MONTREAL PROTOCOL ON SUBSTANCES THAT DEPLETE THE OZONE LAYER

REPORT OF THE TECHNOLOGY AND ECONOMIC ASSESSMENT PANEL

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VOLUME 6

RESPONSE TO DECISION XXXIV/7: STRENGTHENING INSTITUTIONAL PROCESSES WITH RESPECT TO INFORMATION ON HFC-23 BY-PRODUCT EMISSIONS

UN environment programme

Montreal Protocol on Substances that Deplete the Ozone Layer

United Nations Environment Programme (UNEP)
Report of the Technology and Economic Assessment Panel

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Foreword

The September 2023 TEAP Report

The September 2023 TEAP Report consists of three volumes:

Volume 5: *Evaluation of Critical Use Nominations for Methyl Bromide Submitted in 2023 and Related Issues – Final Report*

Volume 6: *Response to Decision XXXIV/7: Strengthening Institutional Processes with Respect to Information on HFC-23 By-Product Emissions*

Volume 7: *Supplement to the May 2023 TEAP Replenishment Task Force Report "Assessment of the Funding Requirement for the Replenishment of the Multilateral Fund for the Period 2024–2026"*

This is Volume 6.

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Executive Summary

This report includes sections responding to each of the following sub-paragraphs of decision XXXIV/7, relating to HFC-23 by-product generation and emissions from the manufacture of Annex C, Group I, or Annex F substances:

(a) Information on the possible chemical pathways that could be used in the production of Annex C, Group I, or Annex F substances that may generate HFC-23 as a by-product;

(b) Compilation of information on the amount of HFC-23 generation and emissions from facilities that manufacture Annex C, Group I, or Annex F substances, the reporting of which is required under Article 7 of the Montreal Protocol; and

(c) Best practices available to control these emissions.

The report includes additional contextual information on other HFC-23 generation and/or emissions, i.e., from chemical pathways used in the production of substances that are not Annex C, Group I, or Annex F substances, and from feedstock and consumptive uses. This additional contextual information was considered useful in understanding the relative importance of chemical pathways used in the production of Annex C, Group I, and Annex F substances that may generate HFC-23 as a by-product, which is the focus of this decision.

Two key terms from the decision are defined as follows:

- *Generation* is defined as the total HFC-23 produced as a by-product, without taking into account abatement of emissions.
- *Emissions* are defined as the total HFC-23 emitted from a facility that generates HFC-23 as a by-product, after any abatement. Although HFC-23 may be emitted via different routes, the dominant emission pathway is direct emissions to atmosphere.

ES.1 Chemical pathways that could be used in the production of Annex C, Group I, or Annex F substances that may generate HFC-23 as a by-product

There are several chemical mechanisms that can, by their nature, generate HFC-23 as a by-product in chemical production processes, including:

- *Over- or under-reaction of chemicals* present in the reaction vessel enroute to the intended product, e.g., HFC-23 is an over-fluorination of HCFC-22.
- *Presence of impurities in the feedstocks that are being reacted*, e.g., the chloroform impurity in dichloromethane feedstock, used to produce HFC-32, is hydro-fluorinated to HFC-23.
- *Unintended side reactions*, where the feedstock follows a different reaction path than the one that is desired to make the product, e.g., cleavage of carbon–carbon bond in the production of HFC-125 from perchloroethylene, with subsequent hydro-fluorination of the resulting mono-carbon molecule to form HFC-23.

