most widely prescribed treatments for asthma in Bangladesh.

There are new developments in injectable drugs, so far for asthma only. The first injectable preventive therapy against Immunoglobulin E (IgE) is now marketed worldwide. However, it has very low uptake outside developed countries, and most often in patients with severe asthma because of its cost (20–24 times the cost of an inhaled corticosteroid). Novel injectable biologic drugs have also been launched, targeting eosinophilic inflammation through different interleukin pathways (IL4, IL5 and IL13[352]) and other pathways will likely be on the market in the next 2 years. These drugs are expensive and are restricted mostly to patients in developed countries to target patients with

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[351] Global Initiative for Chronic Obstructive Lung Disease, 2022, *Global Strategy for Prevention, Diagnosis and Management of COPD: 2022 Report*, 2022. https://goldcopd.org/2022-gold-reports-2/. Accessed November 2022.

[352] Brusselle G.G., Koppelman G.H., Biologic therapies for severe asthma, *N Engl J Med.,* 2022, **386**(2), 157–171. doi: 10.1056/NEJMra2032506.

significant asthma related to those pathways. None of these developments will impact the continued need for inhaled therapies for most patients with asthma and COPD worldwide.

10.1.4 Other disease areas and conditions and their treatment

The overwhelming majority of inhalers are used to treat asthma or COPD, but some other conditions are treated with inhaled therapies.

Cystic fibrosis is an inherited disease that causes repeated or prolonged lung infections and progressive lung damage**.** An estimated 105,000 people have been diagnosed with cystic fibrosis worldwide. Bronchodilators are commonly prescribed, though there is very little evidence to show they are effective. Most inhaled treatments involve saline, antibiotics and DNA-ase via a nebuliser, though inhaled antibiotic DPI formulations are also available

Bronchiectasis is the third most chronic airway disease after COPD and asthma. The most common causes are pneumonia, tuberculosis, and immune system disorders. It is often treated in the same manner as cystic fibrosis, with nebulised mucolytics and antibiotics. Bronchodilators and ICS are commonly prescribed, though both are not normally recommended in guidelines as there is very little evidence to show they are effective.

Pulmonary arterial hypertension is a rare condition where there is high blood pressure in the arteries that supply the lungs (pulmonary arteries). The main treatments are tablets or intravenous, but nebulised prostacyclins are sometimes used.

Influenza may be treated by a neuraminidase inhibitor delivered from a mDPI.

Nicotine addiction— Most electronic nicotine delivery systems (e-cigarettes) deliver an aerosol by heating a solution that users inhale, and no HFC propellants are involved. However, there is interest in using pMDI technology as a nicotine delivery system. One nicotine-containing pMDI was granted a medical license in the United Kingdom but has since been dropped by the manufacturer. Another nicotine-containing pMDI has been shown to help support smoking cessation in a clinical trial. Tobacco companies have invested heavily in inhaler companies recently, so this is a potential area for significant growth in future. However, most international respiratory societies advocate strongly against the use of e-cigarettes.

Other respiratory diseases where drugs delivered by inhalation are in clinical trials include COVID-19, idiopathic pulmonary fibrosis, pneumonia, respiratory syncytial virus infection, lung transplantation and lung cancers.

Medications can be delivered systemically via the lungs to treat other conditions, although none have yet been commercialised on a large scale. Examples include the measles vaccine via a DPI and insulin delivery via DPI or nebuliser. New therapies to deliver cannabinoid products via a pMDI are under development.[353]

Nasal drug delivery— Drugs delivered nasally are predominantly to treat nasal disease, but there is interest in systemic drug delivery via the nasal route. Most nasal treatments use a pump to deliver a spray, but a pressurised HFC-134a containing nasal spray is in use in the United States.

Sublingual-drug delivery— The vast majority of drugs absorbed sub-lingually (under the tongue) are administered as tablets or using a pump spray. A pressurised HFC-134a aerosol is in use to deliver

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[353] Kindeva Drug Delivery, 2022, *Kindeva and BOL Pharma Using Low Global Warming Potential (GWP) Propellant in Development of Inhaled Cannabinoid Products*, May 11, 2022. https://www.kindevadd.com/news/bol-pharma/. Accessed December 2022.

glyceryl trinitrate sublingually in the treatment of angina, for which there are also effective sublingual tablet and pump spray alternatives.[354]

10.2 Technology options for treatment by inhalation

There are two common types of highly portable inhalation devices for the delivery of respiratory drugs: pMDI and the DPI in single- or multi-dose. Other methods of delivering drugs to the lung include the soft mist inhaler (SMI) and nebuliser. The choice of the most suitable treatment method is a complex decision taken between the health care provider and the patient. It is not uncommon for patients to be prescribed a mix of medications in a range of devices. The sections below briefly describe each main type of inhaler and their use.

One feature generally common to the use of inhalers (pMDIs and DPIs) is that patients need to use the correct technique, and this needs training and reinforcement, which unfortunately is rarely provided in routine practice. There is great variation in the quality of inhaler training by healthcare providers. As a result, a large proportion of patients who are prescribed inhaled medications do not use their inhalers correctly.[355] Studies have observed errors defined by the authors as critical in the use of both pMDIs and DPIs.

Complex considerations are necessary when patients and healthcare professionals make an informed choice about a patient's inhaled therapy, taking into account therapeutic options, patient history, patient preference, ability (e.g., dexterity, inspiratory flow, vision) and adherence, patient-borne costs, as well as environmental implications, with the overall goal of ensuring patient health. Patient choice may be enhanced with an increase in publicly available information about the environmental impact of different inhaler products. Healthcare professionals and their patients may benefit from this information to take environmental impact into account in their choice of inhaler.

The patterns of prescribing suggest that the choice of inhalers is based on local economics, access, availability, supply, custom, and practice (the prescribing clinicians' habits). Clinicians and patients have their own preferences based on their own experiences.

There is an increasing trend to involve patients in the informed choice of treatment. This is likely hard to achieve, or has its limitations, in countries where patients have limited access to inhalers because of cost or supply. Also, culturally or for other reasons, not all patients want or expect to be involved and

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[354] Boden, W.E., Padala, S.K., Cabral, K.P., Buschmann, I.R., Sidhu, M.S., Role of short-acting nitroglycerin in the management of ischemic heart disease, *Drug Des Devel Ther*., 2015, **9**, 4793–4805. doi: 10.2147/DDDT.S79116.

[355] It is important to understand how critical training, appropriate use, and patient choice are to adherence. Adherence is central to optimal disease control. The following are a selection of references on the topic:

Bjermer, L., The importance of continuity in inhaler device choice for asthma and chronic obstructive pulmonary disease, *Respiration*, 2014, 346–352.

Bosnic-Anticevich S., *et al*., The use of multiple respiratory inhalers requiring different inhalation techniques has an adverse effect on COPD outcomes, *COPD*, 2016, **12**, 59–71. https://doi.org/10.2147/copd.s117196.

Bosnic-Anticevich, S., Inhaler device handling: have we really started to address the problem? *Eur. Respir. J.*, 2017, **49**, 1700120. http://erj.ersjournals.com/content/erj/49/2/1700120.full.pdf.

Engelkes M., *et al*., Medication adherence and the risk of severe asthma exacerbations: a systematic review, *Eur Respir J*., 2014, **45**, 396–407. https://doi.org/10.1183/09031936.00075614.

Laube, B., *et al*., ERS ISAM Task Force Consensus Statement, *Eur. Respir. J.*, 2011, **37** (6), 1308–1331. http://erj.ersjournals.com/content/erj/early/2011/02/10/09031936.00166410.full.pdf.

Lavorini, F., *et al.*, Effect of incorrect use of dry powder inhalers on management of patients with asthma and COPD, *Respir. Med.*, 2008, **102**(4), 593–604.

Pritchard, J., Nicholls, C., Emerging technologies for electronic monitoring of adherence, inhaler competence, and true adherence, *J. Aerosol Med. Pulm. Drug Deliv*, 2015, **28** (2), 69–81.

defer to the clinician to make the decision. In practice, involving a patient in making informed choices can also be hard to achieve during brief clinician consultations, which can be the case in many countries. Nevertheless, where local circumstances allow, the guidance provided by clinicians is important in supporting the informed decision-making process.

Environmental factors are one of several factors considered in making choices about treatment and are of more importance to patients in some countries than in others.[356][357,358]

In addition to the need for adequate training in the use of a device, clinicians should, in dialogue with the patient, provide the appropriate medication in a device that the patient can most easily use and afford.[359]

10.2.1 Pressurised metered dose inhalers (pMDIs)

A pMDI is a device designed to produce a fine spray of medication for inhalation directly to the airways. These products were first developed over 60 years ago and are particularly suited to administration of therapy when respiratory function is compromised. pMDIs that used CFCs as a propellant were historically the inhaled-delivery device of choice as they were affordable, reliable, and extremely effective. Under the Montreal Protocol, the use of CFCs for pMDIs has been successfully phased out worldwide without significant adverse impact to medical care.

The process of reformulating pMDIs with HFCs began 40 years ago when HFC-134a and HFC-227ea were first proposed as alternatives to CFCs. These HFCs underwent extensive toxicological testing and were deemed to be safe for human use. Since 1994, pharmaceutical companies have gradually replaced the CFC propellants in pMDIs with HFCs (HFC-134a and to a lesser extent HFC-227ea). This has been difficult because the components, formulations and method of manufacture had to be substantially modified to use the HFC propellant. Furthermore, the absence of an acceptable HFC that is liquid at room temperature has meant the development of new manufacturing processes. Each new pMDI product underwent extensive regulatory assessments of safety, efficacy, and quality, much the same as for the development of any new drug product. Development costs for the transition of pMDIs from CFCs to HFCs have been estimated to be more than USD2 billion, and the phase-out of CFC pMDIs took over 20 years to complete. The cost to research and develop a new medicine has been estimated to be just under USD1 billion, although if the cost of new drugs that fail on the grounds of safety or efficacy are included, this estimate can be as high as USD2.8 billion.[360]

Following reformulation, the pMDI remains popular, especially because it is relatively affordable for the short-acting bronchodilator salbutamol, which is the predominant short-term relief or "rescue" treatment for acute symptoms in asthma/COPD worldwide. The low cost of salbutamol pMDIs to the patient has remained relatively constant over 50 years, globally, including for HFC pMDIs; although there have been some notable regional variations over time (e.g., the United States), which is

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[356] Schreiber, J., Sonnenburg, T., Luecke, E., Inhaler devices in asthma and COPD patients – a prospective cross-sectional study on inhaler preferences and error rates, *BMC Pulmonary Medicine*, 2020, **20**, 222. https://bmcpulmmed.biomedcentral.com/articles/10.1186/s12890-020-01246-z.

[357] D'Ancona, G., Cumella, A., Renwick, C., Walker, S., The sustainability agenda and inhaled therapy: what do patients want? *European Respiratory Journal*, 2021, **58**, PA3399. https://erj.ersjournals.com/content/58/suppl_65/PA3399.

[358] Wilkinson, A., Woodcock, A., S63 Partnering patients on climate change; assessing patients' understanding of the carbon footprint of inhalers, *Thorax*, 2022, **77**, A40–A41.

[359] Azeez, N.F., *et al.*, Best practice principles for inhaler prescribing, *The Pharmaceutical Journal*, 2022, **309**, 7964. DOI:10.1211/PJ.2022.1.151334.

[360] Wouters, O.J., McKee, M., Luyten, J., Estimated research and development investment needed to bring a new medicine to market, 2009–2018, *JAMA*, 2020, **323**(9), 844–853. doi:10.1001/jama.2020.1166

influenced by the market availability or otherwise of low-cost generic products. In 2020, the global price per dose was estimated to be around \$0.06, although can be as low as \$0.02 per dose.[361]

Accurate and consistent co-ordination of drug release and inhalation is required for correct use of pMDIs. Studies have shown that some patients do not use pMDIs correctly. For example, they may forget to actuate a priming shot after a period without use, or alternatively, prime the inhaler when not needed. In routine clinical practice as many as 50% of patients fail to use a pMDI correctly, mainly due to poor synchronisation of actuation with inhalation. A valved holding chamber, spacer device or breath-actuated inhaler can be used to overcome most coordination issues; however, breath-actuated inhalers are more costly in many markets, and spacers can be quite large and less portable, which can result in the patient using the pMDI without the spacer. With information and training, poor inhaler technique can be improved, but this requires reinforcement, which is rarely provided on a regular basis in practice. pMDIs with spacers provide a cost-effective option for some patients with severe lung disease and very young children, and for severe asthma attacks (where nebulisers are the alternative). [362]

10.2.2 Dry powder inhalers (DPIs)

DPIs are devices that deliver powdered medication (active ingredient mixed with excipient) without the need for a propellant. There are many different devices that deliver powder medication. Most types of DPI are available exclusively from a single pharmaceutical company that has patented that device, although there are device developers who are offering their devices generically to the industry. Most of the commonly used respiratory drugs have been formulated successfully for DPIs and are now widely available.

DPIs are suitable for many patients and are widely prescribed for the treatment of asthma and COPD. DPIs are often easier to use than pMDIs because drug delivery is driven by the patient's inhalation and does not require patient co-ordination. Given the available options, many patients prefer DPIs to pMDIs because of their ease of use.[363] While DPIs are a suitable option for many patients, younger children and some COPD patients may not always be able to generate an adequate inspiratory flow to ensure optimal medication delivery from high resistance DPIs.[364] The wide variety of different DPI designs, and often used with pMDIs for rescue treatment, can lead to confusion in the correct usage of each inhaler.

Powdered drug particles tend to aggregate; therefore, delivery devices usually contain a mechanism to ensure adequate de-aggregation of the drug powder or separation of drug powder and carrier (where the product contains carrier) so that the drug particles are sufficiently small to be inhaled deeply into the lungs. It is essential that patients handle and use their DPIs properly, for example in humid conditions where excessive powder aggregation otherwise might impair their efficacy.

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[361] Pritchard, J.N., The climate is changing for metered-dose inhalers and action is needed, *Drug Design, Development and Therapy*, 2020, **14**, 3043–3055.

[362] Lavorini, F., Janson, C., Braido, F., Stratelis, G., & Løkke, A., What to consider before prescribing inhaled medications: a pragmatic approach for evaluating the current inhaler landscape, *Therapeutic advances in respiratory disease*, 2019, **13**, 1–28. https://journals.sagepub.com/doi/pdf/10.1177/1753466619884532.

[363] Schreiber, J., Sonnenburg, T., Luecke, E., Inhaler devices in asthma and COPD patients – a prospective cross-sectional study on inhaler preferences and error rates, *BMC Pulmonary Medicine*, 2020, **20**, 222. https://bmcpulmmed.biomedcentral.com/articles/10.1186/s12890-020-01246-z.

[364] Clark, A.R., Hollingworth, A.M., The relationship between powder inhaler resistance and peak inspiratory conditions in healthy volunteers – implications for in vitro testing, *J. Aerosol Med.*, 1993, **6**(2), 99–110. doi: 10.1089/jam.1993.6.99.

DPIs fall into two categories: single-dose and multi-dose.

Single-dose DPIs, which have been in use for more than 60 years, utilise a capsule, containing one dose, inserted into the device. The capsule is opened within the device and the powder is inhaled. The capsule must be discarded after use and a new capsule inserted for the next dose. They are inexpensive but may be more susceptible to humidity than more recently developed multi-dose DPIs. Despite this, they are generally found to be effective. In some developing countries (e.g., India), single-dose DPIs have a major role because they require only simple manufacturing technology, and patients can purchase a small number of doses at an affordable cost. However, this purchasing behaviour, of a small number of doses, has the potential to undermine adherence to treatment for products that are required daily (e.g., corticosteroids or combination therapies), with adverse health outcomes. Correct training in the usage of single-dose DPIs is important (as for all inhalers). They can require a degree of manual dexterity that elderly patients may not have. With information and training, misuse of single-dose DPIs can be minimised.

Multi-dose DPIs (mDPI), which have been in use for over 30 years, typically contain enough doses for at least one month's treatment. There are two types of mDPI, one with individual doses pre-packed during manufacture, and the second that loads a measured amount of medicine for each inhalation from a reservoir in the device. Older reservoir mDPIs can suffer from water ingress in high humidity environments that leads to clumping of the powder formulation. These issues can be partially addressed by supplying the device in a foil pouch opened upon first use and disposed of within the month. Newer mDPIs have improved moisture protection and are available in countries with humid climates, such as experienced in many developing countries.

Substantial development efforts are being pursued in the DPI segment by pharmaceutical companies. Many novel drugs for the last decade have been commercialised in DPI formulations. The challenges and costs associated with the development of new DPI products are like those that were incurred for HFC pMDIs developments. In recent years, mDPIs containing off-patent molecules have entered the European and North American markets from pharmaceutical companies that market generic products.

10.2.3 Nebulisers

Nebulisers are devices that are filled with drug dissolved or suspended in aqueous solution, which is converted to inhalable droplets using compressed air, ultrasonic waves, or vibrating mesh. Historically, the situation has been different to that of pMDIs or DPIs, in that pharmaceutical companies supply drug formulations but not the delivery device. Therefore, in principle, any drug formulation could be used with any nebuliser, with widely different outputs, and dose to the patient. In practice, this has been largely restricted to short-acting beta-agonists, short-acting anti-muscarinics and corticosteroids. The differences in nebuliser performance have led to recommendations for the use of a particular formulation only with selected nebulisers, usually those with clinical data to support their use. More recent drug approvals for nebulised products in the United States have been cross-labelled to a specific nebuliser device. Therefore, nebulisers have generally not been considered as alternatives to pMDIs and are now recommended mainly for the treatment of infants and severely ill patients, where patients can breathe normally, or for situations when larger doses of drug and/or prolonged administration times are desired. A nebuliser takes 3–10 minutes to deliver its dose and is relatively inconvenient to maintain. Until recently, only short-acting bronchodilators, corticosteroids, antibiotics and DNA-ase have been widely available for nebulised use. However, there have been recent launches in the United States of nebulised formulations of long-acting beta-agonists and anti-muscarinics. There are no combinations of long-acting drugs available as nebulised formulations.

Air jet nebulisers use a source of compressed air to provide the energy to break up the liquid into small droplets. Established systems are not readily portable, are powered from compressed gas cylinders or electrically powered compressors, and largely restricted to home or hospital use. Some portable systems have been introduced in their first markets. However, they are still dependent on external power supply and therefore restricted in their use.

Ultrasonic nebulisers utilise a vibrating crystal at the bottom of a nebulising chamber. The crystal vibration causes droplets to form on the surface of the liquid. These can be entrained in a stream of air created either by a fan or by the patient inhaling. Ultrasonic nebulisers are more efficient than air jet nebulisers but still require either a battery or external power source. They tend to be expensive and cannot be used for all drug formulations particularly suspensions, nor with drugs that are thermally labile due to heating of the medication during use.

The most recent development has been to vibrate a mesh containing micron-sized holes at ultrasonic frequencies in portable battery-powered devices. The vibration serves to pump liquid through the mesh creating a respirable spray. The use of electronics also allows introduction of more sophisticated features, such as triggering spray generation only during a portion of the inspiratory manoeuvre, thereby minimising waste and environmental discharge. The initial cost of these devices is substantially more than a pMDI or DPI, and the relative lifetime cost will also depend on the cost of the drug/solution for nebulisation.

For patients with asthma and COPD, drug delivery via nebulised therapy is at least as efficacious as a pMDI plus a valved holding chamber ("spacer") but costs far more. However, in many countries nebuliser use is still seen as optimal treatment in the acute situation in hospital and for chronic severe patients at home. In China, it is often the first-line therapy and initiated at hospital out-patient clinics. Over time, nebuliser use for asthma treatment could largely be replaced using a pMDI plus spacer. However, in at least one study, it has been suggested that use of a nebuliser has a lower carbon footprint than that of an HFC-134a pMDI.[365] In COPD, there may be a role for nebulisers in breathless patients with low inspiratory flow rates especially after hospital admission.

A few companies are exploring particle engineering approaches that allow larger doses of drug to be dispensed with the energy available from the patient's inspiratory manoeuvre; one such product is marketed in many countries to deliver an antibiotic in the treatment of cystic fibrosis.[366] This may also become an alternative to other nebulised treatments in the future.

10.2.4 Aqueous mist (soft mist) inhalers

Small portable devices that produce aerosols of respirable diameter from aqueous formulations have been under development for several years and one SMI[367] is now commercially available from one global pharmaceutical company. This utilises the collision of two liquid jets to generate an aerosol (rather than e.g., relying on a propellant). This novel device took many years to develop and optimise but is now marketed with five different drug or drug combination formulations, although availability of each product may be restricted in certain countries. More recently, a re-usable version has been introduced that allows the patients to refill the device with a further months' therapy on up to five occasions.

These new-generation devices produce an aerosol through mechanisms different from those described for nebulisers. The mechanisms to produce an aerosol include collision of two jets of liquid or forcing liquid through tiny micron-sized holes. They can be distinguished from nebulisers in that they endeavour to deliver a complete dose within one or two breaths. The combination of improved efficiency and smaller aerosol particle size from these devices ensure that the aerosol they generate can be deposited deeply into the lungs and therefore serve as local delivery for treating lung disease or for absorption for systemic delivery. However, the small size some of the orifices/filters used in these

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[365] Goulet, B., Olson, L., Mayer, B.K., A comparative life cycle assessment between a metered dose inhaler and electric nebulizer, *Sustainability*, 2017, **9**(10), 1725. https://doi.org/10.3390/su9101725.

[366] VanDevanter, D.R., Geller, D.E., Tobramycin administered by the TOBI® Podhaler® for persons with cystic fibrosis: a review, *Med Devices (Auckl)*, 2011, **4**, 179–188. doi: 10.2147/MDER.S16360.

[367] Laube, B.L., *et al.*, What the pulmonary specialist should know about the new inhalation therapies, *Eur. Respir. J.*, 2011, **37**, 1308–1417.

devices currently restrict their use to drugs that are capable of being formulated as solutions at sufficient concentration to deliver a dose within 50µl.

The development and regulatory timescales for new aqueous inhaled delivery systems are lengthy and new technical breakthroughs are not common. Even with the same drug already approved in a pMDI or DPI, an aqueous formulation will require full clinical trials to establish dose, safety, and efficacy. As well as conforming to pharmaceutical regulations, novel devices are becoming regulated under device regulations. There are also hybrid approaches in development, whereby a portable mesh nebuliser can be combined with a formulation containing10s–100s µl per dose dispensed from a bottle.

10.2.5 Novel devices

In recent years, there has been development of devices that use heat to vaporize a formulation based around propylene glycol. These have been applied to the inhaled delivery of nicotine and flavourings for recreational and smoking replacement ("vaping"). These are not currently regulated as medicinal products, there is no mechanism to control the dose delivered, nor levels of quality control of performance applied in the way that an inhaler or nebuliser would be assessed. However, there are companies looking at whether the technology can be converted for application in the medical field.

In addition, there is a class of devices that vaporize an excipient-free drug to form a condensation aerosol which, when inhaled, allows for systemic drug delivery. One device is approved for systemic administration of loxapine in the treatment of schizophrenia. This technology will only work with drugs that have relatively low boiling points and are thermally stable.

10.2.6 Regulatory framework for HFCs

As of November 2022, around 144 parties had ratified the Kigali Amendment to the Montreal Protocol, which phases down the production and consumption of HFCs listed in Annex F, including HFC-134a, HFC-152a, and HFC-227ea. In response, parties are adopting HFC phase-downs within domestic legislation.

Japan opted to update its Ozone Layer Protection Law in 2018 to control the manufacture and import of HFCs and is actively managing the process to ensure it meets its targets. Under this legislation, the production and import of quantities of HFCs for pMDIs is designated as an exceptional use, which is allocated based upon individual circumstances and after limiting the use to the intended purpose. The total amount of HFCs for pharmaceutical use needed for the production of pMDI is imported.

The remainder of this section focuses on two regions that account for over 60% of the consumption and emissive use of pMDIs, namely North America and Europe. It should be noted that there are many other aspects of environmental legislation, such as the European Regulations concerning Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), that apply to inhaled therapies, but these are not discussed further here. There is also the prospect of legislation under consideration in the United States and the European Union concerning per- and polyfluoroalkyl substances, which could impact fluorinated propellants in pMDI (see also section 2.7.4).

The American Innovation in Manufacturing (AIM) Act was introduced in December 2020 to allow the U.S. Environmental Protection Agency (U.S. EPA) to manage the phase-down, relative to an established baseline, maximise reclamation and minimise release, and support transition to next-generation technologies with lower carbon impact. The AIM Act specifically provides that six sectors, including pMDIs, should receive 'application-specific allowances' to ensure uninterrupted supply of HFCs. The Allowance Framework establishes a process for pMDI manufacturers to supply data to justify their allowance, which in the case of pMDIs focuses on bulk HFC production, import, and intended use, HFC pMDI production, import, and export. The U.S. EPA program does not require allowances for the import of finished pMDIs from outside the United States. These six designated sectors will receive specific allowances initially for a five-year period; U.S. EPA will review ongoing allocations in the light of available alternative technologies. More recently, the State of California has introduced legislation (Senate Bill 1206) that completely bans the sale of pMDIs containing HFC-227ea from the end of 2030, and those containing HFC-134a from the end of 2032.

Canada updated its ODSs and Halocarbons Alternatives Regulations to enshrine the Kigali phase-down targets in law. There are exemptions for an essential use where a suitable alternative is not available.

The European Union was one of the early movers, introducing legislation to restrict the use of F-gases in 2006, and updated in 2014. The phase-down timetable was more aggressive than that subsequently adopted by Kigali for non-Article 5 parties, although it did exempt medical aerosols from these targets. The United Kingdom adopted similar legislation in 2020, when it seceded from the European Union. In June 2020, the European Commission launched a review consultation on its legislation, which concluded with recommendations made in April 2022. A new, more aggressive phase-down schedule has been proposed, dropping emissions to 24% of baseline by 2024 and 10% of baseline by 2027. It also removes all exemptions (including for pMDIs) that previously accounted for emissions around 5% of baseline. If no progress is made towards finding replacement propellants in pMDIs, this would mean that previously exempted uses would account for half of the allowable 10% of baseline in 2027. If these proposals are enshrined in European Union law, pMDIs are likely, therefore, to make a highly significant contribution to the overall European Union HFC targets within the next 5 years. The United Kingdom has yet to declare if it will enact similar proposals.

10.2.7 New propellants for pMDIs

An inhalation propellant must be safe for human use and meet several other criteria relating to safety, efficacy, and quality. Traditionally the list would include: (i) liquefied gas, (ii) low toxicity, (iii) non-flammable, (iv) chemically inactive and stable, (v) acceptable to patients (in terms of taste and smell), (vi) appropriate solvency characteristics, and (vii) appropriate density. Not all these requirements may be essential for an alternative propellant, but careful study and justification would be required to support any significant change. It is, however, extremely difficult to identify new propellants fulfilling all these criteria, and which are also environmentally acceptable.