The estimated global generation of HFC-23 as a by-product is around 25,000 tonnes per year for the range of chemical pathways considered in this report. This estimate is based on current expert knowledge of production quantities and HFC-23 by-product generation rates by process. HFC-23 generated will only be emitted if it is not captured, used as feedstock, or destroyed before it leaves the process, e.g., by incineration. HFC-23 is primarily generated by the fluorination of chloroform, via the chloroform, HCFC-21, HCFC-22 to HFC-23 pathway in fluorination or hydro-fluorination chemical processes. This process is widely understood to be the main source of global HFC-23 by-product generation, at around 95% of the estimated total global HFC-23 generation. Chemical pathways used in the production of other Annex C, Group I, (other than HCFC-22) or Annex F substances can also generate HFC-23 as a by-product, which in combination, are currently estimated to generate up to around 1% of the total global HFC-23 generation. Some chemical pathways used to produce substances other than Annex C HCFCs or Annex F HFCs are also understood to generate HFC-23 by-product, which in combination, are currently estimated to account for around 3–4% of the total global HFC-23 by-product generation.

For many processes producing fluorinated controlled substances, HFC-23 by-product generation is possible. In the production of HCFC-22, HFC-23 by-product generation cannot be eliminated, with 1–3 wt% HFC-23 generation being typical. For other processes, very low generation rates are possible; with careful design and operation of the process, HFC-23 by-product generation rate can be minimised to less than 0.1 wt%, often less than 0.01 wt%, of production, with emission mitigation reducing the final HFC-23 emission rate further. For many HCFC and HFC production processes, little or no effort has been taken to date to eliminate HFC-23 by-product generation because the "natural" HFC-23 generation rate of the process is so low as to not make it cost-effective. With an effectively operated HFC-23 mitigation step, e.g., thermal oxidation, HFC-23 emission rates can be significantly lower than the HFC-23 by-product generation rates because destruction efficiencies can exceed 99%.

The chemical pathway used to produce HCFC-22, involving the two-step reaction of chloroform and anhydrous hydrogen fluoride to produce HCFC-22, is employed in many plants around the world. HFC-23 generation rates are typically around 1–3 wt%, or 10–30 kg of HFC-23 by-product generated per tonne of HCFC-22, and can be as high as 4 wt%. This process is widely understood to be the main source of global HFC-23 generation, at ***around 95% of the estimated total global HFC-23 by-product generation.***

Chemical pathways used to produce Annex C, Group I, substances other than HCFC-22, and Annex F substances can also generate HFC-23 as a by-product. In combination, these other chemical pathways are currently estimated to generate up to ***around 1% of total global HFC-23 by-product generation***.

Some chemical pathways used to produce Annex C HCFCs and Annex F HFCs have good evidence of HFC-23 generation and its associated rates (e.g., HCFC-22 from chloroform). Other chemical pathways used to produce Annex C HCFCs and Annex F HFCs have more limited evidence of HFC-23 generation, although generation is theoretically feasible (e.g., HFC-32 from dichloromethane, HFC-125 from perchloroethylene, HFC-134a from trichloroethylene). Evidence is limited due to insufficient data, with a lack of emissions reporting and a lack of reference to HFC-23 generation in patents. Nevertheless, HFC-23 generation is theoretically feasible and potentially present in trace amounts. For some chemical pathways, the rate of HFC-23 generation may be so low (practically zero) that HFC-23 would remain undetected in routine analysis.

While noting these uncertainties, for additional context and understanding of the potential relative contributions to HFC-23 by-product generation, the report provides indicative estimations of relative global HFC-23 generation by relevant chemical pathways based on available information and/or expert opinion.

With these data qualifications in mind, the chemical pathways that could be used to produce Annex C HCFCs and Annex F HFCs that *may* generate HFC-23 as a by-product are:

- HCFC-22 from chloroform, including co-production of HCFC-21
- HFC-32 from dichloromethane
- HFC-125 from perchloroethylene, including co-production of HCFC-124 and HCFC-123
- HFC-134a from trichloroethylene, including co-production of HCFC-133a

- HCFC-142b from vinylidene chloride or trichloroethane
- HFC-152a from vinyl chloride
- HFC-143a from trichloroethane
- HFC-227ea from hexafluoropropylene (HFP)
- HFC-245fa from pentachloropropane

Some chemical pathways used to produce substances other than Annex C HCFCs or Annex F HFCs (around 3–4% of global HFC-23 by-product generation), which are outside the scope of decision XXXIV/7, are also understood to generate HFC-23 by-product. The largest contributor of these chemical pathways to global HFC-23 by-product generation is likely to be the pyrolysis of HCFC-22 to make tetrafluoroethylene (TFE) and hexafluoropropylene (HFP), which can be used to produce fluoropolymers. This process is understood to generate up to around 1 kg of HFC-23 per tonne of HCFC-22 consumed (0.1 wt%). Other chemical pathways where HFC-23 by-product generation is theoretically feasible include those used to produce CFCs, namely CFC-113 from perchloroethylene and CFC-114 from perchloroethylene. In combination, these chemical pathways are currently estimated to account for ***around 3–4% of the total global HFC-23 by-product generation.***

ES.2 Compilation of information on the amount of HFC-23 generation and emissions

In response to decision XXXIV/7, paragraph b, this report provides a compilation of information on the amount of HFC-23 generation and emissions from facilities that manufacture Annex C, Group I, or Annex F substances. It draws on several sources for this information, including UNFCCC submissions by Annex 1 countries; the Intergovernmental Panel on Climate Change (IPCC); Article 7 data reported under the Montreal Protocol; data reported to the Executive Committee (ExCom); and the Science Assessment Panel (SAP).

Most reported data for HFC-23 by-product generation are available for HCFC-22 production. Based on IPCC default factors, HFC-23 by-product generation from HCFC-22 production is expected to be in the range of about 15,000 to 30,000 tonnes per year.

HFC-23 emissions data reported under Article 7 are incomplete for 2019, 2020 and 2021 due to the timing of reporting obligations and depending on when parties ratified the Kigali Amendment. The dataset for 2021 is the most complete. The combined HFC-23 emissions reported as by-product from HCFC-22 production (UNFCCC and under Article 7) is 2,572 tonnes in 2021.

Other information on HFC-23 emissions is provided as additional contextual information, including from sources other than facilities that manufacture Annex C HCFC and Annex F HFCs.

The SAP 2022 Assessment reports estimated HFC-23 emissions, derived from atmospheric monitoring, of 17.2 ± 0.8 Gg yr^{-1} (17,200 tonnes) in 2019, and a similar value of 16.5 ± 0.8 Gg yr^{-1} (16,500 tonnes) in 2020. This compares with the combined reported HFC-23 emissions from HCFC-22 production (UNFCCC and under Article 7), which is 2,572 tonnes in 2021.

A range of sources other than facilities that manufacture Annex C HCFC and Annex F HFCs are considered, with associated estimates of a*nnual* HFC-23 emissions, as follows:

- Pyrolysis of HCFC-22 to produce TFE/HFP (~100–1,000 tonnes, based on estimated associated HFC-23 by-product generation without possible emissions abatement)
- Feedstock use of HFC-23 (~10 tonnes)
- HFC-23 present as an impurity in other chemicals that are used in emissive uses (e.g., ~40 tonnes HFC-23 emissions arising from the HCFC-22 bank)

- Fire protection (~50 tonnes)
- Low temperature refrigerant (similar order of magnitude to fire protection)
- Semiconductor and electronics manufacturing (~90 tonnes)

ES.3 Best practices available to control HFC-23 by-product emissions

In response to decision XXXIV/7, paragraph c, the report provides a summary of information on best practices available to control emissions of HFC-23 by-product from facilities that manufacture Annex C HCFCs or Annex F HFCs. These best practices to control emissions of HFC-23 are consistent with those used to control other emissions associated with chemical manufacturing. This report also summarises a sample of measures implemented or being implemented by parties to control emissions of HFC-23 by-product.

ES.4 Recommendation

Uncertainties and data discrepancies have been identified in this report that impact the accurate estimation of global HFC-23 generation and emissions based on currently available data. With improved data, more refined estimates and conclusions could be drawn.

Parties may wish to consider measures to improve the reported data for HFC-23 generation and emissions, including their accuracy and their scope.