At the time of the introduction of the Montreal Protocol, extensive research had already identified the two currently used hydrofluorocarbons as alternative propellants – HFC-134a and HFC-227ea. Two international consortia (IPACT-I and IPACT-II) conducted toxicological testing to ensure that these propellants were safe for inhalation by humans. The direct cost of this testing was tens of millions of dollars. Once identified, the pMDI industry reformulated the CFC pMDIs so that they could use HFCs. The components and formulations were substantially modified to use the new HFC propellants due to the different chemical and thermodynamic properties of HFC versus CFC propellants.[368]

Importantly, pMDIs are subject to extensive regulation by national health authorities to ensure product safety, product efficacy and product quality. Although there are now HFC-based generic products available, at the time of transition, the process for developing HFC pMDIs was essentially identical to the development of a wholly new drug product, involving full safety testing, stability testing and clinical trials for each reformulated pMDI. Research and development for a new product is a lengthy, challenging, costly and resource-intensive process. A safety study for an entirely novel

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[368] Leach, Chet L., The CFC to HFA transition and its impact on pulmonary drug development, *Respiratory Care,* 2005, **50**(9), 1201–8.

pMDI propellant for asthma/COPD treatment likely requires at least 12 months clinical trial experience in hundreds[369] of patients, as well as lifetime studies in laboratory animals.

In summary, the process of bringing a new product to market is time-consuming. While the first new products might reach the prescribing physician in as little as 3 years, global market penetration takes longer. For the CFC pMDI phase-out, after identifying HFC propellants and developing safe products, the final step was to switch millions of patients to reformulated pMDIs and other CFC-free products.[370] In that case, an essential use process under the Montreal Protocol managed the adequate supply of pharmaceutical grade CFCs during transition, which continued for over 20 years on a global basis, with different regions conducting the change at different rates. Conversion time within a region was around 10 years, or longer, e.g., in the European Union, where manufacture continued to supply essential medicines for export markets.

Two low-GWP (global warming potential) chemicals are under development as potential propellants for pMDIs (HFC-152a[371] and HFO-1234ze(E)[372]), although historically, isobutane has also been investigated. Which of these will make it to the market, and the subsequent rate of uptake, is unpredictable. For a new propellant development programme, there is technical risk, significant investment, and no guarantee of commercial success. In contrast to the introduction of CFC-free propellants, the pharmaceutical development of HFC-152a, and HFO-1234ze(E), are being largely supported by the chemical manufacturing companies themselves. For existing products, it might be difficult for a pharmaceutical company to justify an investment in new propellants given the limited benefit to patients (i.e., the active ingredient will remain the same and the performance characteristics are likely to be comparable to current pMDIs). On the other hand, many pharmaceutical companies have committed to being carbon-neutral by 2030, which could be impossible to achieve when the emissive use of current propellants from pMDIs might constitute up to 45% of a company's carbon footprint.[373] The choices to reduce a company's carbon footprint are largely limited to reformulating pMDIs with new propellants and/or develop equivalent DPI formulation options.

The lifecycle of potential propellants, from manufacture through to their environmental fate, including their GWP and atmospheric lifetimes, are considerations for pharmaceutical companies. The atmospheric degradation of some HFCs and HFOs is briefly discussed in section 2.7.4.2, with more detailed information available in the Environmental Effects Assessment Panel's 2022 Assessment Report. Other relevant information is available in the 2005 IPCC/TEAP Special Report.[374] Some manufacturing routes to HFCs and HFOs are discussed in section 2.8.4.4.

10.2.6.1 Isobutane

Under an MLF-funded project, a company in Argentina (Pablo Cassara), undertook research and development to use isobutane as a propellant. While registration for the isobutane-based salbutamol pMDI was initially expected to occur in 2014, no pMDI products containing isobutane have appeared

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[369] The number of patients varies on the clinical trial and/or the country where the trial is conducted. Patient numbers can range from the low hundreds to more than a thousand.

[370] IPCC/TEAP, 2005, *IPCC/TEAP Special Report: Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons*, B. Metz, L. Kuijpers, S. Solomon, S. O. Andersen, O. Davidson, J. Pons, D. de Jager, T. Kestin, M. Manning, and L. Meyer (Eds), 2005, p. 355.

[371] 1,1-difluoroethane

[372] *trans*-1,3,3,3-tetrafluoroprop-1-ene

[373] GSK, 2021, *Our position on: respiratory products and global warming*, October 2021. https://www.gsk.com/media/2962/respiratory-products-and-global-warming-policy.pdf.

[374] IPCC/TEAP, 2005, *IPCC/TEAP Special Report: Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons*, B. Metz, L. Kuijpers, S. Solomon, S. O. Andersen, O. Davidson, J. Pons, D. de Jager, T. Kestin, M. Manning, and L. Meyer (Eds), 2005, Chapter 2, p. 153.

on the market by 2022. Previous studies had reported toxicological concerns for isobutane used in combination with a beta-agonist.[375] Isobutane is flammable, with a lower flammable limit of 1.8 volume percent in air, and therefore its adoption would require pMDI manufacturing to address safety.[376] Safety considerations for manufacturing with flammable chemicals requires significant engineering and investment. The global warming potential of isobutane is <<1 and it has an atmospheric lifetime of about 6 days.[377]

10.2.6.2 HFC-152a

One chemical company has made significant progress in the development of pharmaceutical-grade HFC-152a as a possible pMDI propellant with lower global warming potential than HFC-134a. HFC-152a is a colourless and odourless gas that is already manufactured in large volumes and widely used in several non-medical applications. The toxicology of HFC-152a is well known as an industrial gas (and similar to HFC-134a). Work to fill in gaps in the industrial toxicity was initiated in 2016 and is now successfully completed. A Drug Master File is expected to be completed soon, and a medical grade production facility was opened in March 2022.[378]

Placebo formulations of medical grade HFC-152a have shown no adverse effects in phase I safety and tolerability studies[379], while a more recent study of a combination drug product formulated in HFC-152a has demonstrated acceptable pharmacokinetics.[380] HFC-152a was originally considered as a CFC replacement, alongside HFCs -134a and -227ea, over 30 years ago but was not adopted at the time, possibly because the propellant is flammable with a lower explosive limit (LEL) of 3.9% by volume in air at room temperature. Unlike some ethanolic pMDI formulations, it does not cause flame extension from a standard flame test. Nonetheless, safe manufacturing processes for HFC-152a would need to be developed for pMDIs. Given that billions of aerosol cans are safely filled with isobutane every year, the technology exists to overcome this problem through addition of appropriate control measures to minimise the associated risks when making the formulation and transferring it into the cannister. The first pMDIs containing HFC-152a are expected to launch in 2025.

The global warming potential[381] of HFC-152a is 124, compared with 1,430 for HFC-134a and 3,220 for HFC-227ea. A lifecycle carbon footprint study has shown that the carbon footprint of an HFC-134a pMDI can be reduced by 92% if replaced by an HFC-152a pMDI (1,800 gCO_2e/200 actuation inhaler).[382] Due to the lower liquid density of HFC-152a (compared with the higher GWP HFC

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[375] Final report of the Safety Assessment of isobutane, isopentane, *n*-butane, and propane, *Journal of the American College of Toxicology*, 1982, **1**(4), 127–142. https://doi.org/10.3109/10915818209021266.

[376] For flammability limits of isobutane see: Kondo, S., Takizawa, K., Takahashi, A., Tokuhashi, K., Sekiya, A. Flammability limits of isobutane and its mixtures with various gases, *Journal of hazardous materials*, 2007, **148**(3), 640–647. https://doi.org/10.1016/j.jhazmat.2007.03.021.

[377] WMO (World Meteorological Organization), 2018, *Scientific Assessment of Ozone Depletion: 2018*, Global Ozone Research and Monitoring Project–Report No. 58, 588 pp., Geneva, Switzerland, 2018.

[378] Chiesi, 2022, *Koura opens world's first HFA 152a medical propellant production facility*, Press Release, March 30, 2022. https://www.chiesi.com/en/koura-opens-worldrs-first-hfa-152a-medical-propellant-production-facility/.

[379] Kuehl, P. *et al.*, 2022, Safety, tolerance and pharmacokinetics of HFA-152a in healthy volunteers, *Respiratory Drug Delivery 2022*, eds Dalby, R., *et al.*, 87–95, Virginia Commonwealth University, 2022.

[380] Chiesi, 2022, *First carbon minimal pMDI is on track with the goal to benefit patients and planet*, Press Release, July 27, 2022. https://www.chiesi.com/en/first-carbon-minimal-pmdi-is-on-track-with-the-goal-to-benefit-patients-and-planet/.

[381] According to Montreal Protocol Annex F, 100-year Global Warming Potential, based on IPCC AR4.

[382] Jeswani, H., Corr, S., Azapagic, A., 2017, *Reducing carbon footprints of metered dose inhalers*, Inhalation, CSC Publishing, December 2017. Available at https://www.zephex.com/wp-content/uploads/2019/05/inh_20171201_0036.pdf. Accessed December 2022.

propellants), early indications are that less weight of propellant will be used in HFC-152a pMDIs resulting in additional savings. More data on environmental impacts are provided in section 10.4.3.

HFC-152a is an Annex F HFC, which are subject to Kigali Amendment HFC phase-down measures.

10.2.6.3 Hydrofluoroolefin HFO-1234ze(E)

HFO-1234ze(E) is a much more recent chemical development. It exhibits similar toxicological and key physical properties (density, vapor pressure, moisture solubility, dipole moment) to HFC-134a and HFC-227ea. It is classified as non-flammable (per ASTM E-681 and ISO 10156) and is currently being used as a near drop-in replacement for HFC-134a in other applications, including aerosol applications. Nevertheless, it possesses a flammable range of 8.0–8.5 volume percent in air (at one atmosphere under certain conditions), requiring consideration in manufacturing processes.

Formulation studies show good compatibility with common excipients and active pharmaceutical ingredients (APIs), suggesting comparable performance to current HFC-134a formulations.[383] Completed toxicology studies have been reviewed by the U.S. Food and Drug Administration (FDA) and Committee for Medicinal Products for Human Use (CHMP) and a Drug Master File has been submitted.[384] Phase I clinical trials of HFO-1234ze(E) in a pMDI containing a combination of budesonide, glycopyrronium, and formoterol fumarate showed positive results, providing similar safety, tolerability, and systemic exposure as the corresponding HFC-134a pMDI.[385] Phase III clinical trials are scheduled to proceed, with the first anticipated product launch in 2025.

HFO-1234ze(E) has a much shorter atmospheric lifetime (0.052 years, 19 days) compared with HFC-134a (14 years), HFC-227ea (36 years), and HFC-152a (1.6 years), resulting in a very low GWP[386] of 1.37.

HFO-1234ze(E) is a relatively new propellant. It has a complex chemical synthesis and currently lower consumption than, e.g., HFC-134a or HFC-152a. The cost to manufacture pharmaceutical-grade HFO-1234ze(E) may be higher than for HFC-134a.

10.2.6.4 Summary of progress

At the time of preparation of this report, three pharmaceutical companies and one major contract development and manufacturing organization (CDMO) have announced plans to reformulate their pMDI products with lower-GWP propellants. Together, they account for over 70% of the pMDI market revenues from the United States and Europe.

All four companies aim to begin introducing new pMDIs into the market from 2025. Given the differences in regulatory expectations and the pace of approval in different countries, together with the time it takes to convert both patients and the supply chain, it is currently unlikely that transition in non-Article 5 parties would be completed before 2030, even for this limited number of products announced to date. Nevertheless, it does mean that there will be lower-GWP pMDIs available that contain all major classes of drug used to treat asthma and COPD, including double- and triple-combinations. However, it should be noted that within these developments, there is only one company that has publicly announced reformulation of a reliever pMDI. Salbutamol pMDIs account for well

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[383] Hulse, R. *et al.*, 2022, A journey to net zero using Solstice® Air, *Respiratory Drug Delivery 2022*, eds Dalby, R. *et al.*, 97–101, Virginia Commonwealth University, 2022.

[384] U.S. FDA, DMF number 34607, submitted 26 June 2020.

[385] Aurivillius, M., Dunsire, L., Bednarczyk, A., *et al.*, S61 Reducing the environmental impact of pressurized metered dose inhalers: relative bioavailability of budesonide/glycopyrronium/formoterol fumarate dihydrate with novel propellant formulations in healthy subjects, *Thorax,* 2022, **77**, A39.

[386] Atmospheric lifetimes are from IPCC AR6. HFO-1234ze(E) 100-year GWP is AR6 value as there is no AR4 value.

over half of all inhaled doses of medication. Based only on these announcements, a significant proportion of global production of salbutamol pMDIs could potentially be in the earlier stages of development of replacements. The introduction of low GWP HFC pMDIs will be gradual and is likely to require careful coordination with the phase-down of high GWP HFC pMDIs to ensure continued patient access to essential treatments.

For those with smaller market share, there is a commercial dilemma. As noted above, to reformulate is a lengthy and costly process, and for many companies it is unclear whether this would be financially justified. One key element in this consideration is the scale of clinical studies that would be required. To date, health authorities have not announced specific guidelines for switches in pMDI to lower GWP propellants. Under the CFC to HFC pMDI transition, all health authorities required full-scale phase III clinical studies with 100s of patients and 12 months' safety data. Since then, the regulatory science has advanced and, at least in the European Union, it is possible to gain product approval by performing bioequivalence studies if there is a high degree of similarity between the two products.[387] The difference in time and cost between the two approaches is enormous, and unless the latter approach is accepted, it is likely many companies will not attempt to reformulate all pMDI products. Indeed, one company informed MCTOC that it would only attempt to launch a generic low-GWP pMDI once an innovator low-GWP pMDI had been marketed, to utilise the clinical and safety data from the innovator under a traditional generic pathway.

At the same time, it is likely that the cost of bulk HFC-134a and HFC-227ea propellants will rise substantially over the next few years as other industrial uses decline, and quota mechanisms impact on their availability.[388] This could lead to a shortage of affordable reliever medication, even if allocations of HFCs for pMDIs are set aside under national HFC phase-down requirements.

The projected timescale for the introduction of the lower GWP pMDIs from the 4 companies active in the field may be at risk if the health authorities require full clinical development programmes to be completed for switches of the propellant when there are no other substantial changes in the formulation. Some general guidance on the clinical data requirements is urgently needed, especially given the possibility of accelerated HFC phase-down, such as with the proposed changes to European Union F-gas regulations.

For Article 5 parties, the timetable for phase-down is longer than for non-Article 5 parties. Nevertheless, there are multinational inhaler manufacturers based in these countries that have corporate targets to reduce their carbon footprints and that wish to maintain and build global market access. Accordingly, some are investigating prototype formulations with low-GWP propellants. However, to date, none have announced plans to launch such products. The patent landscape may also play a role in their decision-making because the current suppliers of pharmaceutical grade HFC-152a and HFO-1234ze(E) have several patents pending or granted in this field. Until the strength of these patents is resolved, it is not clear whether alternative propellant manufacturers can enter the field or whether any pharmaceutical company (in non-Article 5 or Article 5 parties) wishing to develop and launch low-GWP pMDIs will need to seek propellant and patent licenses from the current suppliers.

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[387] European Medicines Agency, 2009, Guideline on the requirements for clinical documentation for orally inhaled products (OIP) including the requirements for demonstration of therapeutic equivalence between two inhaled products for use in the treatment of asthma and chronic obstructive pulmonary disease (COPD) in adults and for use in the treatment of asthma in children and adolescents, Doc. Ref. CPMP/EWP/4151/00 Rev. 1, 22 January 2009. https://www.ema.europa.eu/en/documents/scientific-guideline/guideline-requirements-clinical-documentation-orally-inhaled-products-oip-including-requirements_en.pdf.

[388] Pritchard, J.N., 2022, Is the climate right for a new pMDI propellant? *Respiratory Drug Delivery 2022*, eds Dalby, R. *et al.*, 1–12, Virginia Commonwealth University, 2022.

10.3 Global market dynamics for inhaled therapies

Globally, the total inhaled respiratory market has grown in volume by approximately 30% over the past decade. This reflects the continued uptake in use of inhaled medicines in countries that have growing economies. Injectable treatments (biologics) have recently been introduced to treat severe asthma. These have grown significantly in recent year but from a very low base.

Inhaler prices are declining as competition increases, with more multinationals and local companies coming into the market. In less mature markets, the market value is increasing due to increasing numbers of inhalers being used. In some mature markets (e.g., the European Union), the overall market value is declining due to competitive pricing.

10.3.1 Numbers and disposition of inhalers

Based on HFC manufacturing industry estimates[389], approximately 800–825 million HFC pMDIs (assuming a global weighted average fill weight: 14.61 g/HFC-134a pMDI and 11.38 g/HFC-227ea pMDI) are currently manufactured annually worldwide, using approximately 10,700 tonnes HFCs (~10,100 tonnes HFC-134a; ~600 tonnes HFC-227ea) in 2021. This corresponds to direct emissions with a climate impact of approximately 16.4 MMTCO$_2$e. Based on knowledge about DPI raw material inputs, one industry estimate puts the number of DPIs manufactured worldwide at 450 million annually.

10.3.2 Inhaler Market Dynamics

Data on the total respiratory market, provided by IQVIA[390], for respiratory medicines sold worldwide demonstrates that DPI and pMDIs retain the most significant portion of the market (see Figure 10.1). This data is based on an analysis of prescriptions in markets where this information is available, where it should be noted that IQVIA data does not cover all countries around the world.

Compared with 2018, the share of units for both pMDIs and DPIs is very similar in 2021. The market data for inhaler units sold worldwide indicates approximately 60% were pMDIs, 32% were DPIs, and the remaining 8% were either SMIs or nebulised liquids. These percentages have changed little over the past decade. The time series analysis presented in Figure 10.1 is based on available data in previous Medical TOC reports and new data from IQVIA.

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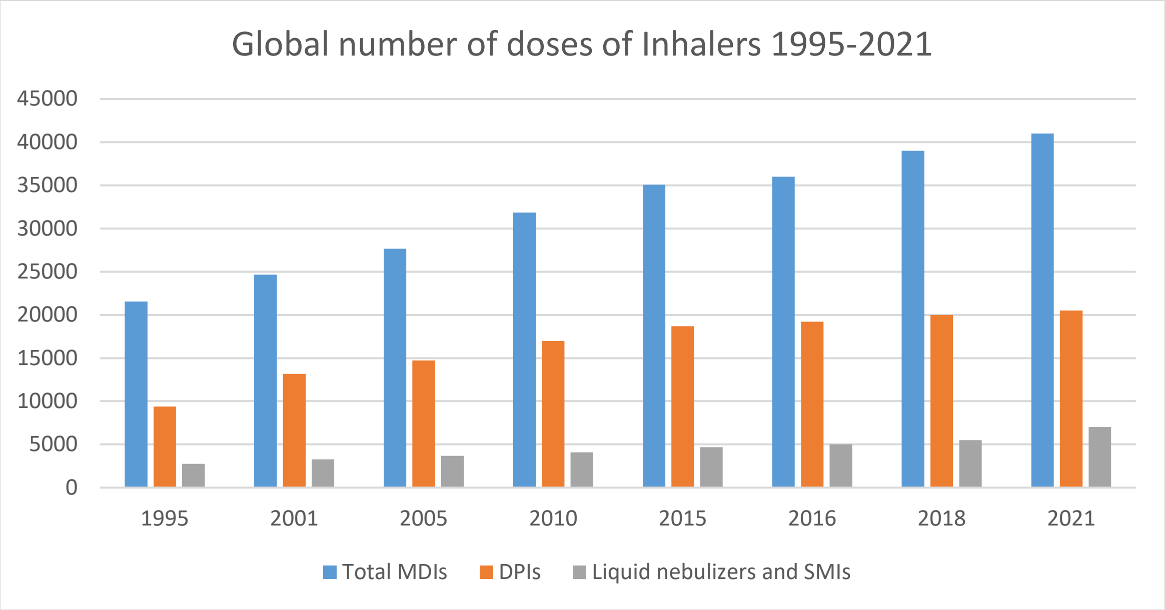
[389] T.J. Noakes, Koura, United Kingdom, personal communications, 2022. HFC propellant consumption data, derived from HFC and cannister manufacturing industry sources, differ from that derived from inhaler market data. For the purposes of this report, the manufacturing industry data has been used to estimate HFC propellant consumption and corresponding estimates for numbers of inhalers.

[390] IQVIA Quarterly MIDAS® data obtained under license by IQVIA, formerly IMS Health and Quintiles, a leading global provider of advanced analytics, technology solutions, and clinical research services to the life sciences industry. AstraZeneca was granted permission to provide IQVIA inhaler sales data to MCTOC for this assessment. Data were adapted for the purposes of MCTOC. MCTOC wishes to acknowledge the assistance of AstraZeneca in sourcing, adapting, and providing IQVIA data.

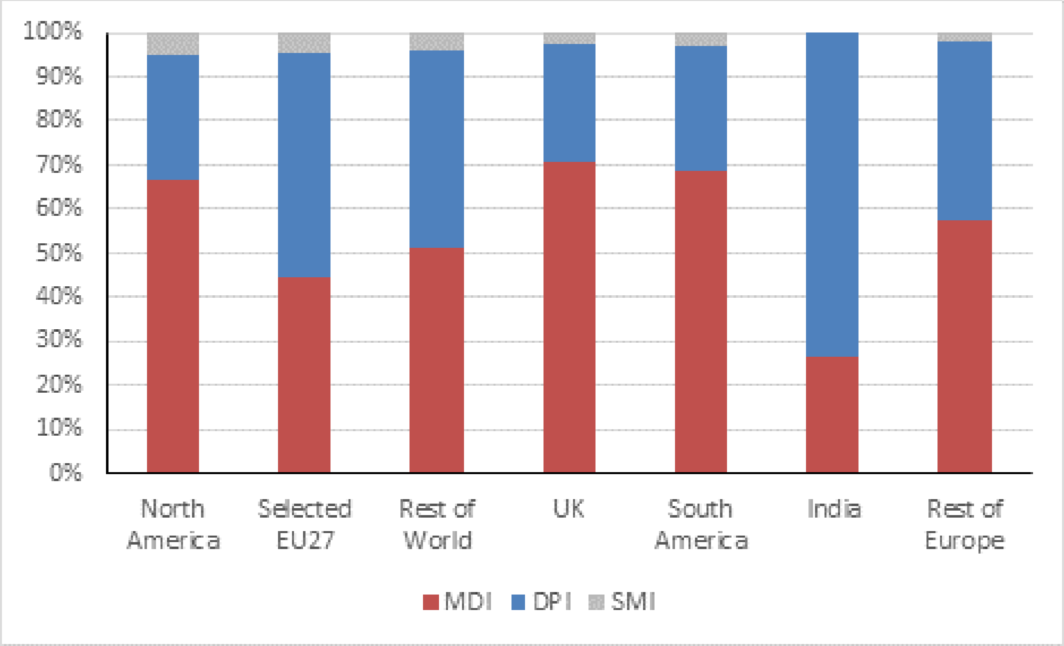
Figure 10.1 **Annual number of doses of pMDI, DPI, liquid nebulised units (including SMIs), 1995–2021**



pMDIs remain the dominant option in most markets for the delivery of inhaled therapy (see Figure 10.2), with exceptions being the European Union, and India, the latter where single-dose DPIs are used extensively. In different markets, the proportion of pMDIs to DPIs and SMIs use differs. These proportions vary for many reasons, including prescribing practices, cost and availability, patient preference, and national government guidance.

Of the total DPI/pMDI/SMI inhalers units sold worldwide in 2021, the dynamics vary for different markets. In the United States, pMDIs dominate with approximately 65% of the market being pMDIs. In the selected EU27 countries (Belgium, Croatia, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Netherlands, Poland, Romania, Spain, and Sweden), approximately 45% of the inhaler units sold were pMDIs. In the United Kingdom, about 70% of the inhaler units sold were pMDIs. In India, nearly 75% of the inhaler units sold were DPIs. An analysis of the rest of the world data indicates that approximately 50% of the units sold are pMDIs.

Figure 10.2 Proportion of pMDI, DPI and SMI units sold in specific regions, 2021[391]



For preventer (or maintenance) therapy only, of the DPI/pMDI/SMI inhalers units sold worldwide in 2021, slightly different market patterns are indicated, reflecting relatively higher usage of DPIs for this type of therapy. DPIs are the dominant option for the delivery of inhaled maintenance therapy in most markets (see Figure 10.3). In the United States, DPIs were approximately 55% of inhalers sold for maintenance therapy. In the selected EU27 countries (see above), approximately 65% of the inhaler units for maintenance therapy sold were DPIs. In the United Kingdom, about 40% of the inhaler units sold for maintenance therapy were DPIs. In India, about 75% of the inhaler units sold were DPIs. An analysis of the rest of the world data indicates that nearly 70% of the units sold for maintenance therapy were DPIs.

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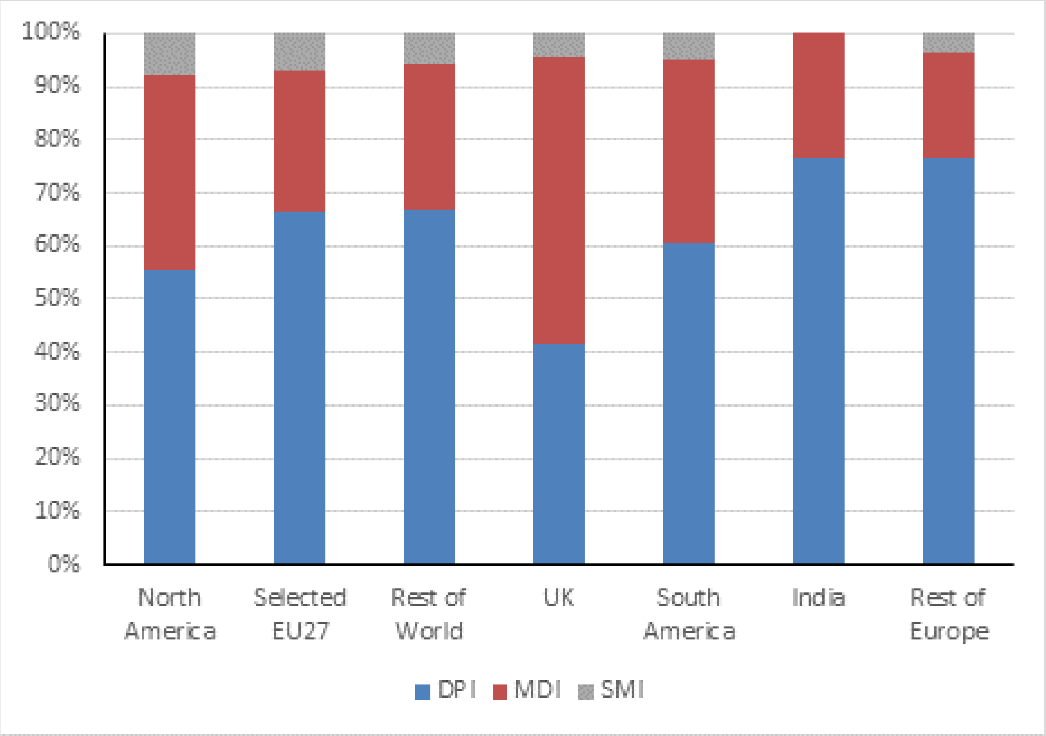
[391] Based on internal analysis by AstraZeneca UK Ltd using data from IQVIA Quarterly MIDAS® for the period 2021. Unit volume sales of AstraZeneca defined Respiratory Total Market limited to Respi Form Groups: Dry Powder Inhaler, P Metered Dose Inhaler, Soft Mist Inhaler, reflecting estimates of real-world activity. AZ defined Markets: North America (U.S. and Canada), Selected EU27 (Belgium, Croatia, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Netherlands, Poland, Romania, Spain and Sweden), Rest of World (Algeria, Australia, East Asia, Egypt, Indonesia, Jordan, Kuwait, Lebanon, Malaysia, Philippines, South Africa, Saudi Arabia, Singapore, Thailand, UAE and Vietnam), South America (Argentina, Brazil, Central America, Chile, Colombia, Dominican Republic, Mexico and Peru) and Rest of Europe (Kazakhstan, Norway, Russia Federation, Switzerland, Turkey and Ukraine). Copyright IQVIA. All rights reserved.

Figure 10.3 Proportion of pMDI, DPI and SMI units for maintenance therapy sold in specific regions, 2021[392]



The distribution of worldwide pMDI sales (Figure 10.4) indicates that North America, the United States in particular, remains the largest global market for pMDIs in terms of units sold, and this remains unchanged from 2018. The market share of the selected EU27 countries, United Kingdom, and rest of the world (RoW) regions fell by around 1% from 2018 to 2021, while the market share of South America and India increased by 2% and 1% respectively.

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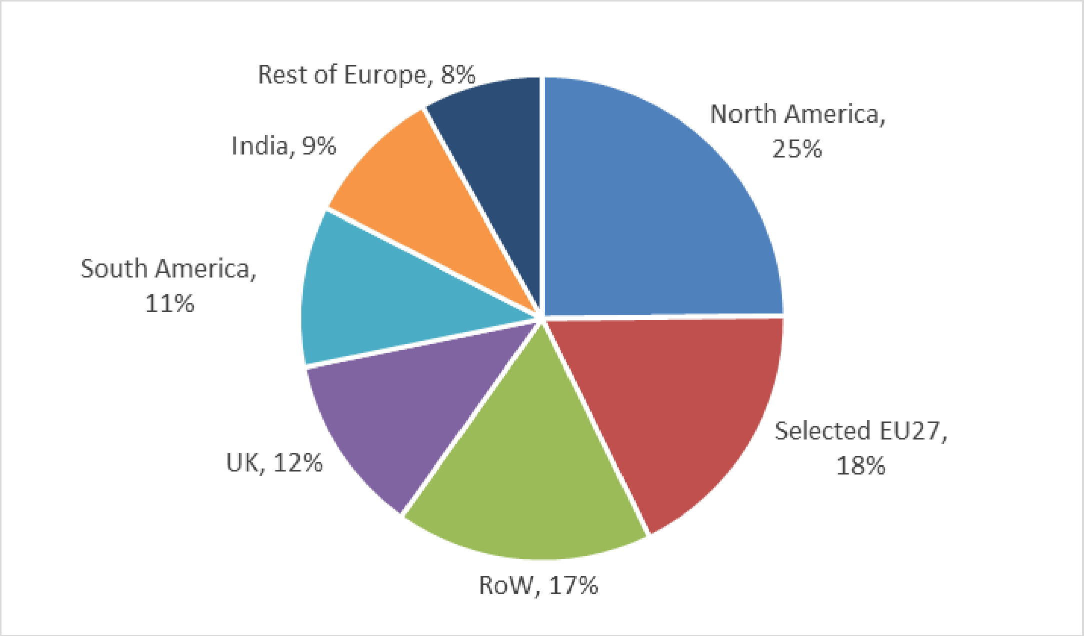
[392] Based on internal analysis by AstraZeneca UK Ltd using data from IQVIA Quarterly MIDAS® for the period 2021. Unit volume sales of AstraZeneca defined Respiratory Maintenance Market limited to Respi Form Groups: Dry Powder Inhaler, P Metered Dose Inhaler, Soft Mist Inhaler, reflecting estimates of real-world activity. AZ defined Markets: North America (U.S. and Canada), Selected EU27 (Belgium, Croatia, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Netherlands, Poland, Romania, Spain and Sweden), Rest of World (Algeria, Australia, East Asia, Egypt, Indonesia, Jordan, Kuwait, Lebanon, Malaysia, Philippines, South Africa, Saudi Arabia, Singapore, Thailand, UAE and Vietnam), South America (Argentina, Brazil, Central America, Chile, Colombia, Dominican Republic, Mexico and Peru) and Rest of Europe (Kazakhstan, Norway, Russia Federation, Switzerland, Turkey and Ukraine). Copyright IQVIA. All rights reserved.

Figure 10.4 **Percentage global pMDI unit sales by selected region and/or country[393], 2021**



Of the pMDI use globally, the largest single molecular entity delivered by pMDI is salbutamol (also known as albuterol). This is a short-acting bronchodilator (SABA) used as reliever medicine for asthma and COPD patients who are undergoing an acute shortage of breath. Recent studies have indicated an overuse of salbutamol that is associated with poor asthma outcomes, of which healthcare professionals are becoming increasingly aware in their prescribing practices.[394] There is projected to be a slow reduction of salbutamol use in the coming years; however, it is currently still a significant portion of overall pMDI use. Several large pMDI manufacturers produce around 230 million salbutamol pMDIs annually. However, some estimates put the total global use of salbutamol pMDIs at around 480–500 million units per annum (or greater than 60% of total pMDI use). Many of these pMDIs may be produced domestically (or by nationally owned pharmaceutical companies) for domestic or regional consumption. An analysis recently presented by Pritchard[395] of pMDI and DPIs doses (not by units sold, and not normalised for population size) indicates that the pMDI dominates the SABA inhaler market in most countries, with regional differences (Figure 10.5).

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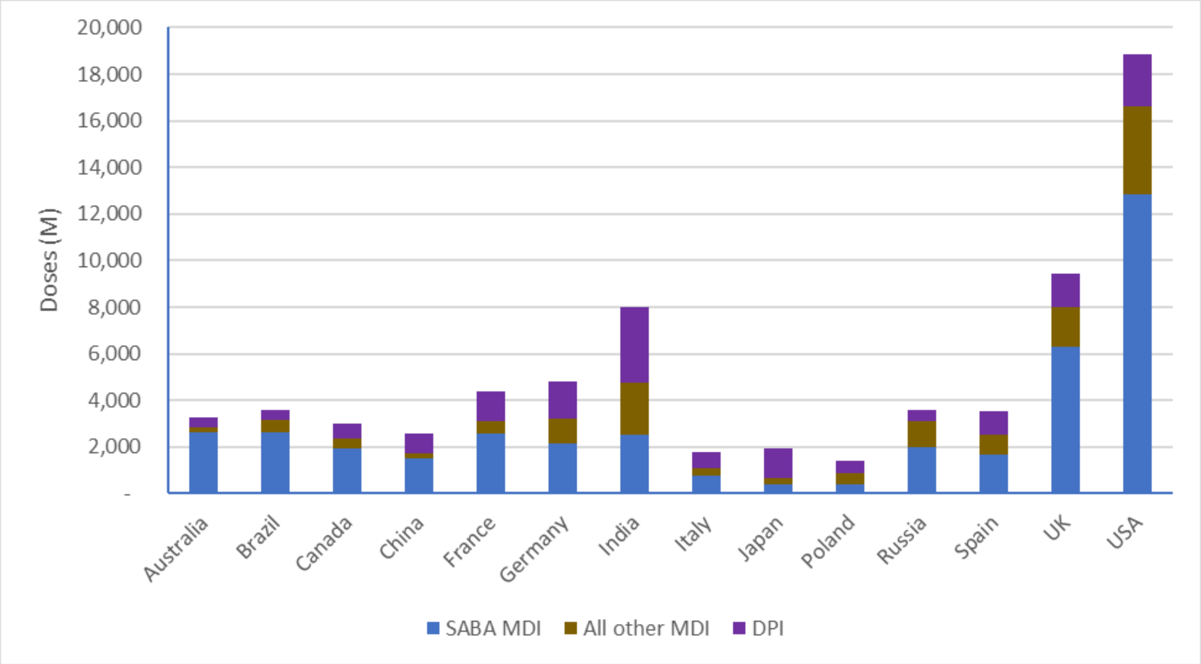
[393] Based on internal analysis by AstraZeneca UK Ltd using data from IQVIA Quarterly MIDAS® for the period 2021. Global MDI unit volume sales of AstraZeneca defined Respiratory Total Market, reflecting estimates of real-world activity. AZ defined Markets: North America (U.S. and Canada), Selected EU27 (Belgium, Croatia, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Netherlands, Poland, Romania, Spain and Sweden), Rest of World (Algeria, Australia, East Asia, Egypt, Indonesia, Jordan, Kuwait, Lebanon, Malaysia, Philippines, South Africa, Saudi Arabia, Singapore, Thailand, UAE and Vietnam), South America (Argentina, Brazil, Central America, Chile, Colombia, Dominican Republic, Mexico and Peru) and Rest of Europe (Kazakhstan, Norway, Russia Federation, Switzerland, Turkey and Ukraine). Copyright IQVIA. All rights reserved.

[394] Janson, C., Maslova, E., Wilkinson, A., Penz, E., Papi, A., Budgen, N., Vogelmeier, C.F., Kupczyk, M., Bell, J., Menzies-Gow, A., Short-acting ß2-agonists and greenhouse gas emissions in Europe and Canada, *European Respiratory Journal*, 2021, **58**, PA3549. DOI: 10.1183/13993003.congress-2021.PA3549.

[395] Pritchard, J.N., 2022, Is the climate right for a new pMDI propellant? *Respiratory Drug Delivery 2022*, eds Dalby, R. *et al.*, 1–12, Virginia Commonwealth University, 2022.

Figure 10.5 Total pMDI and DPI doses in the Top 14 global markets[396]



10.3.3 New inhaled therapies

New therapies have been introduced in the market over the past 5 years. These include products that contain a combination of 3 active ingredients (a long-acting beta agonist, an inhaled corticosteroid and a long acting anti-muscarinic) in a single device. Different companies have introduced these in a range of delivery platforms, both pMDIs and DPIs.

10.3.4 Transition to lower GWP propellants

Based on industry knowledge, MCTOC presents an analysis of possible projected propellant usage under a business-as-usual transition away from high GWP HFC propellants to lower GWP propellants, HFC-152a and HFO-1234ze(E) (see Figure 10.6).

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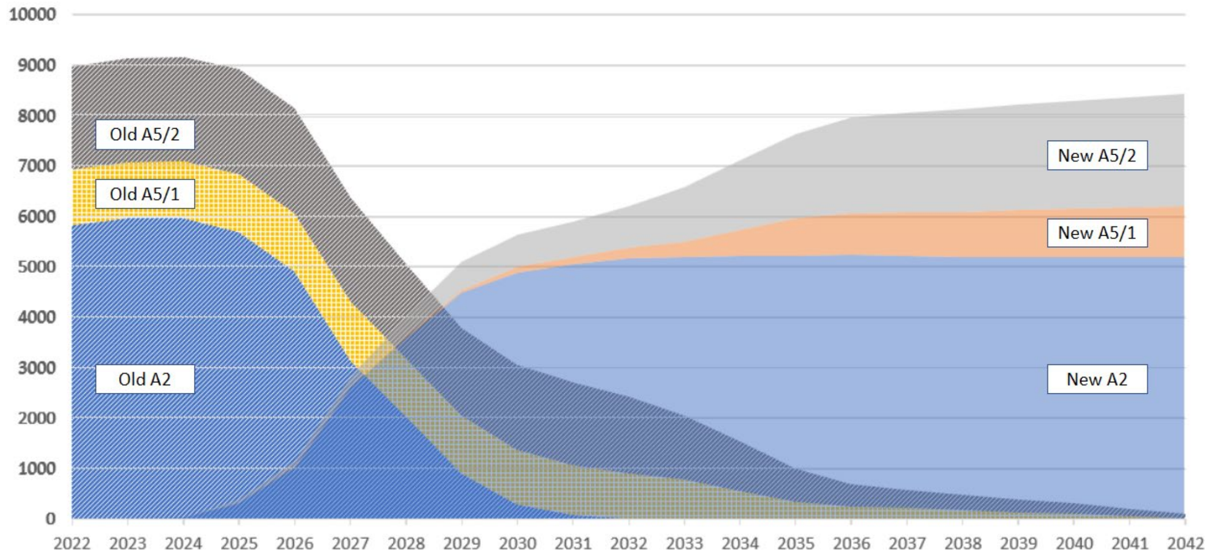
[396] Pritchard, J.N., 2022, Is the climate right for a new pMDI propellant? *Respiratory Drug Delivery 2022*, eds Dalby, R. *et al.*, 1–12, Virginia Commonwealth University, 2022.

Figure 10.6 Projected global propellant usage, 2022–2040 (by volume, m^3)



The scenario outlined in Figure 10.6 is essentially a business-as-usual projection of what the low GWP propellant transition could look like. It assumes no substantial changes in the global pMDI to non-pMDI (i.e., DPI and SMI) ratio. This analysis also includes a slow decline for salbutamol pMDIs, which is anticipated. It also assumes the issues and challenges described in section 10.3.5 below do not significantly delay or disrupt the transition to lower GWP pMDIs. An anticipated reduction in can fill volume is also included, due to the enhanced formulation characteristics of the low GWP propellants, enabling companies to target smaller volumes of propellant per actuation in more concentrated formulations.

The units used are not tonnes, as has been the case in previous reports, but volume of liquefied propellant in cubic metres. This enables different propellants, "Old" propellants HFC-134a and HFC-227ea and "New" propellants HFC-152a and HFO-1234ze(E), to be combined and contrasted in one graphic without distortions occurring due to differing liquid densities and without having to clarify assumptions about future relative market share of HFC-152a versus HFO-1234ze(E) propellants.

The three groupings used on Figure 10.6 refer to country groupings that each have different HFC phase-down commitments under the Kigali Amendment of the Montreal Protocol.

- "A2" includes non-Article 5 parties in North America, Europe, Australia, Japan, New Zealand
- "A5/2" includes Article 5 parties, India, Iran, Iraq, Pakistan, Saudi Arabia (only pMDI manufacturing countries listed here)
- "A5/1" includes all other Article 5 parties not listed above.

The analysis indicates a propellant transition period in non-Article 5 parties starting in 2025, with new product launches, and extending until at least 2032, at the same time while "new" propellants steadily increase. The transition period in Article 5 parties starts later this decade and proceeds more slowly, with "old" propellants extending beyond 2040. This reflects some multinational companies transitioning to maintain their global markets while other companies that lack the resources for major research and development, wait longer for technology transition.

10.3.5 Issues and potential challenges in the transition to lower GWP inhalers

There are a range of issues and potential challenges that could emerge in the transition away from high GWP propellant pMDIs to inhalers with lower GWPs, including pMDIs using lower GWP propellants, DPIs and SMIs.

These issues are summarised below.

- ***Global and national frameworks***— The global and national transition frameworks that were established for the transition to high GWP HFC pMDI, created clear market signals and triggers that managed the transition away from CFC pMDIs. They were developed through industry and stakeholder consultation and were based on technical and economic considerations. They supported global and national market transitions without significant disruptions to the global supply and use of life-saving medicines. These frameworks also addressed challenges as they arose, e.g., the continued supply of CFC pMDIs to countries that had not yet approved the HFC pMDI products. Such considerations may also be needed to coordinate the coming transition to lower GWP pMDIs and other low GWP alternatives, such as DPIs and SMIs. Without similar strategic considerations, there are potential risks of disruption to markets and to patients in the coming transition. Parties may wish to consider the need for global and national coordination in the HFC phase-down and its impact on the transition away from high GWP HFC pMDIs to ensure patient safety.

- ***Pharmaceutical-grade HFC supply chains***— In the transition from high GWP HFCs to lower GWP pMDIs, there is likely to be a point when the continued supply of pharmaceutical-grade HFC-134a and HFC-227ea becomes no longer technically or economically viable. Under an open-ended HFC phase-down, this tipping point is less easy to identify precisely and will be governed more by market forces and the decisions of chemical manufacturers. Prior to that tipping point, the cost of pharmaceutical-grade HFCs is likely to increase substantially due to the complexities and costs of purifying a diminishing supply of HFCs to reach pharmaceutical grade. When HFC supply and demand falls, such as when major HFC-consuming sectors transition or the Kigali phase-down reaches significant step downs, these factors could precipitate the tipping point where supply of pharmaceutical-grade HFC-134a and HFC-227ea becomes no longer technically or economically viable. More detail is provided below. Large-scale stockpiling will also not be technically or economically feasible, with operational difficulties to build and store stockpiles and regulatory frameworks that limit HFC quotas. Some pharmaceutical companies might be left unexpectedly under-prepared, both for the resulting higher HFC prices or for the end to the supply of pharmaceutical-grade HFCs, with associated risks to the continuous global supply of pMDIs and patient health. Parties may wish to consider how to ensure that adequate bulk HFC-134a and/or pMDIs are available in their own markets, and in their export markets, to avoid risks to the continuous supply of pMDIs.

- ***Regulatory approvals*** of the new pMDI products will be a factor in the speed and orderliness of transition and may benefit from a rationalised and coordinated approach. A coordinated approach across government agencies may be needed to facilitate regulatory approvals of the new pMDIs, taking into careful consideration the phase-down of high GWP HFCs and the stability in supply of pharmaceutical-grade HFCs, to ensure continued patient access to essential treatments. In this context, attention may also be needed to global and regional considerations, such as the impacts on global and regional markets of the HFC phase-down on pMDI manufacturing intended for export, especially in the absence of an approved new pMDI product in those export markets, and how regulatory approvals in Europe and the United States could serve as regulatory examples elsewhere. Parties may wish to consider measures that facilitate efficient, timely development while assuring the safety and effectiveness of the new pMDIs.

- ***Exports of pMDIs***— Countries with pMDI manufacturing and export will want to account for high GWP HFCs needed for pMDI manufacture in their own domestic quotas to accommodate the needs of importing countries that have not yet approved the new lower GWP products. .

- ***Market signals***— Unlike the CFC to HFC pMDI transition, an HFC phase-down presents a different set of factors that could impact the transition from high GWP HFC pMDIs to lower GWP propellants. An HFC phase-down lacks the clear market signals that drove the CFC phase-out. Clear market signals create economic certainty for industry and a commercial level playing field; a lack of clear signals creates economic uncertainty and potential market distortions. With an HFC phase-down, innovators making significant investments to transition their pMDIs to lower GWP propellants will be introducing new products that are more likely to compete simultaneously in the market with high GWP HFC pMDIs. Some companies might see little advantage in transitioning their high GWP HFC pMDI products, especially if the cost of new pMDIs from their competitors is even slightly more expensive. Factors related to intellectual property and the existing market reliance on generic pMDIs could impact the transition, where generic manufacturers might not have market access to, or might not actively pursue, new technology. Given the expense of bringing new products to market and the cost sensitivity of salbutamol pMDIs, while pharmaceutical-grade HFCs remain available, an HFC phase-down could set up market conditions, in the short- or medium- term, that lead some companies to delay their transition and gain market advantage. It is difficult to say what the implications of this might be for patients, whether positive or negative. However, a sudden closure in supply of pharmaceutical-grade HFCs would bring about a rapid phase-down of high GWP pMDIs, which could create significant risks to the continuous supply of pMDIs.

- ***Patents***— Patent protection is the opportunity given to innovators to achieve the necessary return on their investments in research and development. Patent protection issues impacted the economics of the transition from CFC pMDIs to HFC pMDIs. In the United States, the first HFC pMDI was approved in 1996, the last HFC pMDI patents expired in 2017, and the first generic HFC pMDI was approved in 2020. Initially, cheaper generic CFC pMDIs were competing on the market simultaneously with more expensive branded HFC pMDIs, until CFC pMDIs were later phased out by regulation. With no access to cheaper generic CFC pMDI, an abrupt cost increase was experienced by patients. A relatively large increase in the mean out-of-pocket costs for salbutamol pMDIs was reported among privately insured patients in the United States that has been attributed to the shift from generic CFC pMDIs to branded HFC pMDIs, with a small but measurable associated impact in lowering pMDI use.[397] Providing patent protection provides incentives for on-going investments in research and development; nevertheless, maintaining access to affordable medicine remains a universal goal in ensuring equitable healthcare.

  One chemical manufacturer of the new lower GWP propellants, with a suite of intellectual property on its propellant and propellant/drug formulations, has indicated an intention to license widely and in a generally non-exclusive way, to avoid impeding the transition from high GWP HFC pMDIs to lower GWP pMDIs. This type of approach would allow access to technology for generic manufacturers, which could facilitate smooth introduction of generics if manufacturers choose to transition or are forced to transition when pharmaceutical-grade HFC supply issues start impacting. This could avoid potential abrupt cost increases to patients and potential disruptions in the transition.

- ***pMDI manufacturing capacity*** with the new propellants may not be able to pivot rapidly to replace global demand for pMDIs using high GWP propellants. The new propellants have

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[397] Jena, A.B., Ho, O., Goldman, D.P., Karaca-Mandic, P., The impact of the U.S. Food and Drug Administration chlorofluorocarbon ban on out-of-pocket costs and use of albuterol inhalers among individuals with asthma, *JAMA Intern Med.*, 2015, Jul, **175**(7), 1171–1179. https://doi.org/10.1001/jamainternmed.2015.1665.

properties that require changes to manufacturing to manage flammability and other changes to production lines, requiring significant plant adjustments or entirely newly built facilities. Supply chains will also need to adapt their manufacturing, e.g., cannisters and metering valves.

- ***mDPI and SMI manufacturing capacity*** may not be able to pivot rapidly to increase global production to replace the demand for pMDIs. Ramping up DPI and SMI production would take time.

- ***Patient and physician information*** might be needed if there are differences in the patient experience of the new lower GWP pMDIs compared with the high GWP pMDIs.

10.3.5.1 Pharmaceutical-grade HFC supply chains

The HFC phase-down and pMDI transition create a complex set of technical and economic issues for pharmaceutical-grade HFC supply chains. These issues will increasingly create instability in HFC supply chains, in turn creating risks for continuous global supply of pMDIs and patient health.

There are currently up to 10 plants that produce technical-grade HFC-134a, with up to 5 (India, Japan, United States, 2 more in China) of those currently actively offering technical-grade HFC for subsequent purification to medical (topical aerosols) or pharmaceutical grade (pMDIs). The plants in Japan and the United States offers technical-grade HFC-134a to a plant in the United Kingdom that has the technical capability to purify to pharmaceutical-grade and supplies globally to pharmaceutical companies. The plant in India offers technical-grade HFC-134a to another plant in India that has the technical capability to purify to pharmaceutical-grade and supplies pharmaceutical companies in the South Asia region. The plants in China supply China, and it is unclear whether purification is to medical or pharmaceutical grade.

There are currently 2 plants (Germany, United States) that produce and offer technical-grade HFC-227ea for subsequent purification to pharmaceutical grade. Both supply technical-grade HFC-227ea that is purified at plants within their own country, and supply globally to pharmaceutical companies. One of those suppliers is decreasing its offerings as it moves to exit the business.

The technical-grade HFC feed plants are large, complex processes designed to run continuously at a normal running rate (i.e., nameplate rate), which is sensitive to change below a certain throughput. The plants do not operate as designed below around 60–70% of nameplate rate. When demand falls below this point, a manufacturer would have 2 options; campaign production, by turning the plant off and on; or rationalising production by closing lines if they have more than one or by entering a rationalisation deal with a competitor, with one company’s plant being closed.

To operate a plant efficiently, it is necessary to run it above a minimum capacity. Once overall product demand falls below a certain point, a plant cannot operate continuously above that minimum capacity without producing more product than is needed to meet the lower demand, which is uneconomic. One option is for the plant to run intermittently above its minimum capacity in production campaigns by turning the plant off and on, in what is called campaign production. Campaign production is very wearing on a plant designed for continuous production and doing so on a regular basis would rapidly destroy the plant, with super-corrosion at start-up being a major issue. It is also less efficient because technical-grade HFCs at the beginning of the campaign need to be rejected due to unacceptable levels of impurities, potentially without a commercial end-use.

Rationalisation is a limited and impractical option when there are so few plants. These HFC plants have running capacity designed to comfortably supply large HFC-consuming sectors, such as RACHP, not small sectors like pMDIs. When global demand diminishes beyond the nameplate rates of the plants, resulting from the HFC phase-down and successful transition to low GWP refrigerants in the RACHP sector, they will be unable to supply the technical-grade HFC feed for pharmaceutical-grade purifiers.

A higher quality, purified technical-grade HFC is needed to feed the pharmaceutical-grade purification plants, meaning that the purifier is married to the feed plants that it uses. It can take 1–2 years to qualify and validate new feed, which may ultimately prove unsuccessful. Registration or validation of the pharmaceutical-grade HFC supplied by the purifiers is also required for use by pharmaceutical companies with a 1 to 3-year process, which again may ultimately prove unsuccessful especially in highly regulated markets for pharmaceuticals. These factors make it impractical or impossible to change suppliers if technical-grade HFC feed plants close.

The purification plants generate a by-product stream containing HFC with a higher-than-normal impurity level. This by-product stream typically represents 20% of the HFC fed through the purification plant. This by-product is sent to industrial sales; the industrial business will eventually collapse as HFC phase-down and transition proceeds.

10.3.5.2 Conclusions

The transition of high GWP HFC pMDIs to lower GWP pMDIs within the global HFC phase-down is a complex manufacturing and marketing transition that requires careful forward planning of the supply chain to avoid patient harm. Market authorisation of the new lower GWP pMDIs by health authorities is another critical factor in a successful transition and could benefit from a coordinated approach.

Bulk pharmaceutical-grade HFC-134a manufactured in the United Kingdom is exported around the world, where pMDIs are then manufactured locally. India, and potentially China, also have the capacity to manufacture pharmaceutical-grade HFC-134a; however, certification by pMDI manufacturers of new supply chains for pharmaceutical-grade HFC-134a is difficult to achieve. Several major pharmaceutical companies manufacture pMDIs in Europe from bulk HFC import allocations, for subsequent export of HFC pMDIs around the world.

To guarantee adequate pharmaceutical-grade HFC-134a during transition, adequate amounts of technical-grade HFC-134a from Japan and/or the United States would need to continue to be supplied to the single purifier of bulk pharmaceutical-grade HFC-134a located in the United Kingdom. Technical-grade HFC-134a plants operate at a minimum capacity below which it becomes technically challenging or impractical to continue to manufacture HFC-134a (below 60–70% of normal running rate).

The Kigali Amendment’s 70% reduction of production and consumption from baseline for Annex F HFCs in non-Article 5 parties in 2029 is likely to impact and limit the global supply of pharmaceutical-grade HFCs for pMDIs, at which time it is also possible that an adequate supply of lower GWP pMDIs might not yet be available to meet patient demand.

How different regions manage their HFC phase-down within the global HFC phase-down will be important in ensuring global, regional, and local management of the supply chains during the transition away from high GWP HFC pMDIs. National implementation of HFC phase-down requirements may have implications for the global HFC and pMDI supply chains, including export markets. Flexibility within global and national HFC phase-down frameworks may need to be considered during the transition from high GWP to lower GWP pMDIs.