1 Introduction

1.1 Decision XXXIV/7: Strengthening institutional processes with respect to information on HFC-23 by-product emissions

At the 34th Meeting of the Parties in 2022, parties agreed decision XXXIV/7.

Decision XXXIV/7: Strengthening institutional processes with respect to information on HFC-23 by-product emissions:

Recalling the provisions under paragraphs 6 and 7 of Article 2J of the Montreal Protocol on Substances that Deplete the Ozone Layer on destruction, to the extent practicable, of HFC-23 by-product emissions from each production facility that manufactures Annex C, Group I, or Annex F substances,

To request the Technology and Economic Assessment Panel to prepare a report for the Thirty-Fifth Meeting of the Parties to include:

(a) Information on the possible chemical pathways that could be used in the production of Annex C, Group I, or Annex F substances that may generate HFC-23 as a by-product;

(b) Compilation of information on the amount of HFC-23 generation and emissions from facilities that manufacture Annex C, Group I, or Annex F substances, the reporting of which is required under Article 7 of the Montreal Protocol; and

(c) Best practices available to control these emissions.

1.2 TEAP's response to decision XXXIV/7

Given the focus of decision XXXIV/7 on chemical pathways used in the production of Annex C, Group I, or Annex F substances generating HFC-23 as a by-product, associated HFC-23 emissions, and best practices available to control these emissions, the Medical and Chemical Technical Options Committee (MCTOC), with its relevant chemical production expertise, has led the preparation of this report on behalf of the Technology and Economic Assessment Panel (TEAP).

To provide a broader context for HFC-23 emissions from chemical pathways used in the production of Annex C, Group I, or Annex F substances, brief information has been provided on other additional HFC-23 emissions, including from consumptive uses. MCTOC has consulted experts within TEAP to address emissions from these sectors.

1.3 Development and structure of this report

MCTOC met to prepare this report from March until late August, including during its face-to-face/hybrid meeting in April and online. To facilitate the drafting of this report, MCTOC formed a drafting sub-group of chemical experts with a range of relevant industry expertise and geographic coverage. During August, a final draft report was reviewed by the full membership of MCTOC and TEAP, followed by a final review of the report incorporating the feedback received.

The report includes sections responding to each of the sub-paragraphs of decision XXXIV/7. It also includes additional contextual information on other HFC-23 generation and/or emissions, i.e., from chemical pathways used in the production of substances that are not Annex C, Group I, or Annex F substances, and from feedstock and consumptive uses. This additional contextual information was considered useful in understanding the relative importance of chemical pathways used in the production of Annex C, Group I, or Annex F substances that may generate HFC-23 as a by-product, which is the focus of decision XXXIV/7.

1.4 Explanation of terms

Several terms are used in decision XXXIV/7 and/or referred to in this report that are explained further below and at relevant places within the report.

A *chemical pathway* (or reaction pathway) describes the specific selected starting materials/feedstocks used to be converted into the desired chemical product. The chemical pathway selected considers factors such as the yield and purity of the final product(s) and minimising unwanted side-products (i.e., by-products) and waste materials. There are other considerations in selecting commercially desirable chemical pathways, including plant design, engineering, safety, the impact of scaling up quantities, reaction time, and cost. For example, there are several chemical pathways used to produce HFC-152a; one chemical pathway uses vinyl chloride as starting material, and another uses acetylene.

A *chemical process* describes the mechanism for how chemicals are transformed or formed, defining its associated chemical reactions and chemical and/or physical conditions. For example, HFC-23 by-product can be generated via different chemical processes, with the potential for that chemical process to occur across a range of different chemical pathways where the right mix of chemicals and conditions allows it (see Chapter 2).

A *by-product* is considered an ancillary product, which is created as the secondary result of a primary process to create an intended product. A by-product is created through chemical processes that are secondary to those creating the primary product. A by-product may be ancillary, but it is not necessarily unwanted if it is commercially valuable and can be economically and efficiently separated from the primary product and any other by-products.

Generation is the formation of a chemical arising from a chemical process used in chemical production. For this report, generation is defined as the total HFC-23 produced as a by-product, without taking into account abatement of emissions (see Chapter 3).

An *emission* is considered as the release of substance into the environment, often describing gas releases of substance to atmosphere but also substance released in solids or liquids. For this report, emissions are defined as the total HFC-23 emitted from a facility that either uses HFC-23 as a feedstock or generates HFC-23 as a by-product, after any abatement (see Chapter 3). Although HFC-23 may be emitted via different routes, the dominant emission pathway is direct emissions to atmosphere.

2 Information on the possible chemical pathways that could be used in the production of Annex C HCFCs and Annex F HFCs that may generate HFC-23 as a by-product

In response to decision XXXIV/7, paragraph a, this section describes information on the possible chemical pathways that could be used in the production of Annex C HCFCs and Annex F HFCs that may generate HFC-23 as a by-product.

2.1 Background to HFC-23 by-production

Section 2.3 of the MCTOC 2022 Assessment Report outlined several chemical pathways and processes that can generate HFC-23.

There are several chemical mechanisms that can, by their nature, generate HFC-23 as a by-product in chemical production processes, including:

- *Over- or under-reaction of chemicals* present in the reaction vessel enroute to the intended product, e.g., HFC-23 is an over-fluorination of HCFC-22.
- *Presence of impurities in the feedstocks that are being reacted*, e.g., the chloroform impurity in dichloromethane feedstock, used to produce HFC-32, is hydrofluorinated to HFC-23.
- *Unintended side reactions*, where the feedstock follows a different reaction path than the one that is desired to make the product, e.g., cleavage of carbon–carbon bond in the production of HFC-125 from perchloroethylene, with subsequent hydrofluorination of the resulting mono-carbon molecule to form HFC-23.

For many processes producing fluorinated controlled substances, HFC-23 by-product generation is possible. In the production of HCFC-22, HFC-23 by-product generation cannot be eliminated, with 1–3 wt% HFC-23 generation being typical. For other processes, very low generation rates are possible; with careful design and operation of the process, HFC-23 by-product generation rate can be minimised to less than 0.1 wt%, often less than 0.01 wt%, of production, with emission mitigation reducing the final HFC-23 emission rate further. For many HCFC and HFC production processes, little or no effort has been taken to date to eliminate HFC-23 by-product generation because the "natural" HFC-23 generation rate of the process is so low as to not make it cost-effective. With an effectively operated HFC-23 mitigation step, e.g., thermal oxidation on the process vents containing HFC-23, HFC-23 emission rates can be significantly lower than the HFC-23 by-product generation rates because destruction efficiencies can exceed 99%.

The design intent of most plants is to minimise the generation of by-products to the extent possible within the limits of inherent chemistry and available applied engineering. This is for financial reasons, where most processes typically seek to minimise generation of unwanted by-products to maximise desired feedstock to product conversion ratios. Unwanted by-products tend to have a detrimental economic effect because they:

- Consume feedstocks that cannot be (made into and) sold as final product.
- May require additional process steps (and cost) to remove them from final product and/or to mitigate emissions of by-product e.g., thermal oxidation.
- Make final product out of specification in some cases.

In some cases, however, 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.

By-product can be present in gaseous, liquid or solid waste streams and as impurities in products and co-products, from which there is potential for emissions. For example, HFC-23 emissions from HCFC-22 production may occur at several stages: direct emissions of HFC-23 from a vent; HFC-23 degassed to atmosphere during subsequent treatment of the aqueous effluent, possibly off-site; and, to a lesser extent, emissions resulting from HFC-23 present as an impurity in the finished HCFC-22 product and its emission.

2.2 Information on the chemical pathway used to produce HCFC-22 that generates HFC-23 as a by-product

HFC-23 is primarily generated by the fluorination of chloroform, via the chloroform, HCFC-21, HCFC-22 to HFC-23 pathway in fluorination or hydro-fluorination chemical processes.