Regulatory approvals of the new pMDI products may benefit from a coordinated approach, taking into careful consideration the HFC phase-down and the stability in supply of pharmaceutical-grade HFCs, to ensure continued patient access to essential treatments. Timely transition and access to new technology, for example in markets reliant on generic pMDIs, could avoid large price increases with the loss of generic salbutamol HFC-134a pMDIs if or when HFC-134a supplies are shut down for technical and economic reasons.

Parties may wish to consider the range of technical and economic issues associated with the transition from high GWP HFC pMDIs to ensure adequate supplies of pMDIs and other inhalers during HFC phase-down.

Parties may wish to consider the need for global and national coordination in the HFC phase-down and its impact on the transition away from high GWP HFC pMDIs to ensure patient safety.

Parties may wish to consider how to ensure that adequate bulk HFC-134a and/or pMDIs are available in their own markets, and in their export markets, to avoid risks to the continuous supply of pMDIs. This necessity may persist for up to 10 years, until full ranges of affordable low GWP pMDIs are available worldwide.

Parties may wish to consider measures that facilitate efficient, timely development while assuring the safety and effectiveness of the new pMDIs.

10.4 Technical and Economic Assessment of pMDIs containing controlled substances and their alternatives

An assessment follows of the technical and economic feasibility of alternatives to Annex F HFCs in aerosol uses. The assessment criteria referenced in decision XXVIII/2 have been slightly modified to remain relevant to this application, using the following criteria:

i. Commercially available and accessible
ii. Technically proven
iii. Environmentally sound
iv. Economically viable and affordable
v. Suitable for high humidity regions
vi. Safety in production and use, considering flammability and toxicity issues
vii. Easy to use

“Commercially available” has been interpreted to include *commercially accessible*, which has a specific relevance and importance for pMDIs and their alternatives. “Safe to use in areas with high urban densities considering flammability and toxicity issues, including, where possible, risk characterization” has been adjusted to *safety in production and use considering flammability and toxicity issues*. “Economically viable and cost effective” has been adjusted to *economically viable and affordable*. “Easy to service and maintain” has been adjusted to *easy to use*. An additional criterion has been added, *suitable for high humidity regions*. Technically proven is interpreted to mean the technology has been proven to work for that application, or an aspect of it.

The assessment below includes only those alternatives considered as direct alternatives to pMDIs, i.e., it excludes oral tablets and nebulisers.

Table 10.1 Technical and economic assessment of use of controlled substances for pMDIs and alternatives

Controlled substances and alternatives	Party	Commercially available and accessible	Technically proven	Environmentally sound	Economically viable and affordable	Suitable for high humidity regions	Safety in production and use	Easy to use
HFC pMDI (HFC-134a, HFC-227ea)	Article 5 parties	🟧[1]	🟩	🟥[2]	🟧[3]	🟧[4]	🟩	🟧[5]
	Non-Article 5 parties	🟩[1]	🟩	🟥[2]	🟩[3]	🟧[4]	🟩	🟧[5]
				Alternatives				
Dry powder inhalers	Article 5 parties	🟧[1]	🟩	🟩[2]	🟧[3]	🟧[4]	🟩	🟧[5]
	Non-Article 5 parties	🟩[1]	🟩	🟩[2]	🟩[3]	🟧[4]	🟩	🟧[5]
Soft-mist inhalers	Article 5 parties	🟧[1]	🟩	🟩[2]	🟧[6]	🟩	🟩	🟧[5]
	Non-Article 5 parties	🟧[1]	🟩	🟩[2]	🟧[6]	🟩	🟩	🟧[5]

🟩 Yes or More acceptable; 🟧 Not always or Less acceptable; 🟥 No or Unacceptable.

1. Although classed by the World Health Organisation as essential medicines, commercial availability and accessibility of inhaled therapy for airways disease is not universal across all products/drugs and regions. This can be due to many reasons, including regulatory drug product approvals, health policy, presence of companies in pharmaceutical markets, as well as patient and prescriber preferences. pMDIs and DPIs can be less accessible in some Article 5 parties/regions than in non-Article 5 parties (see 10.5 below). The range of commercially available medications in SMIs is limited to short or long-acting bronchodilators, either as single drugs or combinations; these are primarily treatments for COPD. SMIs are also likely to be far less commercially available and accessible in Article 5 parties than in non-Article 5 parties, as is the case for pMDIs and DPIs.
2. This assessment of environmentally sound considers relative climate impact only. HFC-134a and HFC-227ea are controlled substances with high GWPs that are subject to the phase-down control measures for Annex F HFC of the Montreal Protocol. Currently available pMDIs have a large carbon footprint, though newer pMDIs with lower GWP propellants are in development, with the first commercially available products planned to be available from 2025, though full availability of lower GWP propellant alternatives to the current pMDIs across regions may take many years beyond. One of those candidate propellants is HFC-152a, which has a relatively low

GWP and is also a controlled substance, subject to the Article 2J phase-down control measures for Annex F HFCs. The most widely used pMDI globally is the salbutamol pMDI, which utilises HFC-134a, where salbutamol constitutes about 60% of all pMDI use, and contributes most to the environmental impact of pMDIs. Further detail is provided in the discussion below about broader environmental impacts, which are less studied than relative climate impacts.

3. Multi-dose DPIs can be less affordable than single-dose DPIs and pMDIs; single-dose DPIs can be more affordable than pMDIs. In Article 5 parties, locally made pMDIs are more affordable than some imported brands. In all parties, the cost of any treatment can be unaffordable for a portion of patients.
4. Older reservoir DPIs and some HFC pMDIs can be affected by high humidity. Newer multi-dose DPIs and a majority of pMDIs do not have sensitivity to high humidity.
5. While most patients can be taught to use any of these devices, some patients may struggle with any device and ideally a range of options should be available so as to assure individual patient needs can be met.
6. SMIs are usually more expensive than pMDIs for short-acting reliever medication, but they can be equally cost-effective as DPIs or pMDIs for some drugs, particularly long-acting bronchodilators. SMIs are generally likely to be unaffordable in Article 5 parties for most patients. The range of commercially available medications in SMIs is limited to short or long-acting bronchodilators, either as single drugs or combinations; these are primarily treatments for COPD. SMIs are increasingly available as refillable devices, making them even more environmentally sound and potentially more affordable.

10.4.1 Commercial availability

There are a wide variety of pMDIs, DPIs (both multidose and the technically simpler single dose), and soft-mist inhalers available globally, albeit with great regional variation in specific availability, accessibility, and in use patterns. In aggregate, these medications provide a broad array of pharmacologic mechanisms and choice for patients with asthma or COPD. While this is true in general, local regulatory requirements, economic considerations as well as practice of medicine/patient preference can lead to considerable regional differences on specific availability, accessibility, and choice of inhaler type.

Pressurised MDIs remain a mainstay of treating respiratory disease in much of the world, a situation further solidified by the COVID-19 pandemic.[398] While the transition from CFCs to HFCs in pMDIs has been successfully completed, there are currently no pMDIs marketed utilizing low GWP gasses, though active research and development is ongoing, as detailed in prior sections.

Dry powder inhalers – both mDPIs and single-dose DPIs are widely available containing a full array of therapeutic classes of treatment, but variably available and used in individual countries/regions. In many countries in Europe, all therapeutic classes are available at little or no extra cost, and a shift from pMDIs to DPIs could be encouraged. In many Article 5 parties, single-dose DPIs providing short-acting relievers can be economically preferable as mDPIs (and pMDIs) require purchasing a relatively large number of doses at once, typically a month's supply or more.

Soft mist inhaler technology, providing an aqueous aerosol without the use of pressurised propellant, is commercially available from one company, although availability is limited in many regions.

10.4.2 Technically proven

HFC pMDI and DPI inhalers are recommended options in national and international guidelines for the treatment of asthma and COPD. Well-established mDPI and pMDI alternatives are available for all key classes of drugs. For SMIs, only bronchodilators (short- and long- acting) are available; these are primary treatments in COPD but play a more limited role in the management of asthma alongside inhaled corticosteroids.

In recent years, once-daily long-acting DPI, and triple combination DPI and pMDI inhalers have become available. These inhalers have the potential to reduce the number of devices needed, simplify therapy and improve outcomes. They are supported by real-world studies and included in national and international guidelines.

Studies on new lower GWP propellants are well underway, but pMDIs utilising these propellants are not yet available for use. The first products are anticipated to come to market in 2025, with some pharmaceutical companies aiming for 2030 to complete the transition of their individual product lines to novel propellants.

10.4.3 Environmentally sound

Since the previous quadrennial report, far more detailed information has been made available about the carbon footprint of inhalers. These published, peer-reviewed studies are discussed here, but readers should note there is potential for publication bias as companies may be more likely to publish life cycle analyses on those inhalers with smaller carbon footprint. Unless otherwise stated these refer

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[398] Bloom, C.I., Wong, E., Hickman, K., *et al.,* Influence of the first wave of COVID-19 on asthma inhaler prescriptions, *NPJ primary care respiratory medicine*, **31**(1), 45. https://doi.org/10.1038/s41533-021-00260-w.

to the currently available HFC-134a and HFC-227ea containing pMDIs and not newer lower GWP propellant pMDIs.

All currently available HFC pMDIs have a far greater carbon footprint than DPIs or SMIs. While manufacturing efforts have mitigated release during production, life cycle assessments consistently demonstrate that the large majority (88–98%) of the carbon footprint of pMDIs is due to propellant release during use or end of life. There are therefore large differences in the carbon footprint depending on the amount and type of propellant used, varying from 50 gCO_2e up to 300 gCO_2e per actuation or 9,900 to 36,500 gCO_2e per device.

DPIs and SMIs are propellant-free inhalers and consequently have far smaller carbon footprints. The largest contributions to their carbon footprints are made by the API and the manufacturing stage. Published life cycle assessments show their carbon footprint to range from 6 to 27g per dose or 359 to 917 gCO_2e per device.

The smallest carbon footprints are seen in reusable SMIs or single-dose DPIs. Re-usable single-dose devices are the most popular devices in some regions due to their affordability. A once-daily single dose DPI could represent a suitable alternative to pMDI for many patients, but with a 200-fold smaller carbon footprint than an HFC-227ea pMDI and 100-fold smaller than an HFC-134a pMDI per day of maintenance treatment. Multi-dose DPIs, which are the most popular type of device amongst patients in some studies, have a carbon footprint of 588–917 gCO_2e per device, though they are not available for use in all countries. [399,400]

Limited information is available on potential new pMDIs in development using lower GWP propellants, though it is clear they will have far smaller carbon footprints. One life-cycle assessment has been performed using HFC-152a as a propellant. The volume of the propellant required in the final product was estimated. The carbon footprint per actuation was estimated to be 9–14 gCO_2e per actuation for a range of steroid or combination pMDIs.[401]

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[399] Schreiber, J., Sonnenburg, T., Luecke, E., Inhaler devices in asthma and COPD patients – a prospective cross-sectional study on inhaler preferences and error rates, *BMC Pulmonary Medicine*, 2020, **20**, 222 https://bmcpulmmed.biomedcentral.com/articles/10.1186/s12890-020-01246-z.

[400] Fulford, B., Mezzi, K., Aumônier, S., *et al.,* Carbon Footprints and Life Cycle Assessments of Inhalers: A Review of Published Evidence, *Sustainability,* 2022, **14**, 7106. https://doi.org/10.3390/su14127106.

[401] Panigone, S., Sandri, F., Ferri, R., *et al.,* Environmental impact of inhalers for respiratory diseases: decreasing the carbon footprint while preserving patient-tailored treatment, *BMJ Open Respir Res,* 2020, **7**(1), e000571. https://doi.org/10.1136/bmjresp-2020-000571.

Figure 10.7 Relative carbon footprints of available controller inhalers (including current HFC pMDIs)

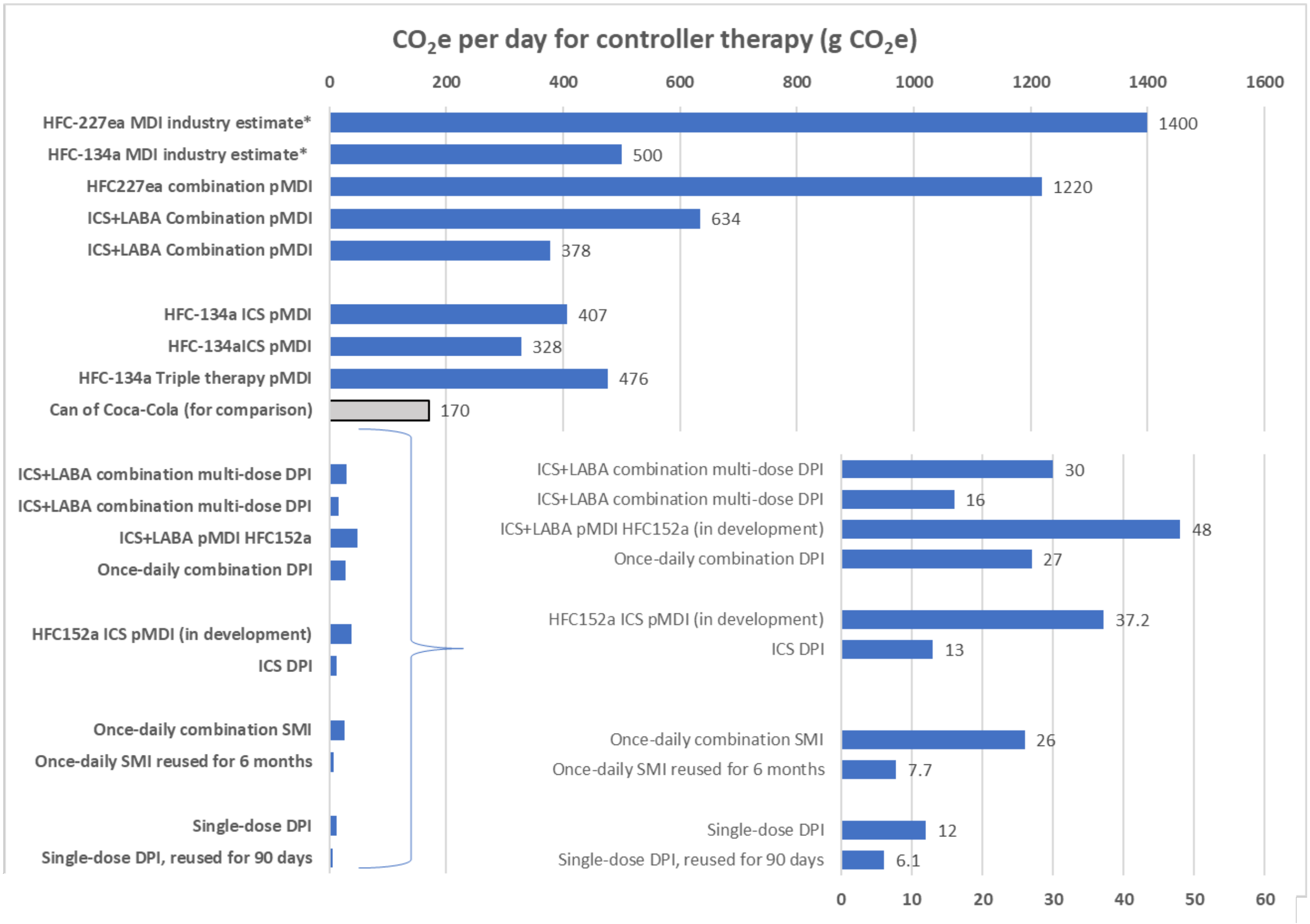

*Figure 10.7: Carbon footprint of maintenance inhalers are based on published life cycle assessments. For all inhalers containing corticosteroids, it is assumed that 2 inhalations twice-daily are used, apart from once-daily devices. Where 2 results are given for the same inhaler, different brands are represented. ICS is inhaled corticosteroid. LABA is long-acting beta-agonist. *Industry estimates given as the midpoint of estimates from 2018 MCTOC Assessment Report. Otherwise, data is taken from Fulford* et al. *(2022).*[402]

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[402] Fulford, B., Mezzi, K., Aumônier, S., *et al.,* Carbon Footprints and Life Cycle Assessments of Inhalers: A Review of Published Evidence, *Sustainability,* 2022,**14**, 7106. https://doi.org/10.3390/su14127106.

Figure 10.8 Relative carbon footprints of available reliever inhalers (including current HFC pMDIs)

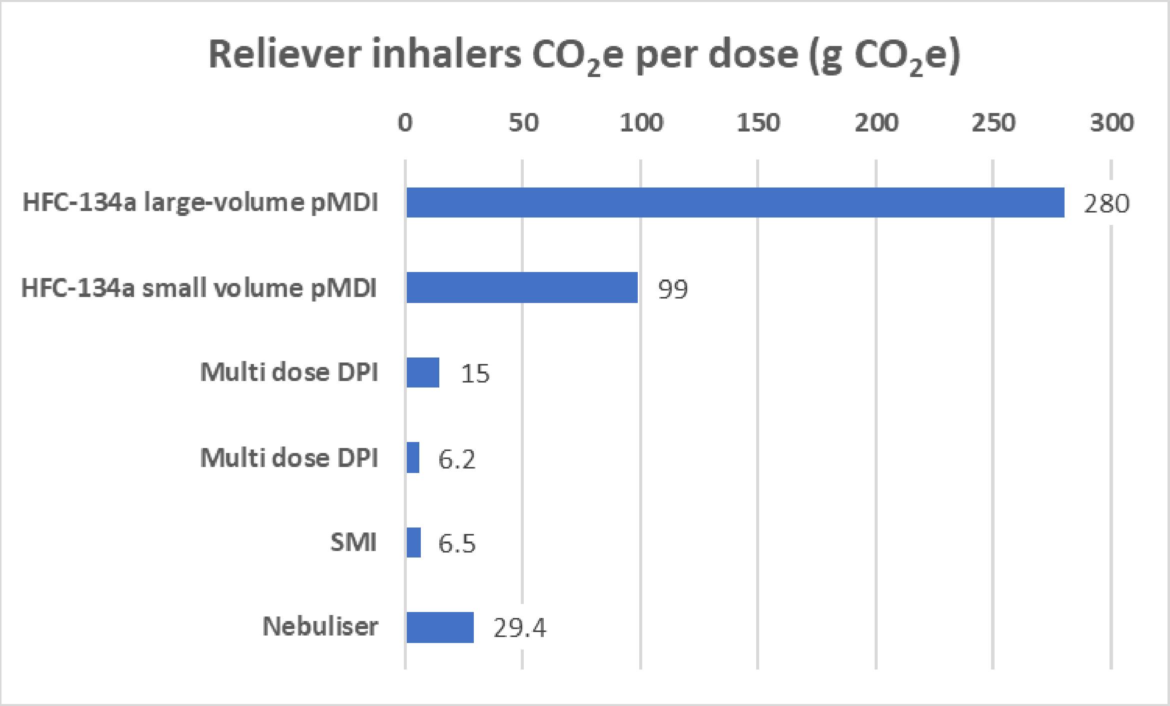

Figure 10.8: Carbon footprint of reliever inhalers are based on published life cycle assessments. The dose of salbutamol (albuterol) is 200mcg for inhalers and 3g for nebuliser. Where 2 results are given for the same inhaler, these represent different brands. Data is taken from Fulford et al. *(2022)*[403] *and Goulet* et al. *(2017)*[404].

The greatest uncertainty about the carbon footprint of pMDIs relates to uncertainty about the carbon footprint of the HFC propellants. In the 2021 IPCC 6th Assessment Report (AR6), the 100-year GWP of HFC-134a was reported as 1,530, up from 1,300 in the previous assessment, with a total uncertainty of 38%. Similarly, the GWP of HFC-227ea increased from 3,350 to 3,600 and HFC-152a from 138 to 164. Using these AR6 GWPs would significantly increase the estimated carbon footprint of pMDIs because most previous analyses use GWPs from the 4th or 5th IPCC Assessment Reports, which leads to differing results. For instance, applying these updated GWPs to a large-volume salbutamol pMDI (the most used pMDI globally) would increase its estimated carbon footprint from 28,000 to 31,500 (20,000–43,500) gCO_2e per device.

10.4.3.1 Impacts other than carbon footprint

To avoid shifting the burden of impact from one category of environmental impacts to another, life cycle impact assessments (LCIA) explore additional impact categories to provide a more comprehensive understanding of environmental impacts. Understanding the relative significance of impacts other than carbon footprint is an evolving area of research, and data on inhalers are limited to two studies; the first examined the relative impacts of one older mDPI versus pMDIs using a range of

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[403] Fulford, B., Mezzi, K., Aumônier, S., *et al.,* Carbon Footprints and Life Cycle Assessments of Inhalers: A Review of Published Evidence, *Sustainability,* 2022, **14**, 7106. https://doi.org/10.3390/su14127106.

[404] Goulet, B., Olson, L., Mayer, B.K., A comparative life cycle assessment between a metered dose inhaler and electric nebulizer, *Sustainability,* 2017, **9**, 1725. https://doi.org/10.3390/su9101725.

propellants – HFC-134a, HFC-227ea and HFC-152a.[405] This study found the mDPI to have greater environmental impacts across most categories but did not consider the relative importance of these impacts or whether the impacts may be specific to the particular mDPI in the study.

Fulford *et al.* found quite different impacts in their LCIA of a single-dose DPI, indicating that these impacts are not generalisable to all DPIs, although they also used different assumptions and databases.[406] "Person equivalents" were used to assess the relative importance of different impact categories. The carbon footprint was found to be the most significant differential impact compared to pMDIs, and the only impact in which the difference between devices exceeded an order of magnitude. At present, there are no public comparable data regarding impacts other than carbon footprint of HFO-1234ze(e). However, for consideration of environmental impacts other than their carbon footprints, HFC-152a pMDIs are estimated to have similar environmental impacts to the best mDPIs.

The life-cycle impact assessments described above by Jeswani and Azapagic and Fulford *et al*. both used the ReCiPe 2016 harmonised LCIA method. This methodology also allows estimation of the relative importance of different environmental impacts by using characterisation factors to convert from emissions into disability adjusted life years (DALYs) and time-integrated species loss (TISL).[407] These are shown in Figures 10.9 and 10.10 below.

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[405] Jeswani, H.K., Azapagic, A., Life cycle environmental impacts of inhalers, *J Clean Prod,* 2019, **237**, 117733. https://doi.org/10.1016/j.jclepro.2019.117733.

[406] Fulford, B., Mezzi, K., Whiting, A., Aumônier S., Life-Cycle Assessment of the Breezhaler® Breath-Actuated Dry Powder Inhaler, *Sustainability*, 2021, **13**(12), 6657. https://doi.org/10.3390/su13126657.

[407] Huijbregts, M.A.J., Steinmann, Z.J.N., Elshout, P.M.F., *et al.,* ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level, *Int J Life Cycle Assess,* 2017, **22**, 138–147. https://doi.org/10.1007/s11367-016-1246-y.

Figure 10.9 **Effects on human health of different environmental impacts from inhaler life cycle impact assessments (disability adjusted life years per dose)**

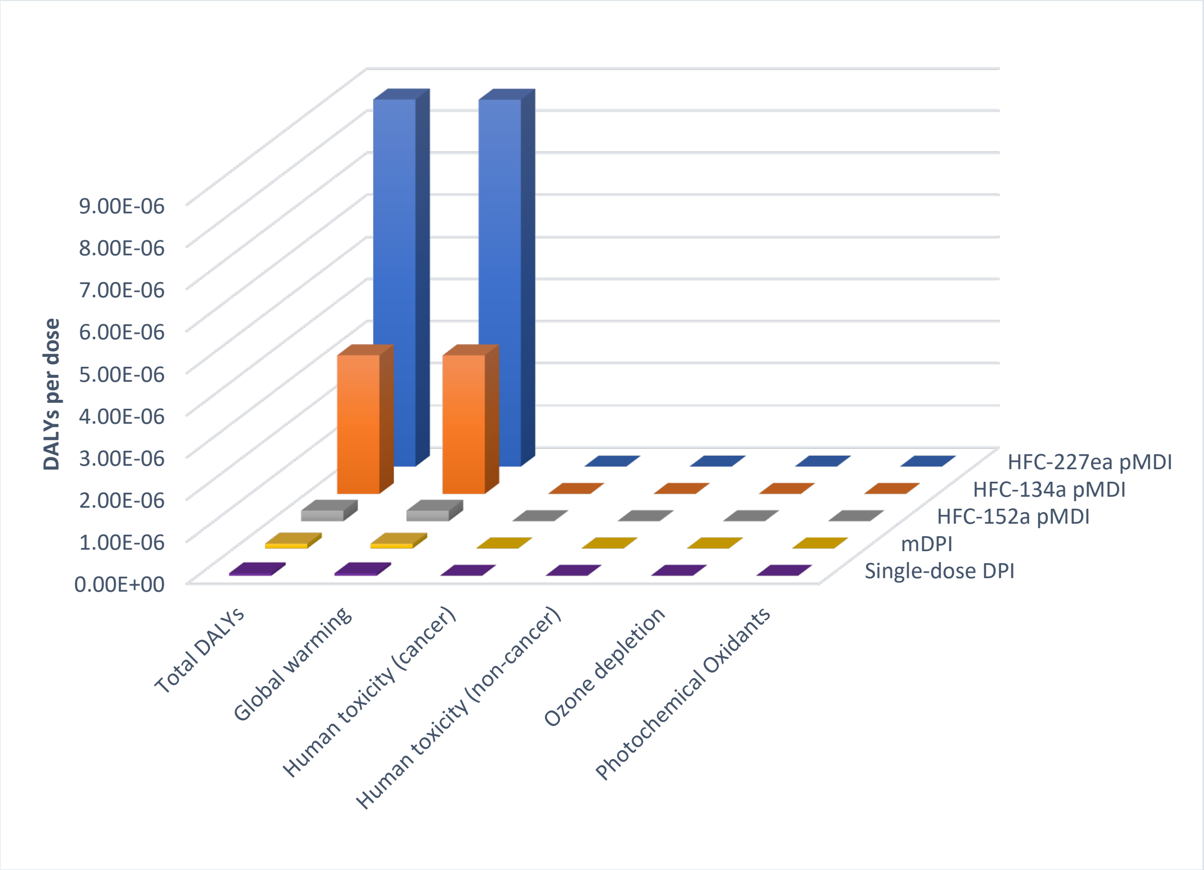

Figure 10.9: Graph showing the relative effects on human health of the different environmental impacts in life cycle impact assessments, expressed as disability adjusted life years per dose. Calculations are based on egalitarian end-point characterisation factors (with unlimited time horizon) from ReCiPe 2016 LCIA method. Note that different assumptions were made for the different inhalers' LCIAs so results may not be directly comparable. Data assumes the single-dose DPI is re-used for 90 days.[408,409]

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[408] Jeswani, H.K., Azapagic, A., Life cycle environmental impacts of inhalers, *J Clean Prod*, 2019, **237**, 117733. https://doi.org/10.1016/j.jclepro.2019.117733.

[409] Fulford, B., Mezzi, K., Whiting, A, Aumônier, S., Life-Cycle Assessment of the Breezhaler® Breath-Actuated Dry Powder Inhaler, *Sustainability*, 2021, **13**(12), 6657. https://doi.org/10.3390/su13126657.