The chemical pathway involving the two-step reaction of chloroform ($CHCl_3$) and anhydrous hydrogen fluoride (HF) to produce HCFC-22 ($CHClF_2$) is employed in many plants around the world.

1. $CHCl_3 + HF \rightarrow CHCl_2F + HCl$

   Chloroform fluorinated to HCFC-21

2. $CHCl_2F + HF \rightarrow CHClF_2 + HCl$

   HCFC-21 fluorinated to HCFC-22 (product)

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 the HCFC-22 can be removed from the reactor.

$CHClF_2 + HF \rightarrow CHF_3 + HCl$

HCFC-22 fluorinated to HFC-23 (by-product or co-product)

This process is widely understood to be the main source of global HFC-23 by-product generation, at around 95% of the estimated total global HFC-23 by-product generation[1]. HFC-23 generation[2] rates are typically around 1–3 wt%, or 10–30 kg of HFC-23 by-product generated per tonne of HCFC-22 and can be as high as 4 wt%.

Section 2.5 below estimates the relative generation rates of HFC-23 per tonne of production and global production for chemical pathways that may generate HFC-23 as a by-product, along with an indication of data quality on which to base estimations of HFC-23 generation rates.

[1] The estimated global generation of HFC-23 by-product based on current expert knowledge of production quantities and HFC-23 by-product generation rates by process is around 25 ktonnes per year, with a range of 16–32 ktonnes per year. HFC-23 generated will only be emitted if it is not captured, used as feedstock, or destroyed before it leaves the process, e.g., by incineration.

[2] HFC-23 generation is assumed to mean the total HFC-23 produced by the process, regardless of whether it is later destroyed by a mitigation stage in the same process, it is captured and destroyed at another location, leaves as an impurity in a final product or is emitted by the plant.

2.3 Information on chemicals pathways used to produce Annex C HCFCs, other than HCFC-22, and Annex F HFCs that may generate HFC-23 as a by-product

Chemical pathways used to produce Annex C, Group I, substances other than HCFC-22, and Annex F substances can also generate HFC-23 as a by-product, either because:

- They have chloroform present as an impurity in the feedstock, where impurity levels are typically less than 100 ppm (often less than 10 ppm) of chloroform, meaning that less than 0.1 kg (often less than 10 grams) of HFC-23 will be generated per tonne of Annex C, Group I, or Annex F substance.
- They can form either chloroform, HCFC-21 or HCFC-22 in their reaction step, e.g., by the chlorination of dichloromethane ($CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$). These species are then hydro-fluorinated to form HFC-23. The chemical pathway that uses dichloromethane as a feedstock to produce HFC-32 generates HFC-23 via this chemical process, estimated at rates less than ~1 kg of HFC-23 per tonne of HFC-32.
- For chemical processes using feedstocks with two or more carbon atoms, such as production of HFC-134a (from trichloroethylene) or HFC-125 (from perchloroethylene), HFC-23 can be formed following the breaking of one of the carbon–carbon bonds. In this case, the quantity of HFC-23 formed is believed to be small, with 0.1 kg, or less, of HFC-23 formed per tonne of product.[3]
- HFC-23 generation is also noted in HCFC-22 plant caustic scrubbers where NaF is present, making the fluorination of HCFC-22 to HFC-23 possible. This is a minor reaction under normal process plant operating conditions, typically increasing HFC-23 in the final HCFC-22 product by at most a few 10s of ppm (i.e., a few 10s of grams) of HFC-23 per tonne of HCFC-22 produced.
- The pyrolysis of HCFC-22 to make tetrafluoroethylene (TFE), which can be used to produce HFC-125, is known to generate small quantities of HFC-23, around 1 kg of HFC-23 per tonne of HCFC-22 consumed.
- The production of hexafluoropropylene (HFP) from HCFC-22, which can be used to make HFC-227ea, is understood to generate small quantities of HFC-23, around 1 kg of HFC-23 per tonne of HCFC-22 consumed. Typically, HFP is co-produced with TFE.
- Disproportionation is understood to occur as a minor reaction in some Annex F production processes (e.g., $2C_2HClF_4$ (HFC-124) $\rightarrow$ C_2H2F_4 (HFC-134a) + $C_2Cl_2F_4$ (CFC-114)). While HFC-23 generation is theoretically feasible, no evidence has been found that indicates that this mechanism leads to HFC-23 generation.