Figure 10.10 Effects on species loss of different environmental impacts from inhaler life cycle impact assessments (time-integrated species loss per dose)

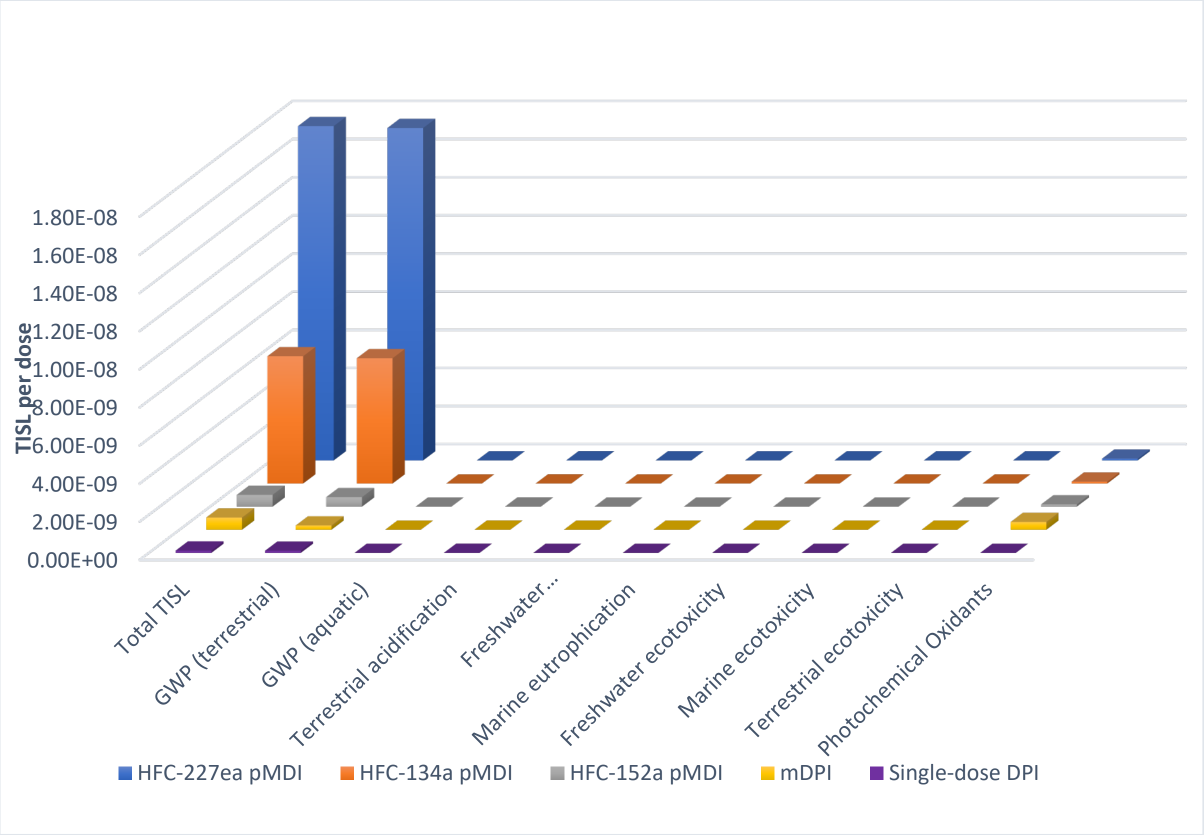

Figure 10.10: Graph showing the relative effects on species loss of the different environmental impacts in life cycle impact assessments expressed as time-integrated species loss per dose. Calculations are based on egalitarian end-point characterisation factors (with unlimited time horizon) from ReCiPe 2016 LCIA method. Note that different assumptions were made for the different inhalers' LCIAs so results may not be directly comparable. Data assumes the single-dose DPI is re-used for 90 days. [410,411]

The science of life cycle impact assessment is rapidly evolving, and small differences between relative impacts should be interpreted with extreme caution. However, these data indicate that by far the most significant life cycle impacts derive from the global warming effects of currently available pMDIs.

10.4.3.2 Recycling and better disposal

Attempts have been made to minimise propellant release at the end-of-life of pMDIs. A national inhaler recycling scheme ran for 9 years in the United Kingdom which recovered and recycled more than 2 million inhalers, although this represents less than 1% of all inhalers used in that period.[412]

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[410] Jeswani, H.K., Azapagic, A., Life cycle environmental impacts of inhalers, *J Clean Prod*, 2019, **237**, 117733. https://doi.org/10.1016/j.jclepro.2019.117733.

[411] Fulford, B., Mezzi, K., Whiting, A., Aumônier, S., Life-Cycle Assessment of the Breezhaler® Breath-Actuated Dry Powder Inhaler, *Sustainability*, 2021, **13**(12), 6657. https://doi.org/10.3390/su13126657.

[412] Clews, G., Inhaler recycling scheme that cut carbon emissions equivalent to more than 8,500 cars is scrapped, *The Pharmaceutical Journal*, PJ July 2020, Vol 305, No 7939, 305(7939). doi:10.1211/pj.2020.20208144.

Smaller recycling schemes are running, though achieving significant returns of inhalers is challenging. Surprisingly large amounts of propellant were found in returned pMDIs, with 48% of doses remaining in discarded pMDIs and 27% of doses in discarded DPIs. Whilst this likely reflects the large number of pMDIs in the United Kingdom, mainly salbutamol-based therapies, that lack dose counters, it also highlights the large potential to reduce emissions through proper disposal of pMDIs. Incineration of used pMDIs has been proposed as a method to reduce emissions of HFCs, and incineration in hazardous medicines waste can degrade HFC-134a into less potent greenhouse gases. The impact of incineration in municipal waste is less certain as the canisters may be punctured before incineration and temperatures involved are typically lower.[413]

10.4.4 Economically viable and cost-effective

Access to affordable inhaled medicines for chronic respiratory diseases is severely limited in low- and middle- income countries, which causes avoidable morbidity and mortality.[414] Generally:

- mDPIs are often less affordable than single-dose DPIs and pMDIs.
- Single-dose DPIs can be more affordable[415] than pMDIs.
- In Article 5 parties, locally made pMDIs are more affordable than some imported brands.
- SMIs are usually more expensive than pMDIs for short-acting reliever medication, but they can be as equally cost-effective as DPIs or pMDIs for some drugs, particularly long-acting bronchodilators. SMIs are generally likely to be unaffordable in Article 5 parties for most patients.
- In all parties, the cost of some or any treatments can be unaffordable for a portion of patients.

In 2022, there are no alternative pMDIs containing low-GWP gasses for the current high GWP HFC-containing products. It is projected that the first of these alternative pMDI products will be in 2025, a full array of inhaled products widely available globally will more likely be accomplished by 2030 or beyond. The speed of introduction will depend on regulatory approvals for inhalers with the new lower GWP propellants and may benefit from a rationalised and coordinated approach. It would be expected that these products will be price competitive with current HFC pMDIs, but costs of development and meeting local regulatory considerations may impact eventual pricing.

Parties may wish to consider measures that facilitate efficient, timely development while assuring the safety and effectiveness of the new pMDIs.

Further, unlike a phase-out, the imperative for uptake of the newer alternative pMDI products may be a barrier to large-scale, rapid transition in the marketplace.

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[413] Mi, T., Han, J., He, X., *et al.,* Investigation of HFC-134a decomposition by combustion and its kinetic characteristics in a laboratory scale reactor, *Environment Protection Engineering,* 2015, **41**(4), 143–150.

[414] Stolbrink, M., Chinouya, M.J., Jayasooriya, S., Nightingale, R., Evans-Hill, L., Allan, K., Allen, H., Balen, J., Beacon, T., Bissell, K., Chakaya, J., Chiang, C-Y., Cohen, M., Devereux, G., El Sony, A., Halpin, D.M.G., Hurst, J.R., Kiprop, C., Lawson, A., Mace, C., Makhanu, A., Makokha, P., Masekela, R., Meme, H., Khoo, E.M., Nantanda, R., Pasternak, S., Perrin, C., Reddel, H., Rylance, S., Schweikert, P., Were, C., Williams, S., Winders, T., Yorgancioglu, A., Marks, G.B., Mortimer, K., Improving access to affordable quality-assured inhaled medicines in low- and middle-income countries, *Int. J. Tuberc. Lung Dis*., 2022, **26**(11), 1023–1032. http://dx.doi.10.5588/ijtld.22.0270.

[415] This is due to the small amount of medication being purchased at any one time, making the single-dose DPI more affordable for the patient; multi-dose DPIs and pMDIs are cheaper overall on a cost per dose basis, where available.

While there are non-pMDI alternatives to HFC-based pMDIs broadly available now (mDPIs, SMIs), consideration of these products replacing a significant proportion of pMDIs is complex, as there are complicated economic considerations, including limitations on the capacity of manufacturing facilities, as well as differences in patient-preference or even effectiveness. [416,417] Furthermore, in many Article 5 parties, even if available, differences in costs may be prohibitive for the use of mDPIs and SMIs compared with generic pMDIs or single-dose dry powder inhalers.

10.4.5 Safety in use

While some of the gasses considered as potential low or lower GWP alternatives to HFC-134a and -227ea have some level of flammability requiring special considerations in manufacturing, it is not anticipated that these considerations would be impactful to pMDIs considering their means of use (i.e., generally not done proximate to ignition sources). However, as with the transition to HFC gasses, toxicology and tolerability testing will be important not only for any novel propellant, but also for any new formulations (surfactants, co-solvents) and leachable/extractable components of the valves and canisters. This testing is anticipated to be conducted and completed successfully in accordance with the usual toxicologic testing for novel inhaled products, and initial safety evaluations of the alternative propellants are encouraging. Clinical testing will explore any potential issues of safety, including impact on airway function in patients (both efficacy as well as any untoward airway tolerability issues).

10.4.6 Ease of use

Incorrect inhaler technique is extremely common in clinical practice and is linked to worsened health outcomes. Moreover, adherence to inhaled maintenance therapy is poor so finding an inhaler that patients can and will use is important for effective treatment.

Different patients find different inhaler devices easier to use, depending on their abilities and preferences, and a range of options can help match the best device to the patient. With DPIs, drug delivery is breath-actuated and does not require the patient to actuate the inhaler in timing with inhalation. Inability to coordinate actuation and inhalation is one of the most common errors with pMDI use and is associated with worsening disease outcomes. It should be noted that breath-actuated pMDIs are available for select drugs that address this issue of coordinated inhalation. While pMDIs and SMIs can be effectively used with very little inspiratory effort, insufficient inspiratory flow through DPIs can result in diminished drug delivery. Most patients with asthma and COPD have sufficient inspiratory force to use DPIs, but patients at the extremes of age may struggle. Given all these considerations, a range of devices is needed to address the needs of all patients.[418,419]

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[416] Kemp, L., Haughney, J., Barnes, N., Sims, E., von Ziegenweidt, J., Hillyer, E.V., Lee, A.J., Chisholm, A., Price, D., Cost-effectiveness analysis of corticosteroid inhaler devices in primary care asthma management: A real world observational study, *ClinicoEcon. Outcomes Res.,* 2010, **2**, 75–85. https://doi.org/10.2147/ceor.s10835.

[417] Wilkinson, A., Braggins, R., Steinbach, I., *et al.*, Costs of switching to low global warming potential inhalers. An economic and carbon footprint analysis of NHS prescription data in England, *BMJ Open*, 2019, **9**, e028763. http://doi.org/10.1136/bmjopen-2018-028763.

[418] Haughney, J., Lee, A.J., McKnight, E., *et al.*, Peak inspiratory flow measured at different inhaler resistances in patients with asthma, *Journal of Allergy and Clinical Immunology: In Practice,* 2021, **9**, 890–896. https://doi.org/10.1016/j.jaip.2020.09.026.

[419] Clark, A.R., Weers, J.G., Dhand, R., The confusing world of dry powder inhalers: It is all about inspiratory pressures, not inspiratory flow rates, *J Aerosol Med Pulm Drug Deliv*, 2020, **33**, 1–11. https://doi.org/10.1089/jamp.2019.1556.

GINA guidelines recommend SABA via pMDI with spacer as the most cost-effective option. Systematic reviews have found that DPIs can be equally effective in exacerbations.[420,421] The evidence for SABA via pMDI with spacer is less clear for life-threatening asthma or hospitalised COPD patients, where nebulised treatment is recommended.[422,423]

Many additional factors influence the overall ease of use and acceptability of an inhaler. Most pMDIs require shaking before use, and many pMDIs have labelling instructing a patient to wait 30–60 seconds between actuations when a second actuation is required, though this may be based on clinical considerations more than technical necessity. It is recommended for many pMDIs that the actuator be washed through regularly with warm water and dried thoroughly to keep them clean. Many pMDIs have no dose counter making it harder to know when to replace them. This can result in patients unknowingly using empty or near-empty inhalers with ineffective drug dosing or discarding part-used inhalers.[424,425]

A range of aids are available to assess technique and aid with inhaler technique training. Some of these include whistles when inspiratory flow is correct and are available for DPI placebo and as add-ons to pMDIs. Most pMDI placebos use HFC propellant and so have a large carbon footprint without direct therapeutic benefit, although an HFC-free device has also been developed.[426]

To effectively use single-dose DPIs requires sufficient manual dexterity to load the capsule, and numerous steps are required to effectively prepare the inhaler, as well as a clear understanding the capsules are not meant to be ingested. Multi-dose DPIs generally have the fewest steps involved in preparing the medication, take the least time to use, and in one study were found to be the most popular class of device when a wide range of options are offered.[427,428]

10.4.6.1 Changing treatment paradigms

GINA guidelines on the treatment of asthma underwent a significant change in 2019 when treatment with short-acting bronchodilators alone was no longer recommended.[429] Instead, combination therapy

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[420] Selroos, O., Borgström, L., Ingelf, J., Use of dry powder inhalers in acute exacerbations of asthma and COPD, *Ther Adv Respir Dis*, 2009, **3**, 81–91. http://doi.org/10.1177/1753465809103737.

[421] Rodrigo, G.J., Neffen, H., Colodenco, F.D., *et al.*, Formoterol for acute asthma in the emergency department: a systematic review with meta-analysis, *Annals of Allergy, Asthma and Immunology*, 2010, **104**, 247–252. http://doi.org/10.1016/j.anai.2009.11.064.

[422] GINA, 2022, *2022 GINA Report, Global Strategy for Asthma Management and Prevention*, 2022. https://ginasthma.org/gina-reports/. Accessed July 2022.

[423] GOLD, 2002, *2022 Global Strategy for Prevention, Diagnosis and Management of COPD*, 2022. https://goldcopd.org/2022-gold-reports/. Accessed December 2022.

[424] Conner, J.B., Buck, P.O., Improving asthma management: the case for mandatory inclusion of dose counters on all rescue bronchodilators, *The Journal of Asthma*, 2013, **50**(6), 658–663. https://doi.org/10.3109/02770903.2013.789056.

[425] Price, D.B., Román-Rodríguez, M., McQueen, R.B., *et al.*, Inhaler Errors in the CRITIKAL Study: Type, Frequency, and Association with Asthma Outcomes, *Journal of Allergy and Clinical Immunology: In Practice,* 2017, **5**(4), 1071–1081.e9. https://doi.org/10.1016/j.jaip.2017.01.004.

[426] Clement Clarke International, *Trainhaler pMDI training system*. https://www.haag-streit.com/clement-clarke/products/inhaler-technique/trainhaler/. Accessed September 2022.

[427] Schreiber, J., Sonnenburg, T., Luecke, E., Inhaler devices in asthma and COPD patients – a prospective cross-sectional study on inhaler preferences and error rates, *BMC Pulmonary Medicine*, 2020, **20**, 222. https://bmcpulmmed.biomedcentral.com/articles/10.1186/s12890-020-01246-z.

[428] Sanchis, J., Gich, I., Pedersen, S., Systematic review of errors in inhaler use: Has patient technique improved over time? *Chest*, 2016, **150**(2), 394–406. https://doi.org/10.1016/j.chest.2016.03.041.

[429] GINA, 2022, *2022 GINA Report, Global Strategy for Asthma Management and Prevention*, 2022. https://ginasthma.org/gina-reports/. Accessed July 2022.

containing the fast-acting bronchodilator formoterol and inhaled steroids became the first-line approach. This treatment strategy ensures patients' airway inflammation is addressed at the same time as promptly controlling their symptoms. It can simplify treatment plans for patients, reduce the risk of severe exacerbations, and reduce reliance on systemic steroids. It can also reduce the number of inhalers used and reduce over-reliance on short-acting salbutamol pMDIs, which are the most used inhalers worldwide. Many combination inhalers for such use are mDPIs so the potential benefits of this strategy include simplified treatment, improved disease control and reduced carbon footprint. However, these combination inhalers can cost more than 10 times that of reliever pMDIs, such as salbutamol pMDIs, and so affordability is an important consideration for some patients and payors.[430]

An alternative strategy is to use inhalers that combine relievers and corticosteroids in a single device. In a large real world study asthma control was improved, and total carbon footprint more than halved, with a single daily dose of a combined ICS/LABA in an mDPI compared to usual care.[431] However, 12% of patients switched back to a pMDI during this study, supporting the continued need for a range of treatment options. In COPD there is increasing emphasis on personalised care, with greater reliance on bronchodilators, with inhaled steroids being reserved for those patients with evidence of eosinophilic airways inflammation.[432] The emergence of once-daily long-acting mDPIs and SMIs and triple-therapy combination DPIs and pMDIs can potentially simplify treatment and reduce the number of devices needed. A once-daily triple therapy combination DPI has also been shown to improve the health status and lung function of COPD patients compared to using multiple inhalers, again suggesting simplified treatment can be achieved by combination inhalers alongside improved disease control and reduced environmental impact.[433]

10.4.7 Other pMDIs that are medical aerosols

In some markets, there are available HFC-based pMDIs intended for nasal administration of corticosteroids. It must be noted that there are widely available metered, aqueous pump sprays with a large variety of active moieties, all that can be considered acceptable and affordable alternatives to these pMDIs, there seems to be very little rational for HFC-based nasal pMDIs from the standpoint of public health.

10.5 Inhaled therapy in different countries

The over 120 Article 5 parties cover a wide range of health systems, economies, population sizes and medicine availability and affordability. The prevalence of asthma and other respiratory diseases which are treated by inhalers also varies from country to country. The effects of climate change, however, reflected by increased numbers of forest fires, droughts, floods, and heatwaves may trigger or worsen symptoms of asthma and COPD in people with these conditions. Increasing pollution from burning

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[430] Pritchard, J. N., The climate is changing for metered-dose inhalers and action is needed, *Drug Design, Development and Therapy*, 2020, **14**, 3043. https://doi.org/10.2147/DDDT.S262141.

[431] Woodcock, A., Vestbo, J., Bakerly, N. D., New, J., Gibson, J. M., McCorkindale, S., Jones, R., Collier, S., Lay-Flurrie, J., Frith, L., Jacques, L., Fletcher, J. L., Harvey, C., Svedsater, H., Leather, D., and Salford Lung Study Investigators, Effectiveness of fluticasone furoate plus vilanterol on asthma control in clinical practice: an open-label, parallel group, randomised controlled trial, *Lancet*, 2017, **390**(10109), 2247–2255. https://doi.org/10.1016/S0140-6736(17)32397-8.

Woodcock, A., Janson, C., Rees, J., *et al.*, Effects of switching from a metered dose inhaler to a dry powder inhaler on climate emissions and asthma control: post-hoc analysis, *Thorax*, 2022, **77**(12), 1187–1192. https://doi.org/10.1136/thoraxjnl-2021-218088.

[432] GOLD, 2002, *2022 Global Strategy for Prevention, Diagnosis and Management of COPD*, 2022. https://goldcopd.org/2022-gold-reports/. Accessed December 2022.

[433] Halpin, D.M.G., Worsley, S., Ismaila, A.S., *et al.*, INTREPID: single- versus multiple-inhaler triple therapy for COPD in usual clinical practice, *ERJ Open Research*, **7**(2), 00950–2020. http://doi.org/10.1183/23120541.00950-2020

fossil fuels in motor vehicles and coal fired power stations are also known to trigger or worsen symptoms.

In most countries, pMDI and DPI use had been increasing but the effect of the COVID-19 pandemic is likely to have affected supply chains, which may not yet have fully recovered. In countries affected by war, of which there are a number, inhalers and other medications are unlikely to be easily available for combatants, the remaining population, and refugees. There appears to be a global economic downturn following the pandemic and other global instabilities. Prices for common commodities are rising steeply in many countries, which may also impact medicines although recently these prices have been falling for other macro-economic reasons. For these many reasons, in the foreseeable future inhaler use may not continue to increase at previous rates despite the work of dedicated health professionals and the spread of knowledge about asthma best practice.

A recent development is the European Union’s review of its rules on F-gases and potential impacts on the global supply of pMDIs. The European Union-based pMDI industry exports 75% of manufactured pMDIs to the rest of the world, particularly to many Article 5 parties. The European Union’s review proposes to reduce greenhouse gases to 10%% of baseline in 2027 and 5% by 2030 and achieve European Union greenhouse gas neutrality by 2050. As it is not yet clear when a reasonable array of lower GWP propellant pMDIs will be on the market globally, likely not by 2030, there is potential for disrupted patient access to pMDIs in Europe and beyond.

Global warming consequences, such as floods and forest fires, cause significant disruption. People may become homeless and lose access to healthcare and their medications including inhalers. Formerly flooded homes and temporary accommodation may be damp with a high mould content. Indoor mould is a common trigger of asthma. Forest fire smoke and debris can trigger asthma symptoms affecting volunteer firefighters, emergency personnel, the community, and media representatives. People in surrounding areas may also be affected as winds carry smoke and ash particles for long distances.

Prescribing patterns for respiratory diseases vary considerably in Article 5 parties. Affordability of medicines remains a problem for many and may become more of a challenge with recent economic pressures. Generally, salbutamol pMDIs remain the most used affordable inhalers. In several countries, inexpensive oral medications are still used. In others, single-dose DPIs are used because they are cheaper than mDPIs. In others, the full range of pMDIs and DPIs are available but not affordable by all patients, who may have greater access to oral therapy and salbutamol pMDIs if affordable.

As the transition to pMDI propellants with lower GWPs occurs, no patient should lose access to their pMDI and patients should have the option to use pMDI or DPI, depending on their individual needs, the advice of their healthcare practitioner, and price. A patient with uncontrolled asthma may have a significant excess carbon footprint due to increased use of healthcare facilities and reliever medication.

Informal consultation with patient groups indicates little patient awareness of the environmental and climate impacts of pMDIs or DPIs, despite general awareness of climate change issues.

The following information describes some experiences of inhaled therapy from a selection of countries.

Africa

Informal feedback was gathered for the following African countries, as exemplars: Ethiopia, Ghana, South Africa, Zimbabwe; and comments general to all African countries were also provided.

	Question:	Country Response				
		Zimbabwe	South Africa	Ethiopia	Ghana	Inferences/Comments
1.	Do the majority of asthma and COPD patients have access to inhalers? What proportion of asthma/COPD patients have access to inhalers?	The majority do not have access to inhalers especially in the public sector. 30% may have access in public sector and possibly 60% in private sector.	No, perhaps 40–50% have access to inhalers.	No, only 10–20% have access to inhalers.	No, maybe a third of patients are on inhalers.	Overall, most asthma and COPD patients in African countries do not have access to inhalers. Furthermore, there are inequities in distribution access driven by factors such as family wealth, asthma knowledge, prescribers' expertise, and patient preferences.
2.	What is the proportional cost of monthly treatment with inhalers in relation to wages? Are they affordable for all patients?	In public sector inhalers are not readily available and proportional cost would be about 20% of the average wages.	Available on essential drug list for free to those who cannot pay.	Very costly and most of the inhalers are not available at government facilities.	Generally, these medicines are not affordable in Ghana. Monthly costs could be 40–60% or more of minimum monthly wages depending on the source of purchase and health insurance coverage. With souring economic inflation in recent times costs will be increasingly prohibitive.	Monthly treatment costs with inhalers are significantly high, largely unaffordable, and unsustainable for the average family. (Many asthma patients eventually resort to using treatments intermittently rather than daily to prolong refill periods). This situation is likely to worsen soon given the effect of current global inflation.
3.	Which are most commonly used pMDIs, DPIs? (Proportions of use by patients?)	pMDIs (DPIs not used).	pMDIs: It is critical to know that for most patients DPIs are not available at primary care so switching of devices would not be	pMDI only.	pMDI – ICS/LABA DPIs – 2 ICS/LABA	pMDIs are most used in many African countries. Single-dose DPIs are largely unavailable in most African countries. The few, available ICS/LABA DPI treatments are relatively much more expensive than SABA in any form.

			feasible for most patients at present.			
4.	Which asthma COPD medications are most used by proportion?	SABA (others not readily available).	Unable to answer this.	Commonly used, SABA, ICS, montelukast, oral and injectable ICS. Rarely: ICS nebules, ICS/LABA	SABA	Note that patients do not always stick with the prescription for cost-cutting reasons.
5.	Is there much use of combination therapy?	20%	Yes, at secondary and tertiary level care.	Combination inhaler use is <5%.	They are available maybe 30% of patients with asthma are on combination therapy.	Less than 30% of patients are on combination therapies in several countries. SABA pMDIs are used much more commonly among patients than combination therapies. (The heavy dependence on inhaled SABA – rather than ICS – for asthma management in African countries leads to poor asthma control in most patients, and to asthma deaths in these countries).
6.	How environmentally aware/concerned are health professionals, patients, healthcare systems regarding effect of medications on the environment?	Very little if at all.	The concern is over access to affordable medication as well as the regulatory processes that would be required to have patients access newer devices that are more environmentally friendly. At this stage access is low and change to devices would significantly impact	Very low.	Quite low.	Awareness of the effect of medications on the environment is very low among health professionals, patients, healthcare systems. In the absence of varieties and alternatives for asthma drug treatments, environmental concerns about production and use of currently available asthma drugs do not seem a priority to all parties.

			the poorest in this context.			
7.	Would there be interest in/concern about the Global Warming Potential (GWP) of current pMDIs?	Not sure, most of them not sure that this is relevant.	Yes, but this must be done in a thoughtful way to ensure that the inequities in access to medicines are not widened as occurred with Covid 19 vaccines.	Not well known.		There should be concerns/interests about the Global Warming Potential (GWP) of current pMDIs. However, since survival from asthma is of utmost priority to patients and healthcare givers, GWP interest may increase only when effective affordable alternative treatments are available.
8.	The GWP is, of course, not just the propellant but the life cycle of the pMDI. Pharmaceutical companies are responsible for the production and distribution. Health professionals and patients for use. But who is responsible for end-of-life cycle disposal and destruction? This is another likely cost for waste disposal systems. Are you aware of any developments in this area i.e., environmentally sound inhaler disposal?	Not aware of any development in this area.	Only one company in South Africa recycles old pMDIs.	Not aware of any.	There should be concerns/interests about the Global Warming Potential (GWP) of current pMDIs possibly because of increasing concerns about effects of climate change including increasing prevalence of non-communicable diseases, and the contributing factors.	There are no asthma drug pharmaceutical companies in many African countries. Waste disposal is a major environmental concern in many African countries. However, there are no specific establishments for special/segregated (including medical) waste disposal in most African countries, except perhaps for South Africa. Perhaps disposal of asthma drug wastes in African countries should be promoted as a special part of existing waste disposal and quality assurance initiatives in African hospitals.

9.	Are health professionals and patients aware of the nature and health implications of propellants in pMDIs? Will the rollout of pMDIs with another propellant cause confusion?	We are not aware of the health implications of propellants in pMDIs. I do not think another propellant will cause any confusion if the medication is delivered where needed.	Yes, there would be confusion and regulatory gaps in access if slow regulatory and procurement processes break the supply chain.	Not aware of this.	Very few are possibly aware.	Awareness about the nature and health implications of propellants in pMDIs is low. Rollout of pMDIs with another propellant should not cause confusion once there has been enough education on the purpose. Other propellants can be introduced if there is enough education on their safety and environmental benefits. The introduction should certainly be gradual.

Argentina

Population: 47.3 million

Prevalence: Asthma 9% COPD 14.5%.

Medication Use: DPIs used are ICS, LABA, ICS/LABA, LAMA, LAMA/LABA. The most used DPI is ICS/LABA. pMDIs used are SABA, SAMA, SABA/SAMA, ICS, LABA, ICS/LABA. The most used inhalers are SABA pMDI and ICS/LABA DPI.

Current Trends: Currently, there is an increasing use of DPIs rather than pMDIs, although DPIs are more expensive. The pharmaceutical companies have some commercial policies to reduce the final price of the product through vouchers.

Consumer/Patient Issues: DPIs and pMDIs are affordable for patients with private or social security coverage. However, public health coverage has supply limitations. There are some initiatives to reduce the prices by creating patient loyalty programs through vouchers for the purchase of certain drugs. The vouchers increase the percentage discount on the final price of the product.

Environmental Issues: Patients are not aware of the environmental issues concerning inhalers and their safe destruction.

Austria

Population: 9 million

Prevalence: Asthma 5.5% and COPD 8%.

Medication Use: 30% use pMDIs and 70% use DPIs. pMDIs are SABA, LABA, ICS, ICS/LABA, LAMA. DPIs are multi-dose SABA, LABA, ICS, LAMA, SAMA. 10% use nebulized therapy and 3% use oral medications like montelukast and theophylline.

Current Trends: DPI use remains very high.

Consumer/Patient Issues: All inhalers are an affordable price. The most used are salbutamol pMDI (because of use in pre-schoolers and children up to 10 years) and tiotropium bromide DPI.

Environmental Issues: The previous transition to HFCs in pMDIs initiated a trend towards DPIs.

Australia

Population: 26 million

Prevalence: Asthma 11% and COPD 5% >45 years.

Medication Use: pMDIs are used by 95% of asthma patients and 100% of COPD patients because of over reliance on SABA pMDI. pMDI inhalers are SABA, SAMA, ICS, ICS/LABA, ICS/LAMA/LABA. DPI use is increasing in asthma. Most COPD patients also use a DPI. DPIs are mostly used in COPD as until recently, all LAMAs were only available in DPI. As stated, COPD patients also rely on SABA pMDI. DPIs are SABA, LABA, LAMA, ICS, ICS/LABA, ICS/LAMA/LABA, LAMA/LABA. Most of these are multi-dose but a few DPIs are single dose. A very low percentage of patients would use nebulisers regularly. Nebulised therapy is mostly used only in hospital for severe or acute disease. Montelukast or low dose ICS may be used in children and in some severe adult asthma. Theophylline is rarely used.

Current Trends: SABA pMDI is still overused despite many educational campaigns promoting best practice asthma management. SABA inhalers are available for purchase in pharmacies without a prescription and sales are not recorded although pharmacists follow strict protocols to supply these products. SABA inhalers are much cheaper than other inhalers. SABA pMDI use aside, DPI use in Australia is increasing.

Consumer/Patient Issues: Most prescription medicines, including inhalers, are subsidised by the Australian Government though not to the full price. However, if several family members have asthma, inhalers may be difficult to afford. People who have a government concession card pay much less for their inhalers and other medicines.

Environmental Issues: Patients are not generally aware of the GWP of inhalers, but no national awareness campaigns have yet been undertaken. The Return Unwanted Medicines (RUM) program has a bin in every pharmacy for unwanted medicines and inhalers, but no national awareness campaign has yet been undertaken for safe disposal and destruction of inhalers.

Bangladesh

Population: 165 million

Prevalence: Asthma 6.9% (~5 million) and COPD 4.24% (~6 million).[434,435]

Medication Use: DPIs used are SABA, LAMA, LABA, ICS/LABA, LABA/LAMA, ICS/LAMA/LABA. pMDIs used are SABA, ICS, ICS/LABA, ICS/SABA, SABA/SAMA, ICS/LABA/LAMA. The inhaler most used by asthma patients is a pMDI with spacer (26%) or without spacer (74%). 11% of asthma and COPD patients use single use DPIs: ICS/LABA.[436] The most used inhalers overall are pMDI SABA and pMDI ICS/LABA. Over 90% of asthma and COPD patients use oral medication. Currently, no data is available for nebulised therapy use but it is used in all emergency and acute medicine departments. Nebulized therapy is also used in some home-based treatment. Bangladesh has 8 local pharmaceutical companies manufacturing pMDIs and DPIs. No inhalers are imported.

Consumer/Patient Issues: Capsules for single-use DPIs are the cheapest treatment. Then, pMDIs which range from a low to relatively high price. mDPIs (60 doses) are the most expensive inhalers.

Current Trends: There is increasing DPI use. Some pharmaceutical companies offer a reduced price for inhalers in exchange for returned used canisters. Patients benefit economically and are disinclined to switch to another brand.

Environmental Issues: The last environmental inhaler awareness campaign was for the transition from CFC to HFC inhalers.

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[434] Hassan, M.R., Kabir, A.R., Mahmud, A.M., Rahman, F., Hossain, M.A., Bennoor, K.S., Amin, M.R., Rahman, M.M., Self-reported asthma symptoms in children and adults of Bangladesh: findings of the National Asthma Prevalence Study, *Int J Epidemiol*, 2002, **31**(2), 483–488. PMID: 11980822.

[435] Hasan, M.R., Rahman, M.M., Hossain, M.A., Mahmud, A.M., Ahmed, M.M., Bennor, K.S., *et al.*, *Burden of Obstructive Lung Disease in Bangladesh (BOLD-BD), Report of National COPD Study*, Bangladesh Lung Foundation, Dhaka, 2007.

[436] Md. Abdur Rafi, Mohammad Jahid Hasan, Sabrina Jahan Mily, *et al.*, Assessment of inhaler using technique among adult asthma patients in Bangladesh: a facility-based cross-sectional study, 02 September 2022, PREPRINT (Version 1) available at Research Square https://doi.org/10.21203/rs.3.rs-1994549/v1.

China

Population: 1.4 billion

Prevalence: >20 years Asthma 4.2% (>45.7 million), COPD 8.6% (>100 million).

Medication Use: 2% of asthma and COPD patients use pMDIs and 30% use DPIs. 68% of asthma and COPD patients use nebulizers. 9% of asthma and COPD patients use montelukast. pMDI are SABA, LABA, ICS, SAMA. DPI inhalers are LABA, ICS, LAMA. 20 pharmaceutical companies in China manufacture inhalers. Inhalers are also imported.

Current Trends: Decreasing pMDI use, increasing nebulised therapy use and overuse of corticosteroids.

Consumer/Patient Issues: Inhalers are an affordable price. Since 2021, China has had a centralized procurement policy, which has greatly reduced the cost of medicines. Also, the National Medical Products Administration has issued a series of guiding principles to speed up the review and approval of drugs urgently needed in clinical practice and encourage low-cost domestic drugs to be launched as soon as possible. The most used pMDI is SABA and the most used DPI is ICS/ LABA.

Environmental Issues: The latest survey results in 2018 indicated that 70% of the public were aware of the GWP of pMDIs and DPIs. Also, that that CFCs have caused the hole in the ozone layer.

Denmark

Population: 6.0 million

Prevalence: Asthma 8%, COPD 7%.

Medication Use: 25% of asthma and COPD patients use pMDIs and 75% use DPIs. Many patients with asthma and COPD are undiagnosed and untreated so pMDI and DPI use would be higher if they were. pMDIs are mostly SABA, ICS and ICS/LABA. DPIs are SABA, ICS/SABA, LABA/LAMA, ICS/LABA/LAMA. The DPIs are multi-dose. Less than 5% of patients use nebulised therapy and less than 5% use oral medications.

Current Trends: A stable pMDI/DPI ratio with combination therapy use increasing.

Consumer/Patient Issues: There is not much price difference between pMDIs and DPIs. The most used pMDIs are two ICS. The three most used DPIs are one for ICS LABA, another for SABA or LABA or ICS or ICS/LABA and the other for ICS/LABA or ICS/LABA/LAMA.

Environmental Issues: Patients have little awareness of the GWP of pMDIs and DPIs.

Greece

Population: 10.7 million

Prevalence(estimated): Asthma 8.6%, COPD 8.40–10.6%.[437]

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[437] https://myasthma.gr/chrisimes-plirofories/to-asthma-stin-ellada/.

Tzanakis, N., Anagnostopoulou, U., Filaditaki, V., Christaki, P., Siafakas, N., and COPD group of the Hellenic Thoracic Society, Prevalence of COPD in Greece, *Chest*, 2004, **125**(3), 892–900. https://doi.org/10.1378/chest.125.3.892.

Medication Use: No data available for the use of pMDI, DPI, nebulised therapy and oral medication. pMDIs used are SABA, ICS, and combination therapies. DPIs used are SABA, ICS and combination therapies and are available in multi-dose and single-dose DPIs. Greece has 5–10 pharmaceutical companies manufacturing inhalers. Inhalers are also imported.

Current trends: Increasing DPI use and overuse of SABA in asthma. SABA pMDIs are the most used inhaler and then DPI for ICS.

Consumer/Patient Issues: Inhalers are expensive especially DPIs. The cost of this medication may be 25% of the weekly pension on which many people depend.[438]

Environmental Issues: There is probably no awareness of the GWP of inhalers.

Iran

Population: 84 million

Prevalence: Asthma 11% children, 9% adults, COPD 4.9% adults >18 years.

Medication Use: pMDIs are used by 80% of asthma and COPD patients. pMDIs are SABA, LABA, ICS, SAMA. DPIs are used by 20% of asthma and COPD patients. DPIs are LAMA, LABA, ICS/LABA. The most used DPI is a LAMA. Nebulised therapy is used by 10% of asthma and COPD patients. Montelukast is used by 30% of asthma patients and theophylline used by 10%. Iran has four local pharmaceutical companies manufacturing inhalers.

Current Trends: More pMDIs are being used.

Consumer/Patient Issues: pMDIs and DPIs are affordable and accessible. Due to the current situation, there is a move to increase the price of both DPIs and pMDIs.

Environmental Issues: There is very little awareness of the GWP of inhalers.

Japan

Population: 125 million

Prevalence: Asthma 3.5%, COPD 8.6% adults >40 years.

Medication Use: A wide range of active ingredients and combination therapies are available in pMDIs, DPIs and SMIs. DPIs became available early on and have been approximately 70% of inhaler use since the CFC phase-out in 2005. Several pharmaceutical companies in Japan manufacture inhalers. Inhalers are also imported.

Current Trends: Deaths have decreased since the introduction of ICS in the 1970s and are now below 2000 yearly. But, with 5.3 million COPD patients over 40, there are 18,500 deaths yearly.

Kourlaba, G., Hillas, G., Vassilakopoulos, T., & Maniadakis, N., The disease burden of chronic obstructive pulmonary disease in Greece, *International journal of chronic obstructive pulmonary disease*, 2016, **11**, 2179–2189. https://doi.org/10.2147/COPD.S110373.

[438] Tsiligianni I. G., COPD patients trapped in the financial crisis in rural Crete, *The Lancet. Respiratory medicine*, 2013, **1**(10), e31–e32. https://doi.org/10.1016/S2213-2600(13)70227-3.

Tsiligianni I., Respiratory health in Greece, *The Lancet. Respiratory medicine*, 2020, **8**(7), e65–e66. https://doi.org/10.1016/S2213-2600(20)30276-9.

Consumer/Patient Issues: Patients who can use DPIs and SMIs are encouraged to switch from pMDIs.

Environmental Issues: Imported pMDIs have HFC-134a and HFC-227ea as propellants, and pMDI manufacturers are recovering HFCs from expired products or defective products during manufacturing. In addition, the amount of HFC propellants of some pMDIs has been reduced through formulation improvement. Although the development of pMDIs using low-GWP propellants is considered important, there are issues that have not yet been resolved, including safety testing of propellants, functionality of formulations, and stability. Japanese pharmaceutical companies will pursue this issue with international cooperation.

Pakistan

Population: 220 million

Prevalence: Asthma 10% in children, COPD 5% in men >40 years.

Medication Use: pMDIs are 36.74% of the inhalation market. pMDIs are SABA, LABA, SAMA, ICS, ICS/LABA, ICS/SABA. DPIs are 44.19% of the inhalation market. DPIs are SABA, ICS, LAMA, ICS/LABA, ICS/SABA, LABA/LAMA. Single dose DPIs are the most used, 91% (2,559 840 064) of the total DPI market. Multi-dose DPIs are 9% (246, 778, 251) of the DPI market. 8 local companies manufacture DPIs in Pakistan and 6 local companies manufacture pMDIs in Pakistan. Inhalers are also imported. Nebulised therapy is 19.08% of the inhalation market.

Current Trends: Overuse of SABA as first line therapy. DPI use is increasing, and all new launches and formulations are DPIs. Single-dose DPIs are preferred to multi-dose DPIs.

Consumer/Patient Issues: Single-dose DPIs are affordable, as a small number of doses can be purchased at a time. pMDIs are more expensive and less affordable because they contain multi-doses and are priced accordingly. Compared to other medications, inhalers are an economical price. The most used inhaler is a DPI with LABA/ICS.

Environmental Issues: There is no awareness of the GWP of inhalers.

Portugal

Population: 10.3 million

Prevalence: Asthma 6.8% current 10.5% lifetime**,** COPD 14.2% ≥40 years (~7.8% of general population).

Medication Use: About 45% of asthma and COPD patients use pMDIs and about 55% use DPIs. pMDIs are SABA, ICS, ICS/LABA. DPIs used are ICS and combination therapy. Less than 3–4% use nebulized therapy and less than 5% use oral medications. Portugal has 2 companies manufacturing inhalers. Inhalers are also imported.

Current Trends: Mild SABA overuse. Slow increase in DPI use.

Consumer/Patient Issues: pMDIs and DPIs are funded by the National Health Service so patients only pay 31% of the market price. All drug prices are regulated and controlled by the Portuguese Medicines Agency (Infarmed). For a new brand to get authorisation for the Portuguese market, one of the requirements is that the selling price cannot exceed the medium price of the three cheapest medicines from the same therapeutic class. The most used pMDI is SABA and the most used DPI is multi-dose ICS/LABA.

Environmental Issues: Very few are aware of the GWP of inhalers. The issue of safe disposal of inhalers is very slowly being introduced.

Romania

Population: 1.8 million

Prevalence: Asthma 5% (est.), COPD 8.2% (national inquiry).

Medication Use: 50% of asthma and COPD patients use pMDIs and 50% use DPIs. pMDIs used are SABA, LAMA, ICS/LABA. DPIs used are multi-dose LAMA, ICS/LABA, LAMA/LABA. 2–5% of asthma and COPD patients use nebulised therapy and 5% use oral medications. Romania has one pharmaceutical company manufacturing inhalers. Inhalers are also imported.

Current Trends: Overuse of SABA and overuse of ICS.

Consumer/Patient Issues: The price of inhalers is covered up to 70% by health insurance. The most used inhalers are ICS/LABA and SMI.

Environmental Issues: No awareness of the GWP of inhalers. Five years ago, a pharmaceutical company and the National Institute of Pneumology conducted a campaign on safe inhaler disposal.

Singapore

Population: 5.45 million

Prevalence: Asthma 12.9% COPD estimate 2–26% (>55 males)

Medication Use: There are no data for pMDI, DPI, nebulised therapy and oral therapy use by asthma and COPD patients. All current pMDIs and DPIs are available.

Current Trends: Markedly reduced use of SABA.

Consumer/Patient Issues: There is a wide range of prices for inhalers and the basic ones are heavily subsidized.

Environmental Issues: No evidence of awareness of the GWP of inhalers. Seem to be no actions providing safe disposal of inhalers.

Turkey

Population: 84.7 million

Prevalence: Asthma >15 years 8.9%, COPD 7.1%.[439]

Medication Use: 31% of asthma and COPD patients use pMDIs and 29% use DPIs. pMDIs used SABA, SAMA, ICS, ICS/LABA, ICS/LABA/LAMA. DPIs used LABA, LAMA, ICS/LABA, LABA/LAMA, ICS/LABA/LAMA. 56% of DPI use is single dose and 44% is multidose. 40% use nebulised therapy and 19% use oral medications. Turkey has 21 pharmaceutical companies which manufacture inhalers. Inhalers are also imported.

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[439] https://data.tuik.gov.tr/Bulten/Index?p=Turkey-Health-Survey-2019-33661. Accessed December 2022.

Current Trends: Increasing DPI use and overuse of SABA.[440]

Consumer/Patient Issues: 79.5% of drug expenses are paid by the Social Security Institution (SSI) and private insurance, and 20.4% of drugs are paid out of pocket. All inhaler drugs are also included in the scope of payment within the framework of a certain price policy determined by SSI which sets the public drug price for drug reimbursement. Depending on the SSI drug reimbursement policy, prices are accessible compared to the prices in other countries. The most used inhalers are ICS, ICS/LABA.

Environmental Issues: Some awareness of the GWP of inhalers. Like all medical wastes, pharmaceutical wastes are expected to be disposed of within the scope of the Waste Medical Control Regulation updated on 25 January 2017 but there is no special legislation.

Ukraine

Population: 39.4 million

Prevalence: Asthma 5, 042 per 100 adults (2017), COPD no data.

Medication Use: SABA, LABA, LAMA, ICS, combination therapy, are used in DPIs. SABA, ICS used in pMDIs.

Current Trends: No data but likely overuse of SABA pMDI for asthma as fully reimbursed by the National Health Service of Ukraine (NHS) so it is free to patients.

Consumer/Patient Issues: Affordability varies from very affordable for SABA pMDIs to unaffordable for LABA/ICS DPI. NHS provides partial or full reimbursement for asthma, ICS pMDI and ICS DPI depending on the manufacturer. Reimbursement for COPD patients planned for end of 2022 for LABA/ICS DPI and pMDI.

Environmental Issues: Patients not aware of environmental issues of inhalers. No knowledge of any environmental actions for safe inhaler disposal.

United Kingdom

Population: 67 million

Prevalence: Asthma 8 million diagnosed, 5.4 million treated. COPD 1.2 million diagnosed, est. 3 million may be undiagnosed.

Medication Use: 70% of inhalers used are pMDIs, 29% are DPIs and 1.4% are SMIs. Many cases of COPD go undiagnosed and so patients receive no treatment. Adherence to medication as in many long-term conditions is inconsistent so it is hard to get true figures on inhaler use. Much of this is true for asthma too. A very wide range of ICS, SABA and combination therapies for asthma and COPD are available as pMDIs and DPIs. Multi-dose DPIs are more common than single dose, although both are in wide-spread use. Less than 1% of asthma patients use nebulised therapy. Montelukast is used by an estimated 7% of asthma patients and theophylline by an estimated 0.1% of asthma and COPD patients. The United Kingdom has 3 companies which manufacture inhalers. Inhalers are also imported.

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[440] Bayar, B., Kutkan, N. U., Şafak Yılmaz, E., Tolun, Ç., Doğan, E., Atikeler, E. K., Vural, E. H., Babacan, S., Karabekmez, N., Beyan, A., Vural, İ. M., Oğuzülgen, İ. K., Bektemür, G., Malhan, S., Kahveci, R., Altın, S., Alkan, A., Eroğlu, H., Gürsöz, H., Cost Evaluation of Inhaler Therapies Used in Respiratory Diseases: 1998–2015 Period in Turkey, *Value in health regional issues*, 2017, **13**, 31–38. https://doi.org/10.1016/j.vhri.2017.07.004.

Current Trends: There have been significant changes in inhaler device type in the United Kingdom over the last 20 years. In asthma, two thirds of ICS inhalers were DPI in 2000 but only 9% in 2017. Similarly, SABA pMDIs which have gone from 40% to about 7% DPI. These changes to pMDIs for ICS and SABAs appear to have been done to reduce the cost of medication. Unfortunately, patients switched to cheaper pMDIs without appropriate clinical advice and education may have experienced worsening asthma control.

Consumer/Patient Issues: For patients inhalers cost the same. Some patients pay a prescription charge which is the same regardless of the medication they receive, be it pMDI reliever or DPI combination preventer/controller. Many patients who struggle to pay, who are over 60, or who have certain co-morbidities will be exempt from any charges. pMDIs are by far the most used, with salbutamol pMDI being the most common inhaled medication. As with other European countries SABA pMDI is the most used inhaler and contributes most to greenhouse gases. In the United Kingdom, SABA use and greenhouse gas emissions are approximately treble those of other European countries where greater proportions of DPI preventer/controller medication are used.[441]

Environmental Issues: Patients do not really understand the GWP of inhalers but there is some awareness. The biggest patient survey of over 12,000 United Kingdom asthma patients found that 60% of pMDI users said they would change their inhaler for environmental reasons, while a further 21% indicated they might. This was despite very low awareness of the environmental impact of inhalers.[442]

There is a national social media campaign to encourage patients to return used pMDIs to pharmacy. There was previously a national inhaler recycling scheme run for 8 years by a pharmaceutical company. In that time >1million inhalers were recycled, although this represents a <1% of all pMDIs prescribed during that period. Currently there are smaller local schemes running, in part to investigate the best ways to recycle medicines.

Recent efforts have tried to reduce the carbon footprint of healthcare alongside general reductions in greenhouse gas emissions. This involves 4 financial incentives paid to primary care networks for

- Reducing the "carbon intensity of salbutamol" by prioritising SABA pMDIs with a lower carbon footprint. This could include DPIs, or pMDIs which contain a smaller amount of HFC-134a.
- Using a greater proportion of DPIs for preventer/controller therapy where clinically appropriate.
- Reducing the proportion of asthma patients who are over-reliant on SABA pMDI (i.e., using 6 or more SABA pMDIs per year)
- Increasing the proportion of asthma patients using 3 or more ICS inhalers per year – as it is anticipated this will improve disease control and reduce over-reliance on SABA pMDIs.[443]

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[441] Wilkinson, A., Menzies-Gow, A., Sawyer, M., *et al.*, S26 An assessment of short-acting β2-agonist (SABA) use and subsequent greenhouse gas (GHG) emissions in five European countries and the consequence of their potential overuse for asthma in the UK, *Thorax*, 2021, **76**, A19.

[442] D'Ancona, G., Cumella, A., Renwick, L., *et al.*, 2021, *The sustainability agenda and inhaled therapy: what do patients want?* ERS International Conference, 2021.

[443] Good asthma control has a carbon footprint 1/3 that of poorly controlled asthma. See Wilkinson, A., Maslova, E., Janson, C., Radhakrishnan, V., Quint, J.K., Budgen, N., Tran, T.N., Bell, J.P., Menzies-Gow, A., Greenhouse gas emissions associated with asthma care in the UK: results from SABINA CARBON, *European Respiratory Journal*, 2021, **58**, OA76. DOI: 10.1183/13993003.congress-2021.OA76.

United States[444]

Population: 333 million

Prevalence: Asthma 8.4% (28 million), COPD 5% (16.6 million)

Medication Use: There is not well delineated data for pMDI or DPI use in patients with asthma or COPD. pMDIs are used for relievers, including over the counter (OTC) epinephrine, and combination therapies for asthma and COPD. There are not any reliever DPIs. DPIs, which are generally multi-dose, are used for combination therapies of preventers and controllers and triple therapies that also include long-acting muscarinics. Data on the use of nebulized therapy are unavailable, but it is more often used for COPD and young asthmatics (or bronchiolitis patients). Oral medications like montelukast (for which 32 million scripts written in 2019 but not known if for allergic rhinitis and/or asthma)[445], theophylline (not much used for asthma or COPD) and oral ephedrine (sold OTC for asthma but a niche product) have little data available. 1.5% of asthma patients use daily oral corticosteroids[446] but while also commonly used in COPD, the prevalence of its use is not well documented. The United States has 5 companies that manufacture inhalers. Inhalers are also imported.

Current Trends: With triple combination therapy, DPI use is increasing, but is still limited (U.S. EPA estimates 25% of inhaler use in the United States is DPI, 75% pMDI as of the pre-pandemic period). Total use is 55.3 million pMDIs, 18.9 million DPIs.

Consumer/Patient Issues: This is a difficult question for the United States, where universal coverage is not the reality, and the answers are very different for differing drugs. If one is having to self-pay, outside of generic SABA or OTC epinephrine, inhalers are not very affordable. For instance, an ICS/LABA is priced at well above USD100 per month vs. USD15 for SABA generics. An ICS/LABA/LAMA is as high as USD563 per month self-pay and an ICS >USD225 per month, many of which have no generic competition. The FDA is trying to enhance approval pathways for complex generics, including inhalers and particularly combination inhalers. SABA pMDI is the most used inhaler.

Environmental Issues: Judging from publications of patient groups/medical patient-targeted publications, there is very little awareness of the GWP of inhalers. Most of the focus is on climate change’s effects on asthma/allergies, not on the use of inhaled medications and their climate footprint.

Vietnam

Population: 97.3 million

Prevalence: Asthma 4%, COPD 4.2% people >40 years.

Medication Use: 60% of asthma and COPD patients use pMDIs and 30% use DPIs. pMDIs used are relievers and combination therapy. DPIs used are relievers, preventers/controllers and combination therapy. Single dose and multi-dose are used. The most used DPI is single dose SABA. 10% of

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[444] U.S. EPA, 2021, *Market Characterization of the U.S. Metered Dose Inhaler Industry*, Prepared by ICF, September 2021. https://www.epa.gov/sites/default/files/2021-03/documents/epa-hq-oar-2021-0044-0002_attachment_1-mdis.pdf.

[445] Statista, 2022, Number of montelukast prescriptions in the U.S. from 2004 to 2020, Oct 14, 2022. https://www.statista.com/statistics/782089/montelukast-prescriptions-number-in-the-us/. Accessed December 2022.

[446] Ekström, M., Nwaru, B. I., Hasvold, P., Wiklund, F., Telg, G., & Janson, C., Oral corticosteroid use, morbidity and mortality in asthma: A nationwide prospective cohort study in Sweden, *Allergy*, 2019, **74**(11), 2181–2190. https://doi.org/10.1111/all.13874.

asthma patients use nebulized therapy, 80% use montelukast and 5% use theophylline. 5% of COPD patients use theophylline.

Current Trends: SABA MDI is still being overused. Increasing use of ICS as preventer/controller.

Consumer/Patient Issues: Inhalers are affordable because of insurance. Initiatives are being undertaken to reduce the cost of inhalers.

Environmental Issues: There is no awareness of the GWP of inhalers.

11 Sterilants

11.1 Background

The provision of good quality health services requires effective disinfection or sterilization of health care products to prevent transmission of infection. Sterilization is defined as validated processes used to render products free from viable microorganisms, while disinfection is considered as a microbial reduction but not necessarily an eradication process. Sterilization, in particular, requires strict application of the principles of quality management to ensure validation of the selected process and implementation of effective routine control; reliable equipment; and knowledge of materials compatibility and biocompatibility. Sterilization of materials, including medical devices and pharmaceutical products and packaging, can be performed in facilities ranging from industrial settings with large outputs of similar items (e.g., by manufacturers of sterile medical devices such as single-use syringes, or specialist contractors offering a sterilization service to medical device manufacturers) and dissimilar items (such as procedure packs and kits), to smaller facilities including hospitals and dental clinics with much smaller outputs but great diversity of items. Process requirements for these settings are essentially similar but the types of sterilization processes used, and the challenges presented to assuring sterility, differ.

There is a range of commercially available sterilization methods including: heat (moist heat or dry heat), ionizing radiation (gamma ray, electron beam, x-ray), alkylating processes (such as ethylene oxide, formaldehyde) and oxidative processes (including hydrogen peroxide gas, gas plasma systems, liquid or gaseous peracetic acid, and ozone). Further sterilization methods based on these and other chemical agents are under continuing investigation for commercialisation.

Sterilization using ethylene oxide (EO) under controlled conditions is used to treat heat, or radiation sensitive medical devices, which are packaged in breathable materials that maintain sterility once the product is removed from the sterilization chamber. EO can penetrate many types of packaging materials and internal areas of medical devices, inactivate micro-organisms, and be removed from the product through the package. Following exposure, adequate aeration is essential after processing to achieve acceptable levels of residues. EO is toxic, mutagenic, carcinogenic, flammable, and explosive, and stringent regulations are applied to protect the environment and ensure worker safety. In the last 20 years alternatives to the use of EO have been developed, particularly for smaller medical device applications in healthcare facilities where the potential for personnel exposure is of greater concern. The fact that EO is still used widely used as sterilant, and its use grows in the industrial sector, is evidence that for numerous applications the benefits of its use outweigh these disadvantages.

EO can be used as a sterilant either alone or diluted with other gases to make non-flammable mixtures. A mixture of 12% by weight EO and 88% dichlorodifluoromethane (CFC-12) (12/88) was once widely used for this purpose. On an industrial scale, non-flammable mixtures can be created *in situ* within the sterilizer chamber using nitrogen. Non-flammable EO mixtures can also be supplied for use in industrial or healthcare facilities with carbon dioxide (CO_2) as a diluent. Hydrochlorofluorocarbons (HCFCs) were initially introduced as drop-in replacement for EO/CFC-12 mixtures but have been phased out in Europe and the United States; HCFC/EO may continue to be used in Article 5 Parties, but this also continued to be phased out over time. Hydrofluorocarbons (HFCs) were investigated as alternative replacement diluents but were not widely adopted for technical reasons and the environmental impact of the use of HFCs.

Some hospitals and other healthcare facilities continue to rely on EO sterilization and new sterilizers are used more efficiently than the previous EO/CFC units. Currently, all major suppliers of EO in these situations do not use CFCs or HCFCs. The overall use of EO sterilization at healthcare facilities has dramatically reduced due to the development of alternative sterilization methods and use of disposable medical devices. In addition, there has been increased efficiency by centralising the provision of sterilization facilities, enabling use of a smaller number of sterilizers under controlled conditions and reducing overall sterilant consumption. Furthermore, improvements in validation practices have enabled the use of processes that efficiently use lower EO concentrations, reducing sterilant usage, and overall decreasing levels of residues in processes and products. It is best practice to use abatement equipment in conjunction with EO sterilizers to reduce emissions to below acceptable safety levels.

11.2 CFC, HCFC, and HFC use for sterilization worldwide

The use of EO/CFC blends for sterilization has been successfully phased out in non-Article 5 Parties, and in most, if not all, Article 5 Parties, and only then from any remaining stockpile. Although it is difficult to be certain, global total use of CFCs for this application is believed to be zero.

EO/HCFC mixtures (10% by weight EO in a mix of HCFC-124 and HCFC-22) were virtual drop-in replacements for the 12/88 mixture using CFC and were introduced as transitional products for sterilization in those countries that employed 12/88 extensively. Estimated global use of HCFCs in sterilization was estimated to be less than 50 metric tonnes over 10 years ago, which amounts to less than 2 ODP tonnes worldwide. These use levels have continued to significantly decline since that time due to more efficient use of EO/HCFC using less gas per sterilizer load, the now predominant use of 100% ethylene oxide (or other alternatives), and by significant hospital conversion to other technologies.

There is no reason for not converting any potentially remaining sterilization equipment or processes in industrial or healthcare facilities in non-Article 5 parties. Medical device manufacturers that previously used EO/HCFC have converted to alternatives, with the major providers in the United States and other countries now using 100% EO-based processes, to the best of our current knowledge. European Union regulations banned the use of HCFCs as carrier gas for sterilization in closed systems from 1 January 1998. In the United States, HCFC-22 production, import, and export were restricted on 1 January 2010 and the HCFC-124 blend was phased out on 31 December 2014.[447] Since 1 January 2010, HCFC-22 cannot be produced or imported for uses other than servicing existing appliances. Whilst there was an exception for the continued use of HCFC-22 as a sterilant when the HCFC was produced prior to 1 January 2010, this exception only applied until 31 December 2014.

The complete phase-out of HCFCs in sterilization is readily achievable in Article 5 Parties to meet the Montreal Protocol schedule. In addition, the useful lifetime of any existing EO/HCFC sterilizers originally estimated in 2010 is about 20 years when well maintained. Therefore, by 2030, at the latest, any remaining sterilizers in Article 5 parties should be ready for replacement with available alternative technologies that do not use ozone-depleting substances. Industrial and healthcare facility procurement should take into consideration the HCFC phase-out, redundancy of EO/HCFC sterilization equipment, and lack of availability of HCFC-containing blends, in making future investment decisions.

HFC mixtures (10.4% by weight EO in a mix of HFC-125 and HFC-227) used in existing sterilization equipment with modified process controls were initially tested in the United States. Technical problems were identified that would require re-engineering, and potentially new equipment, in addition to validation of the new process. The technical problems include higher vapour pressure mixes requiring higher pressure feed lines and ancillary equipment; tendency of the mix to separate; and, for users that recover fluorocarbons, more complicated, less efficient operation unless the entire recovery system is re-engineered and rebuilt. HFC blends have not been broadly adopted or used worldwide, although initially some sterilization service providers in Asia continued to explore the potential application. In the European Union, there are restrictions on certain uses of HFCs, for example as refrigerants. While the use of HFCs in sterilizing equipment is not explicitly excluded

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[447] U.S. EPA, 2020, *Protection of Stratospheric Ozone: Adjustments to the Allowance System for Controlling HCFC Production, Import, and Export; Final Rule*, Federal Register, Volume 74, No. 239, December 15, 2009 (74 FR 66445-66446).

from these restrictions, MCTOC is also not aware of any widespread use. One company in Poland was found to supply EO/HFC-134a (5.6% by weight EO and 94.4% HFC-134a) but only as an option and in addition to 100% EO as a primary recommendation.[448] EO/HFC blends have also been investigated in the past to replace EO/methyl bromide blends to fumigate, *inter alia*, archives and antiquities.[449] In general, such fumigation systems based on EO, methyl bromide and aldehydes (e.g., formaldehyde) have been replaced with alternative technologies such as those based on hydrogen peroxide and chlorine dioxide.[450]

11.3 Available options for replacing ozone-depleting substances

Methods for sterilization of medical devices developed differently in each country due to the respective regulations on fire protection and occupational safety; requirements on process validation; liability considerations; availability of sterilization equipment and materials; and medical practices. Over time, these differences have become less due to international standardisation and harmonisation.

An effective infection control strategy requires the availability of sterile medical devices. Validation of sterilization processes is important to ensure product safety and functionality including the attainment of sterility, biocompatibility, and avoidance of material compatibility problems. No single sterilant or sterilization process is compatible with the range of potential products or materials, be they designed for single-use or designed to be processed in healthcare facilities and used multiple times. The nature and complexity of items and loads to be sterilized will vary according to the user requirements. Some items are more robust than others regarding pressure, temperature, moisture, and radiation dose. Therefore, several different processes are available for use, and each will offer specific advantages depending on the need.

Opportunities and technologies that can be considered to avoid processes using ozone-depleting EO/HCFC blends include use of heat-sterilizable devices, use of single-use devices sterilized by alternative heat, radiation or other chemical technologies, use of 100% EO sterilization processes, and a range of other methods that will sterilize most of the heat sensitive medical devices used in healthcare or industrial settings. Alternative low temperature processes for disinfection and particularly sterilization that have been commercialised include hydrogen peroxide gas (used with or without the generation of plasma during the process), humidified ozone gas, nitrogen dioxide gas, liquid phase peracetic acid formulation and low temperature steam-formaldehyde processes. Other low temperature methods have routinely reported but have yet to be widely deployed.

A summary of alternatives to reduce or phase out the use of ozone-depleting substances (ODS) follows. Several processes and systems have been described or are under development, but the examples described herein do not represent an exhaustive list of such developments. These are further

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[448] Wytwórnia Sterylgaz, 2022, http://www.sterylgaz.com.pl/en/main.php?k0=PRODUCTS&k1=GS-1z. Accessed November 2022.

[449] Methyl bromide or mixtures of methyl bromide and EO are used for de-infestation of historical artefacts, archives and antiquities. Methyl bromide is also an ODS, and its use is controlled under the Montreal Protocol. Blends of HFCs and EO have been validated to replace methyl bromide and EO fumigation blends. There is also a range of other alternatives that can be suitable for these fumigation uses depending on the infestation, including: nitrogen (insects); carbon dioxide (insects); sulfuryl difluoride (insects); heat (fungi); irradiation (fungi). There may be rare occasions where no alternative to methyl bromide is appropriate.

[450] McDonnell, G., Hansen, J., 2020, *Block's Disinfection, Sterilization, and Preservation*, 6th Edition, Wolters Kluwer Philadelphia, August 12, 2020.

considered in other reference materials.[451] This summary updates information included in the 2014 and 2018 Assessment Reports.[452]

11.3.1 Heat

Dry heat – This process is non-toxic, economical, and relatively safe. Devices must be able to tolerate exposure to a temperature typically greater than 150ºC to use the process for sterilization.

Moist heat (e.g., steam) – This process can be non-toxic and relatively safe. Pressurized steam is a particularly effective and well-used sterilization method. Available sterilizing equipment ranges from small self-contained bench-top sterilizers to large installations requiring supporting utilities. Devices must be able to tolerate a temperature greater than 115ºC, very high moisture levels and often changes in pressure to use the process.

11.3.2 Radiation

Ionising radiation— Ionising radiations (gamma rays, x-rays, and accelerated electrons) are widely used for sterilization, but only in large, industrial facilities; governments often operate these facilities in some Article 5 Parties. Operation of ionising radiation facilities is not generally appropriate for hospitals or centralised sterilization facilities supplying hospitals due to complexity, costs and safety implications. Not all materials are compatible with radiation, for these will depend on the radiation dose and material formulation. *Gamma radiation* and *electron beam* are well established, with now an increasing use of x-ray as an alternative. Facilities using gamma radiation need to dispose of spent isotopes used as radiation sources. Systems using low energy electron beams have been introduced for in-line treatment of certain materials such as those being introduced into the aseptic processing of pharmaceuticals, thereby reducing the need for treatment with gaseous sterilants. An increasing number of facilities using *x-ray* sterilization equipment are now operated commercially.

Ultraviolet (UV) radiation and intense pulsed light— UV radiation has been widely employed for disinfection of water systems and air. The lack of penetration and shadowing effect limit the application to exposed surface treatment. Specialised industrial applications for sterilization of certain medical devices have been developed and small-scale units for specific applications have been commercialised. Intense pulsed light, including a significant element in the UV range of the spectrum, has also been investigated for specific industrial sterilization applications.

11.3.3 Alkylating agents

100 percent EO— Despite being a flammable and hazardous gas, 100% EO can be effectively used when proper safety requirements are met (such as installation requirements, ventilation, personal protection equipment, etc.). Equipment ranges from large industrial sterilizers to small sterilizers used in healthcare facilities. On an industrial scale, the use of deep vacuum cycles and/or nitrogen may also be used or added to the sterilizer chamber during the sterilization process to render the process non-flammable. 100% EO processes typically operate at sub-atmospheric pressures to ensure adequate penetration of EO. The increased safety measures employed when using 100% EO, and updated

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[451] McDonnell, G., Hansen, J., 2020, *Block's Disinfection, Sterilization, and Preservation*, 6th Edition, Wolters Kluwer Philadelphia, August 12, 2020.

AAMI, 2021, Industrial Sterilization Process Optimization and Modality Changes, *Biomed Instrum Technol.*, 2021 Mar 1, **55**(s3), 1–88.

[452] UNEP, 2014, *2014 Report of the Medical Technical Options Committee, 2014 Assessment Report*, February 2015. https://ozone.unep.org/sites/default/files/2019-05/MTOC-Assessment-Report-2014.pdf

UNEP, 2018, *2018 Report of the Medical and Chemical Technical Options Committee, 2018 Assessment Report*, December 2018. https://ozone.unep.org/sites/default/files/2019-04/MCTOC-Assessment-Report-2018.pdf.

technologies to limit worker exposure and environmental issues, have been major factors in the increased use and resurgence of pure EO in the industrial marketplace.

Blends of EO and CO_2— Carbon dioxide (CO_2) is used to produce flammable and non-flammable mixtures with EO. Those containing more than 8.5% by weight EO are flammable. In the past, EO/CO_2 mixes were generally not used to replace other non-flammable mixes, but more recently, due to the declining use of other EO blends, there is a renewed interest in considering CO_2 blends. Sterilant container pressures are about ten times higher than for 12/88 EO/CFC mixtures, and chamber pressures are about three times higher. Additionally, processes include phases operating both below atmospheric pressure (to ensure penetration of EO) and pressure in excess of 3 atmospheres (to achieve the required EO concentration[453]). Use of EO/CO_2 blends has other disadvantages, such as composition changes during the use of a single tank or cylinder, potential for increased EO polymerization, and compatibility and corrosion problems caused by the acidity of CO_2.

Aldehydes— Formaldehyde, in combination with steam at sub-atmospheric pressure, is used mainly in northern Europe, China and parts of South America for materials that can withstand temperatures of up to 80–85ºC and high levels of moisture, although uses at 60–65ºC have also been reported. Sterilization processes include humidification, formaldehyde exposure and aeration. Formaldehyde is toxic and a suspected carcinogen, and this technology has not been widely accepted in many countries due to these concerns. Other aldehydes, such as liquid formulations of glutaraldehyde and ortho-phthalaldehyde (OPA), are widely used for high level disinfection purposes, but the use of these is also decreasing due to concerns with operator safety and bacterial resistance.

11.3.4 Oxidising agents

Hydrogen peroxide gas (or vapor — Sterilization processes based on hydrogen peroxide gas are commercially available. These are mostly vacuum-based processes that use hydrogen peroxide gas for sterilization. Some of these systems use plasma generation during the process for the removal of residual gas/liquid from the load. Low energy plasma may also be used for heating or vaporization purposes, depending on the specific sterilizer design. A wide variety of sterilization processes are in commercial use with many sterilizers sold worldwide, mostly to healthcare facilities, and these systems continue to be used extensively. They offer shorter cycle times in comparison to traditional EO systems, depending on the sterilization cycle design. This is now the predominant method of low temperature sterilization used in hospitals.

Liquid peracetic acid— Available equipment uses cassettes in which items to be sterilized (e.g., endoscopes) are placed. The cassette is designed to provide a chamber for exposure to a peracetic acid containing solution (with dedicated flow to internal components) for sterilization, followed by rinsing with sterile (or extensively treated) water, followed by draining. Sterilized items are not, to date, packaged for storage. It is recommended that they be used immediately after removal from the cassette to ensure safety at point of use. Gaseous peracetic acid systems have also been described.

Low temperature plasmas— a variety of methods of surface treatment with plasmas generated from different gases/combinations of gases have been investigated for their antimicrobial effectiveness. Examples of systems under investigation that use plasma directly for sterilization are nitrogen and nitrogen/oxygen gas plasma. Systems using low temperature plasma are under development for in-line treatment of certain materials being introduced into the aseptic processing of pharmaceuticals. None have yet reached commercial application.

Ozone— One process operating at less than 30°C has become recently available for use in hospitals, but, to date, has had limited commercial success. Ozone is generated within the sterilizer from an

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[453] These are also necessary for blends of EO/HCFCs, and blends of EO/HFCs.

oxygen source. The humidified process must be carefully controlled to ensure effectiveness, and it can also have the potential to affect surface materials.

Peracetic acid/gas plasma— A specific process was commercialised but was unfortunately associated with patient injuries when ophthalmic surgical instruments inappropriately sterilized with this system were used. The intended process had not received U.S. FDA approval for this specific application and a global recall was mandated. Despite this, the method has continued to be safely used for the industrial sterilization processes. Alternative peracetic acid gas processes have been the subject of investigations but to date no further processes or equipment have been commercialised.

Chlorine dioxide— A system for sterilizing medical devices using humidified chlorine dioxide was initially developed and patented but was not successful commercially. Chlorine dioxide is generated *in situ*, for example from sodium chlorite and chlorine gas in a nitrogen carrier. Gaseous chlorine dioxide is drawn into an evacuated chamber to achieve the required concentration at the appropriate temperature and relative humidity. These systems are widely used for fumigation (area disinfection) applications but have not found widespread use to date for sterilization applications.

Nitrogen dioxide gas— A United States-based sterilisation equipment supplier has developed a nitrogen dioxide (NO_2) gas sterilisation process. NO_2 sterilisation is performed on products in primary packaging, prior to final packaging in boxes. Product is aerated as part of the exposure cycle, which is typically between 60 and 90 minutes in duration. Some medical device polymers are incompatible with the NO_2 sterilisation process including polyurethanes, nylon and polyacetal. Cellulosic materials such as paper and cardboard are also incompatible, similar to other oxidizing agent-based methods.

Combination processes— Combinations of oxidising agents such as hydrogen peroxide and ozone or nitric oxide and nitrogen dioxide in combination have been investigated and developed but have had limited commercial success to date.

Supercritical carbon dioxide— Carbon dioxide in a supercritical state[454] has been reported as having activity against vegetative micro-organisms. However, it has little activity against bacterial spores without further chemical additives in the process, thus limiting its application as a sterilizing agent. No processes or equipment have reached commercial application at this time.

11.4 Conclusions

Sterilization is an important process in the provision of good quality healthcare services. It is also a process that requires strict application of the principles of quality management, reliability, biocompatibility materials compatibility and safety. Therefore, any alternative to the use of any remaining ozone-depleting substances needs to be well proven and tested to avoid putting the health of patients unnecessarily at risk. It is legal requirement in pharmaceutical and medical devices industries that any change in manufacturing processes, including sterilization, must be validated using appropriate guidelines before implementation.

CFC-12 use in the sterilization sector has been phased out in non-Article 5 Parties, and in most, if not all, Article 5 Parties, and only then from any remaining stockpile. Alternative EO/HCFC blends have small ozone depletion potentials (ODP) (0.03) and have been used as virtual drop-in replacements for EO/CFC blends. These are not widely used and MCTOC believes any remaining use is currently extremely limited and approaching zero. The complete phase-out of HCFCs in sterilization uses to meet the Montreal Protocol schedule is readily achievable. EO/HFC mixtures have not been broadly adopted or used worldwide. There are a wide variety of viable alternatives, based on high and low temperature technologies, including the continued safe use of EO gas. Many of these alternative

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[454] Carbon dioxide in a supercritical state is where the liquid and vapour phases become indistinguishable and is formed at temperatures around 32°C and pressures above 74 atmospheres.

technologies provide significant advances, such as better safety profiles and turn-around times, and reduced cost per cycle.

MCTOC believes that sterilization applications using controlled substances are no longer a relevant risk for the Montreal Protocol. Unless circumstances change, MCTOC proposes not to include sterilization in its technical updates in the next quadrennial assessment. Sterilization technologies and applications continue to move to deploy environmentally safer processes as best practice, in parallel with meeting the essential needs for patient safety.

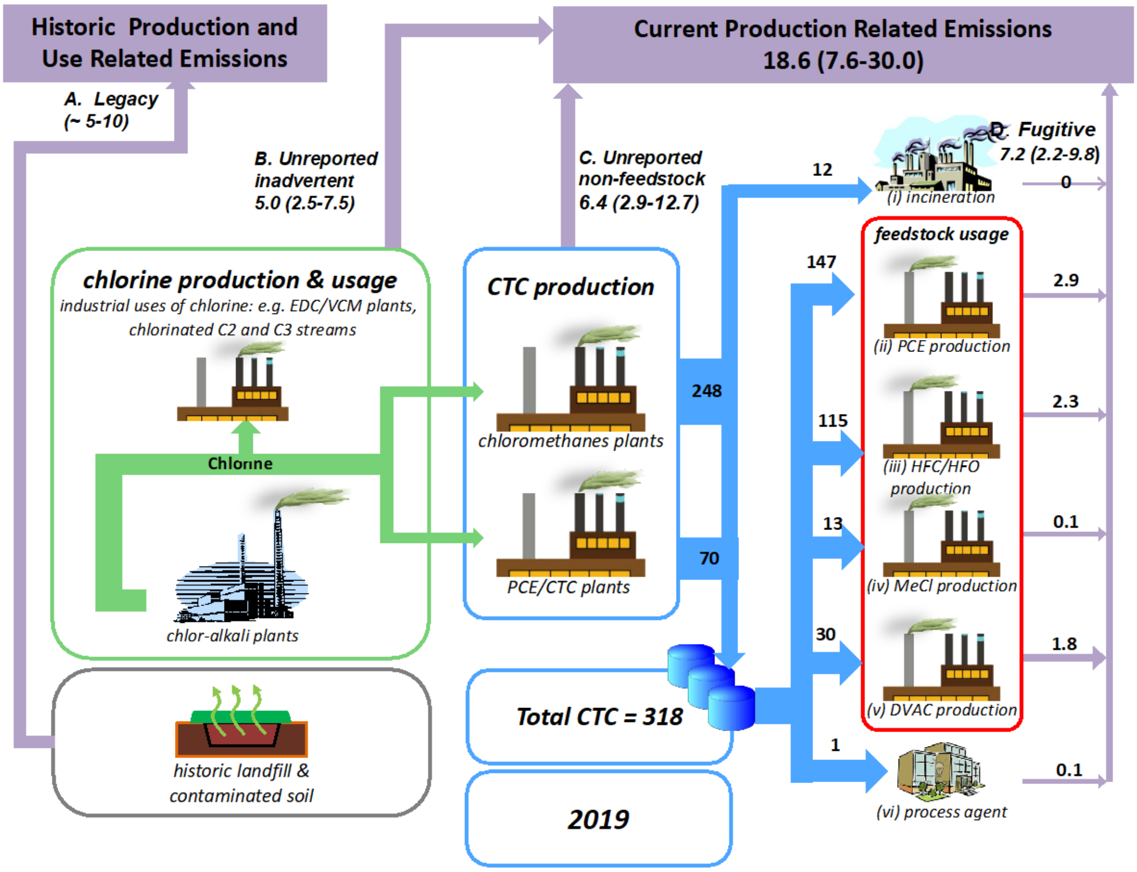
Appendix 1: Supplementary information on carbon tetrachloride

A1.1 Estimations of CTC production and emissions, 2014 and 2019

The following figures provide estimations of CTC production and emissions for the years 2019 and 2014 (SPARC Report, 2016[455]), for comparison with Figure 2.5 for the year 2020 (see Chapter 2, section 2.8).

In 2019, total global emissions of CTC related to current production and historic production and use are estimated to be 26.1 ktonnes (12.6–40.0 ktonnes) (Figure A1.1).

Figure A1.1 Estimated global CTC production, usage, and emissions, 2019 (ktonnes)



**This analysis is based on third-party interpretation of CTC use and is NOT based on reported Article 7 data. No assumption is made in this table for the quantity of CTC that may have been produced as feedstock to the unexpected emissions of CFC-11 (2013–2018).*

The various flow lines and differences between 2019 and 2020 are described in section 2.8.4.

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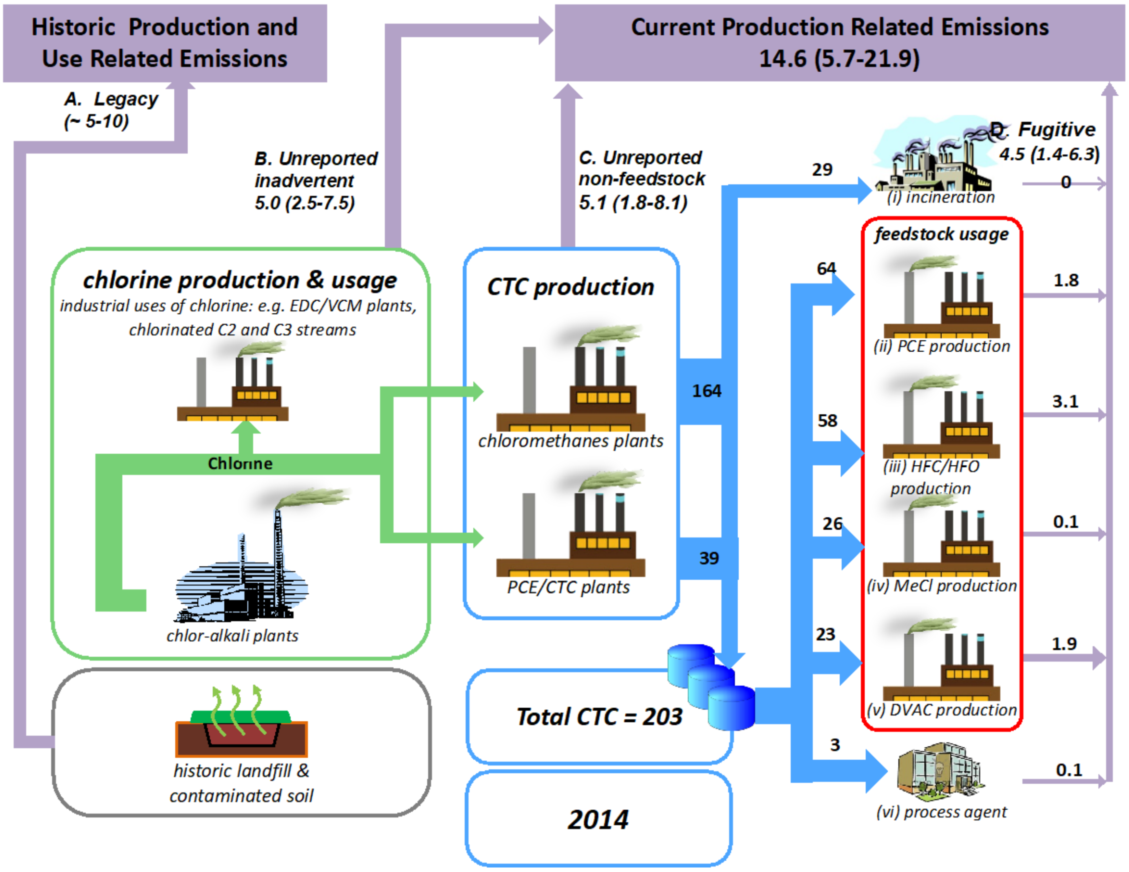
[455] Liang, Q., Newman, P.A., Reimann, S. (eds.), 2016, *SPARC Report on the Mystery of Carbon Tetrachloride*, SPARC Report No. 7, WCRP-13/2016, 2016.

Figure A1.2 **Re-estimated global CTC production, usage, and emissions, 2014 (ktonnes)** (SPARC (2016)[456] analysis for the year 2014, re-estimated using MCTOC emission factors, Chapter 2)



New emissions factors developed by MCTOC for production and feedstock uses have been used to re-estimate global CTC production, usage, and emissions for 2014, which is a revision of the original analysis for the year 2014 that appeared in SPARC (2016) (Figure A1.2). The revision for 2014 results in updated possible emissions, with the mean of concurrent production related emissions being 14.6 ktonnes within a range of 5.7–21.9 ktonnes. Legacy emissions from historic production and use add 5–10 ktonnes to these estimations. The mid-point of revised total global estimated CTC emissions for 2014 is 22.1 ktonnes within a range of 10.9–31.9 ktonnes.

The original SPARC (2016) estimations of CTC emissions are displayed in Figure A.1.3. In the earlier study, prior to the revision above, total global emissions of CTC were estimated to be 29.2 ktonnes, of which 48% was attributed to concurrent production related emissions.

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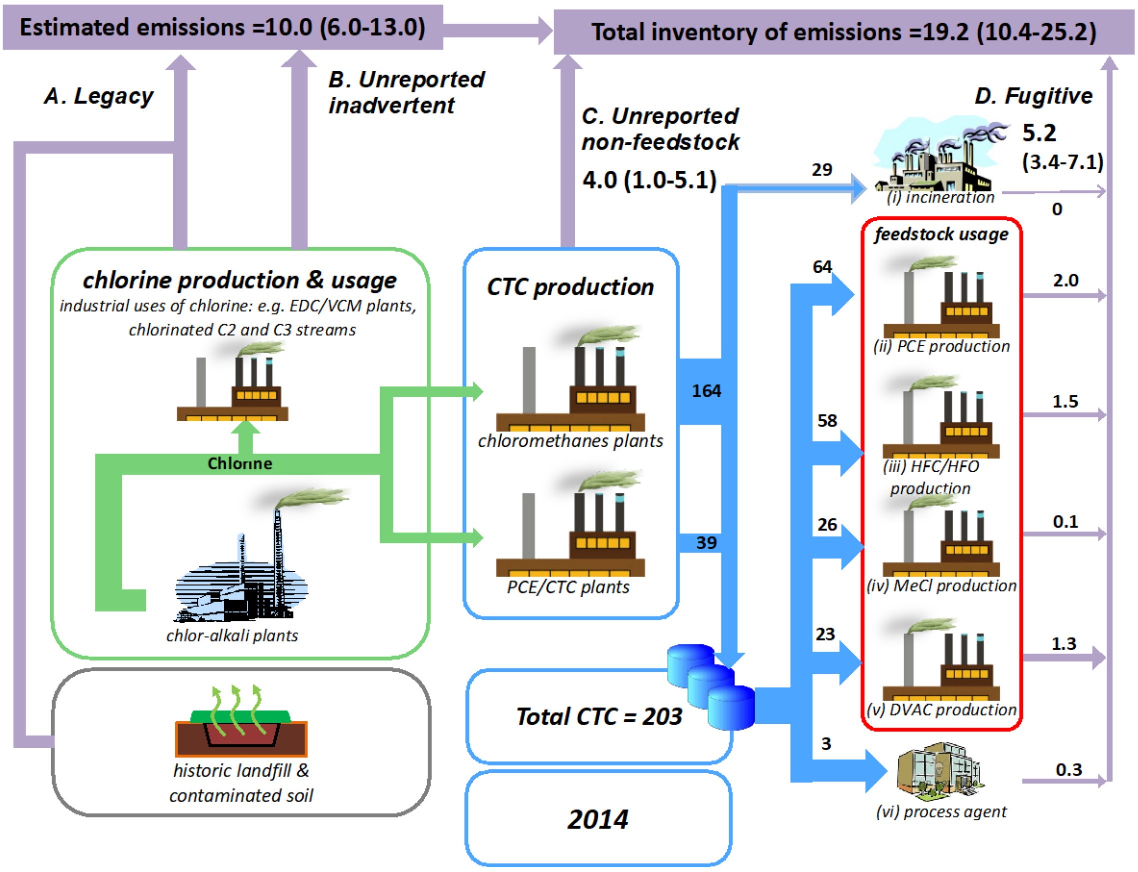
[456] Liang, Q., Newman, P.A., Reimann, S. (eds.), 2016, *SPARC Report on the Mystery of Carbon Tetrachloride*, SPARC Report No. 7, WCRP-13/2016, 2016.

Figure A1.3 Estimated global CTC production, usage, and emissions, 2014 (ktonnes) (SPARC (2016))



The main differences are:

- (B) —Estimated emissions of CTC from anthropogenic sources, excluding chloromethanes and PCE/CTC plants, e.g., EDC/VCM, are now added to the total inventory of emissions and have been more precisely defined as belonging to other chlorination reactions.

- (C) —Estimated emissions from chloromethanes plants and PCE/CTC plants are updated using MCTOC emissions factors (see Chapter 2), and include production plant emissions, transfers from intermediate production tanks to main bulk storage, and the transfer of packaged CTC to the production plant fence line.

- (D) —All emissions caused during transportation from the production plant to the user's premises, unloading and sending to bulk and intermediate storage, and in-process reactions, are attributed to the user industry.

A1.2 Analyses of ethylene dichloride waste streams

Two analyses of ethylene dichloride (EDC) light waste streams are provided in Tables A1.1 and A1.2, the former from Germany and the latter from Spain.[457] These show indicative proportions of CTC present in EDC lights waste streams.

Table A1.1 EDC Lights Analysis (Germany)

Substance	Percentage % of stream
1,1-Dichloroethane	1.40
1,2-Dichloroethene (***trans***)	2.82
1,2-Dichloroethene (***cis***)	1.20
Benzene	0.73
Carbon Tetrachloride	**15.92**
Trichloroethylene	5.10
Monochlorobutadiene (approx.)	10.0
1,1-Dichloroethane	2.91
Chloroform	18.34
1,2-Ethylene dichloride	41.86

Table A1.2 EDC Lights Analysis (Spain)

Substance	Percentage % of stream
1,1-Dichloroethane	1.40
1,2-Dichloroethene (***trans***) and 1,2-Dichloroethene (***cis***)	11.0
2-Chloro-1,3-butadiene	10.0
Carbon tetrachloride	**21.0**
Trichloroethylene	5.8
Ethyl chloride	0.1
Vinyl chloride	0.1
Monochlorobutadiene	10.0
1,1-Dichloroethane	6.0
Chloroform	18.0
1,2-Ethylene dichloride	28.0

EDC heavy streams generally have some content of EDC, at around 40%, and usually also contain mixed percentages of carbon tetrachloride, 1,1,2-trichloroethane, dichlorobutadienes and

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[457] References are available but would disclose the companies' names.

dichlorobutanes, perchloroethylene, tetrachloroethanes, and mixed hexachloroethanes, butadienes and benzene.

The amount of waste generated by the vinyl chain has steadily reduced from >1% of EDC production in the late 1990s and is currently 0.3–0.9% of all EDC production. In many countries regulation requires the destruction of such waste streams; however, *de minimis* emissions are possible.

Appendix 2: Relevant decisions for laboratory and analytical uses

This collation of relevant decisions, or parts thereof, is not exhaustive.

Annex II of the report of the 6th Meeting of the Parties in relation to Decision VI/9

Conditions applied to exemption for laboratory and analytical uses

5. Laboratory purposes are identified at this time to include equipment calibration; use as extraction solvents, diluents, or carriers for chemical analysis; biochemical research; inert solvents for chemical reactions, as a carrier or laboratory chemical and other critical analytical and laboratory purposes. Production for laboratory and analytical purposes is authorized provided that these laboratory and analytical chemicals shall contain only controlled substances manufactured to the following purities:

	%
CTC (reagent grade)	99.5
1,1,1-trichloroethane	99.0
CFC-11	99.5
CFC-13	99.5
CFC-12	99.5
CFC-113	99.5
CFC-114	99.5
Other w/Boiling P >20º C	99.5
Other w/Boiling P <20º C	99.0

6. These pure controlled substances can be subsequently mixed by manufacturers, agents, or distributors with other chemicals controlled or not controlled by the Montreal Protocol as is customary for laboratory and analytical uses.

7. These high purity substances and mixtures containing controlled substances shall be supplied only in re-closable containers or high-pressure cylinders smaller than three litres or in 10 millilitre or smaller glass ampoules, marked clearly as substances that deplete the ozone layer, restricted to laboratory use and analytical purposes and specifying that used or surplus substances should be collected and recycled, if practical. The material should be destroyed if recycling is not practical.

8. Parties shall annually report for each controlled substance produced: the purity; the quantity; the application, specific test standard, or procedure requiring its uses; and the status of efforts to eliminate its use in each application. Parties shall also submit copies of published instructions, standards, specifications, and regulations requiring the use of the controlled substance.

Decision VII/11: Laboratory and analytical uses

5. To adopt an illustrative list of laboratory uses as specified in Annex IV of the report of the Seventh Meeting of the Parties to facilitate reporting as required by decision VI/9 of the Sixth Meeting of the Parties;

6. To exclude the following uses from the global essential-use exemption, as they are not exclusive to laboratory and analytical uses and/or alternatives are available:

   a) Refrigeration and air-conditioning equipment used in laboratories, including refrigerated laboratory equipment such as ultra-centrifuges;

   b) Cleaning, reworking, repair, or rebuilding of electronic components or assemblies;

   c) Preservation of publications and archives; and

   d) Sterilization of materials in a laboratory;

Annex IV of the Report of the Seventh Meeting of the Parties

Categories and examples of laboratory uses *–(This list is not exhaustive)*

1. Research and development (e.g., pharmaceutical, pesticide, CFC and HCFC substitutes)

1.1 Reaction solvent or reaction feedstock (e.g., Diels-Alder and Friedel-Craft Reactions, RuO_3 oxidation, allelic side bromination, etc.)

2. Analytical uses and regulated applications (including quality control)

2.1 Reference

- Chemical (ODS monitoring, volatile organic compound (VOC) Detection, Equipment Calibration)
- Toxicant
- Product (adhesive bond strength, breathing filter test)

2.2 Extraction

- Pesticide and heavy metal detection (e.g., in food)
- Oil mist analysis
- Colour and food additive detection
- Oil detection in water and soil

2.3 Diluent

- Zinc, copper, cadmium detection in plants and food
- Micro-chemical methods to determine molecular weight or oxygen
- Measuring drug purity and residual determination
- Sterilization of lab equipment

2.4 Carrier (Inert)

- Forensic methods (e.g., fingerprinting)
- Titration (cholesterol in eggs, drug chemical characteristics, "Iodine value", e.g., in oils and chemical products)
- Analytical equipment (Spectroscopy (Infra-red, Ultra-violet, Nuclear Magnetic Resonance, fluorescence), chromatography (High-pressure liquid chromatography, gas chromatography, thin-layer chromatography)

2.5 Tracer

- Sanitary engineering

2.6 Miscellaneous (including testing)

- Ingredient in material for testing (e.g., asphalt, metal fatigue and fracturing)
- Separation media (separation of extraneous materials such as filth and insect excreta from stored food products)

3. Miscellaneous (including biochemical)

3.1 Laboratory method development

3.2 Sample preparation using solvent

3.3 Heat transfer medium

Decision XV/8: Laboratory and analytical uses

1. To extend the global laboratory and analytical use exemption under the conditions set out in annex II of the report of the Sixth Meeting of the Parties until 31 December 2007;

2. To request the Technology and Economic Assessment Panel to report annually on the development and availability of laboratory and analytical procedures that can be performed without using the controlled substances in Annexes A, B and C (group II and group III substances) of the Protocol;

Decision XIX/18: Laboratory and analytical-use exemption

1. To extend until 31 December 2011 the global laboratory and analytical-use exemption, under the conditions set out in annex II of the report of the Sixth Meeting of the Parties and decisions XV/8, XVI/16, and XVIII/15, for the controlled substances in all annexes and groups of the Montreal Protocol except Annex C, group 1;

Decision XXI/6: Global laboratory use exemption

1. To extend the applicability of the global laboratory and analytical use exemption also to countries operating under Article 5(1) from 1 January 2010 until 31 December 2010 for all ODS except those in Annex B Group III, Annex C Group I and Annex E.

2. To extend the global laboratory and analytical use exemption beyond 31 December 2010 until 31 December 2014:

(a) for Parties operating under Article 5(1) for all ODS except those in Annex B Group III, Annex C Group I and Annex E, and

(b) for Parties not operating under Article 5(1) for all ODS except those in Annex C Group

Decision XXVI/5: Global laboratory and analytical-use exemption

1. To extend the global laboratory and analytical-use exemption until 31 December 2021, under the conditions set out in annex II to the report of the Sixth Meeting of the Parties and decisions XV/8, XVI/16 and XVIII/15, for the controlled substances under the Montreal Protocol in all annexes and groups except Annex C, group 1;

2. To request the Technology and Economic Assessment Panel to report no later than 2018 on the development and availability of laboratory and analytical procedures that can be performed without using controlled substances under the Montreal Protocol;

3. To encourage parties to continue to investigate domestically the possibility of replacing ozone-depleting substances in laboratory and analytical uses and to share the resulting information;

Decision XXXI/5: Laboratory and analytical uses

1. To extend the global laboratory and analytical-use exemption indefinitely beyond 2021, without prejudice to the parties deciding to review the exemption at a future meeting;

2. To request the Secretariat to include information on production and consumption trends of ozone-depleting substances for laboratory and analytical uses in the annual report on Article 7 data submitted to the parties;

3. To further request the Secretariat to make available to the parties, through its website, the consolidated indicative list of laboratory and analytical uses of ozone-depleting substances that are globally exempted and the list of uses that the parties have agreed are no longer exempted;

4. To invite parties to consider the information provided by the Medical and Chemicals Technical Options Committee in the Technology and Economic Assessment Panel’s 2018 assessment report on uses that can be performed without using ozone-depleting substances;

5. To remind parties that the production and consumption of ozone-depleting substances for laboratory and analytical uses is limited to those uses which are not excluded from the laboratory and analytical-essential-use exemption;

6. To encourage parties to further reduce their production and consumption of ozone-depleting substances for laboratory and analytical uses and to facilitate the introduction of laboratory standards that do not require such substances;

7. To request the Technology and Economic Assessment Panel to report in its quadrennial report on any progress made by parties in reducing their production and consumption of ozone-depleting substances for laboratory and analytical uses, on any new alternatives to those uses, and on laboratory standards that can be performed without such substances, on the understanding that, should new compelling information become available, including opportunities for significant reductions in production and consumption, that information should be reported in its annual progress report;

8. That paragraph 7 of the present decision supersedes the request to the Technology and Economic Assessment Panel relating to reporting on laboratory and analytical uses in paragraph 4 of decision XXX/15.

Appendix 3: Non-exhaustive list of standards that do not use ODS

Determination of hydrocarbons (oil, grease, etc.) in water

Standard number	Standard Title	Alternative or alternative procedure
ASTM D7066-04(2017)	Standard Test Method for dimer/trimer of chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination	Dimer/trimer of chlorotrifluoroethylene (S-316)
ASTM D7575-11(2017)	Standard Test Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination	Membrane
ISO 17993:2002	Water quality-Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction	Hexane
ISO 9377-1:2000	Water quality — Determination of hydrocarbon oil index — Part 1: Method using solvent extraction and gravimetry	Petroleum ether
ISO 9377-2:2000	Water quality — Determination of hydrocarbon oil index — Part 2: Method using solvent extraction and gas chromatography	*n*-Hexane
ISO 15680:2003	Water Quality — Gas-chromatographic Determination of a Number of Monocyclic Aromatic Hydrocarbons, Naphthalene and Several Chlorinated Compounds Using Purge-and-trap and Thermal Desorption	Purge-and-trap
ISO 20595:2018	Water quality — Determination of selected highly volatile organic compounds in water — Method using gas chromatography and mass spectrometry by static headspace technique (HS-GC-MS)	HS-GC-MS
ISO 10301:1997	Water quality — Determination of highly volatile halogenated hydrocarbons — Gas-chromatographic methods	Pentane, hexane, petroleum ether, heptane or xylene
US EPA Method 502.2 Revision 2.1	Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series	Purge-and-trap

Standard number	Standard Title	Alternative or alternative procedure
US EPA Method 524.2 Revision 4.1	Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry	GC-MS
US EPA Method 3560	Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons (TRPHs)	Supercritical CO_2
US EPA Method 1664 Revision A	N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry	Hexane
US EPA 3510C	Separatory funnel liquid-liquid extraction	Dichloromethane
US EPA 3535A	Solid-phase extraction (SPE)	Solid-phase extraction
US EPA 3540c	Soxhlet extraction	Acetone/hexane, dichloromethane /acetone, toluene/methanol
US EPA 3810	Headspace gas chromatography	Methyl alcohol
US EPA 3820	Hexadecane extraction and screening of purgeable organics	Hexadecane
US EPA 5021B	Volatile organic compound in various sample matrices using equilibrium headspace analysis	Headspace analysis
US EPA 8021B	Aromatic and halogenated volatiles by gas chromatography using photo-ionisation and/or electrolytic conductivity detectors	GC
US EPA 5030B	Purge-and-trap for aqueous samples	Purge-and-trap
US EPA 8015C	Non-halogenated organics by GC/FID	GC/FID
US EPA 8260D	Volatile organic compounds by gas chromatography/mass spectrometry	GC-MS
HJ 637-2018	Water quality — Determination of petroleum, animal fats and vegetable oils — Infrared spectrophotometry	Perchloroethylene
HJ 970-2018	Water quality — Determination of petroleum — Ultraviolet spectrophotometric method	Hexane

Determination of hydrocarbons (oil, grease, etc.) in air, soil or sediment

Standard number	Standard Title	Alternative
ISO 16703：2004	Soil quality — Determination of content of hydrocarbon in the range C10 to C40 by gas chromatography	Heptane
ISO 15009：2016	Soil quality — Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons — Purge-and-trap method with thermal desorption	Methanol
ISO 10694:1995	Soil quality -- Determination of organic and total carbon after dry combustion (elementary analysis)	Elementary analysis
ISO 18287:2006	Soil quality — Determination of polycyclic aromatic hydrocarbons (PAH) — Gas chromatographic method with mass spectrometric detection (GC-MS)	Acetone/petroleum ether
ISO 16558-1:2015/Amd 1:2020	Soil quality — Risk-based petroleum hydrocarbons — Part 1: Determination of aliphatic and aromatic fractions of volatile petroleum hydrocarbons using gas chromatography (static headspace method) — Amendment 1	Methanol
ASTM D5765-16	Standard practice for solvent extraction of total petroleum hydrocarbons from soils and sediments using closed vessel microwave heating	Acetone/hexane
US EPA 9071B	*n*-Hexane extractable material (HEM) for sludge, sediment, and solid samples	*n*-Hexane
US EPA Method 8261A	Volatile organic compounds by vacuum distillation in combination with gas chromatography/mass spectrometry (VD/GC/MS)	VD/GC/MS
US EPA 3550B	Ultrasonic extraction	Acetone/ dichloromethane or acetone/hexane
EN 14039:2004	Characterization of waste — Determination of hydrocarbon content in the range of C10 to C40 by gas chromatography	Heptane
EN 14345:2004	Characterization of waste — Determination of hydrocarbon content by gravimetry	Acetone/petroleum

HJ 1020-2019	Soil and sediment — Determination of petroleum hydrocarbons(C6-C9) — Purge and trap/gas chromatography	Methanol
HJ 1021-2019	Soil and sediment — Determination of petroleum hydrocarbons(C10-C40) — Gas chromatography	Hexane or hexane-acetone
HJ 1051-2019	Soil — Determination of petroleum oil — Infrared spectrophotometry	Perchloroethylene
HJ 1077-2019	Stationary source emission — Determination of oil fume and oil mist — Infrared spectrophotometric method	Perchloroethylene

Determination of Iodine value or Bromine value

Standard number	**Standard Title**	**Alternative**
ISO 3961:2018	Animal and vegetable fats and oils — Determination of iodine value	Cyclohexane/glacial acetic acid
ASTM D5768 -02(2018)	Standard Test Method for Determination of Iodine Value of Tall Oil Fatty Acids	*iso*-Octane/cyclohexane
ASTM D1492-21	Standard Test Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration	Glacial acetic acid/ methanol
ASTM D5554 -15(2021)	Standard Test Method for Determination of the Iodine Value of Fats and Oils	Glacial acetic acid/cyclohexane
ASTM D5776-21	Standard Test Method for Bromine Index of Aromatic Hydrocarbons by Electrometric Titration	1-Methyl-2-pyrrolidinone
ASTM D4252 -89(2017)	Standard Test Methods for Chemical Analysis of Alcohol Ethoxylates and Alkylphenol Ethoxylates	Chloroform

Determination of moisture and water

Standard number	**Standard Title**	**Alternative**
ISO 662:2016	Animal and vegetable fats and oils — Determination of moisture and volatile matter content	Heating method

ISO 934:1980	Animal and vegetable fats and oils — Determination of water content — Entrainment method	Xylene
ISO 8534:2017	Animal and vegetable fats and oils — Determination of water content — Karl Fischer method (pyridine free)	Methanol
ISO 3733:1999	Petroleum products and bituminous materials — Determination of water — Distillation method	Aromatic solvent, petroleum distillate solvent, paraffinic solvents
ISO 6296:2000	Petroleum products — Determination of water — Potentiometric Karl Fischer titration method	Sodium dioctyl sulfosuccinate
ISO 12937:2000	Petroleum products — Determination of water — Coulometric Karl Fischer titration method	Sodium dioctyl sulfosuccinate

Determination of phenol in water

Standard number	Standard Title	Alternative
ASTM D1783-01(2020)	Standard test methods for phenolic compounds in water	Chloroform
ISO 6439:1990	Water quality — Determination of phenol index — 4-Aminoantipyrine spectrometric methods after distillation	Chloroform
US EPA Method 9065	Phenolics (Spectrophotometric, Manual 4-AAP With Distillation)	Chloroform
HJ 676-2013	Water quality — Determination of phenolic compounds Liquid-liquid extraction gas chromatography	Dichloromethane and ethyl acetate
HJ 744-2015	Water quality — Determination of phenols compounds — Gas chromatography mass spectrometry	Dichloromethane and hexane

Determination of metal content

Standard number	Standard Title	Alternative
ASTM D3237-17	Standard Test Method for Lead in Gasoline by Atomic Absorption Spectroscopy	Methyl isobutyl ketone

Appendix 4: Non-exhaustive list of standards that still use ODS

Standard No.	**Standard Title**
ASTM D3467 -04(2020)	Standard Test Method for Carbon Tetrachloride Activity of Activated Carbon
ASTM D1783 -01(2020)	Standard Test Methods for Phenolic Compounds in Water
ASTM D3124 -98(2019)	Standard Test Method for Vinylidene Unsaturation in Polyethylene by Infrared Spectrophotometry
ASTM E2106 -00(2019)	Standard Practice for General Techniques of Liquid Chromatography-Infrared (LC/IR) and Size Exclusion Chromatography-Infrared (SEC/IR) Analyses
ASTM C799-19	Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Nuclear-Grade Uranyl Nitrate Solutions
ASTM D5160 -95(2019)	Standard Guide for Gas-Phase Adsorption Testing of Activated Carbon
ASTM D4448 -01(2019)	Standard Guide for Sampling Ground — Water Monitoring Wells
ASTM D297-21	Standard Test Methods for Rubber Products — Chemical Analysis
ASTM D3703-18	Standard Test Method for Hydroperoxide Number of Aviation Turbine Fuels, Gasoline and Diesel Fuels
ASTM D1505-18	Standard Test Method for Density of Plastics by the Density-Gradient Technique
ASTM C761-18	Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride
ASTM F2459-18	Standard Test Method for Extracting Residue from Metallic Medical Components and Quantifying via Gravimetric Analysis
ASTM D3326 -07(2017)	Standard Practice for Preparation of Samples for Identification of Waterborne Oils
ASTM E50-17	Standard Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
ASTM F1147 -05(2017)e1	Standard Test Method for Tension Testing of Calcium Phosphate and Metallic Coatings

ASTM E169-16	Standard Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis
ASTM C169 -16(2022)	Standard Test Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass
ASTM D5226-21	Standard Practice for Dissolving Polymer Materials
ASTM D3698 -04(2020)	Standard Practice for Solvent Vapor Degreasing Operations
ASTM F754 -08(2015)	Standard Specification for Implantable Polytetrafluoroethylene (PTFE) Sheet, Tube, and Rod Shapes Fabricated from Granular Molding Powders
ASTM C670-15	Standard Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials
ASTM E2036-15	Standard Test Method for Nitrogen Trichloride in Liquid Chlorine by High Performance Liquid Chromatography (HPLC)
ASTM D3869-15	Standard Test Methods for Iodide and Bromide Ions in Brackish Water, Seawater, and Brines
ASTM D629-15	Standard Test Methods for Quantitative Analysis of Textiles
ASTM E1683 -02(2014)e1	Standard Practice for Testing the Performance of Scanning Raman Spectrometers
ASTM D460 - 91(2014)	Standard Test Methods for Sampling and Chemical Analysis of Soaps and Soap Products
ASTM B322-99(2020)e1	Standard Guide for Cleaning Metals Prior to Electroplating
ASTM F218 - 13(2020)	Standard Test Method for Measuring Optical Retardation and Analyzing Stress in Glass
ASTM D1574 - 22	Standard Test Method for Extractable Matter in Wool and Other Animal Fibers
ASTM E1982 - 98(2021)	Standard Practice for Open-Path Fourier Transform Infrared (OP/FT-IR) Monitoring of Gases and Vapors in Air
ASTM E1252 - 98(2021)	Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis
ASTM D2008 - 12(2018)	Standard Test Method for Ultraviolet Absorbance and Absorptivity of Petroleum Products

ISO 1183-1:2019	Plastics — Methods for determining the density of non-cellular plastics — Part 1: Immersion method, liquid pycnometer method and titration method
ISO 1183-2:2019	Plastics — Methods for determining the density of non-cellular plastics — Part 2: Density gradient column method
ISO 15001:2010	Anaesthetic and respiratory equipment — Compatibility with oxygen
ISO 5796:2000	Rubber compounding ingredients — Natural calcium carbonate — Test methods
ISO 6439:1990	Water quality — Determination of phenol index — 4-Aminoantipyrine spectrometric methods after distillation
ISO 7523:1985	Nickel — Determination of silver, arsenic, bismuth, cadmium, lead, antimony, selenium, tin, tellurium and thallium contents — Electrothermal atomic absorption spectrometric method
ISO 7106:1985	Liquefied anhydrous ammonia for industrial use — Determination of oil content — Gravimetric and infra-red spectrometric methods
ISO 3705:1976	Sulphur for industrial use — Determination of arsenic content — Silver diethyldithiocarbamate photometric method
ISO 2961:1974	Aluminium oxide primarily used for the production of aluminium — Determination of an adsorption index

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