These chemical processes may be present in a range of chemical pathways used to produce Annex C HCFCs and Annex F HFCs (and other substances not controlled by the Montreal Protocol), meaning that a range of chemical pathways may generate HFC-23 as a by-product.

Some chemical pathways used to produce Annex C HCFCs and Annex F HFCs have good evidence of HFC-23 generation and its associated rates (e.g., HCFC-22 from chloroform). Other chemical pathways used to produce Annex C HCFCs and Annex F HFCs have more limited evidence of HFC-23 generation, although generation is theoretically feasible through any of the above chemical processes (e.g., HFC-32 from dichloromethane, HFC-125 from perchloroethylene, HFC-134a from trichloroethylene). Evidence is limited due to insufficient data, with a lack of emissions reporting and a lack of reference to HFC-23 generation in patents. Nevertheless, HFC-23 generation is theoretically

[3] HFC-23 generation was not found in at least one HFC-152a plant indicating that detectable HFC-23 generation by this route may require a fully halogenated carbon atom when the carbon–carbon bond is broken.

feasible and potentially present in trace amounts. For some chemical pathways, the rate of HFC-23 generation may be so low (practically zero) that HFC-23 would remain undetected in routine analysis.

With these data qualifications in mind, the chemical pathways that could be used to produce Annex C HCFCs other than HCFC-22 and co-produced HCFC-21 and Annex F HFCs that *may* generate HFC-23 as a by-product are:

- HFC-32 from dichloromethane
- HFC-125 from perchloroethylene, including co-production of HCFC-124 and HCFC-123
- HFC-134a from trichloroethylene, including co-production of HCFC-133a
- HCFC-142b from vinylidene chloride or trichloroethane
- HFC-152a from vinyl chloride
- HFC-143a from trichloroethane
- HFC-227ea from HFP
- HFC-245fa from pentachloropropane

In combination, these chemical pathways used to produce Annex C HCFCs other than HCFC-22 and Annex F HFCs are currently estimated to generate up to around 1% of total global HFC-23 by-product generation.[4]

Section 2.5 below estimates the relative generation rates of HFC-23 per tonne of production and global production for chemical pathways that may generate HFC-23 as a by-product, along with an indication of data quality on which to base estimations of HFC-23 generation rates.

2.4 Information on chemicals pathways used to produce substances other than Annex C HCFCs or Annex F HFCs that may generate HFC-23 as a by-product

Some chemical pathways used to produce substances other than Annex C HCFCs or Annex F HFCs, which are outside the scope of decision XXXIV/7, are understood to generate HFC-23 by-product. In combination, these chemical pathways are currently estimated to account for around 3–4% of the total global HFC-23 by-product generation. The largest contributor of these chemical pathways to global HFC-23 by-product generation is likely to be the pyrolysis of HCFC-22 to make TFE and HFP, which can be used to produce fluoropolymers. This process is understood to generate small quantities of HFC-23, up to around 1 kg of HFC-23 per tonne of HCFC-22 consumed (0.1 wt%)[5]. Other chemical pathways where HFC-23 by-product generation is theoretically feasible include those used to produce CFCs, namely CFC-113 from perchloroethylene and CFC-114 from perchloroethylene.

The production routes of other fluorochemicals outside of the scope of the decision have similarities to the chemical processes used to produce Annex C HCFCs and Annex F HFCs and hence could conceivably generate HFC-23 by similar mechanisms. The HFC-23 generation rate could be expected to be similar to other chemical pathways used to produce Annex F HFCs (typically less than 0.01 wt%). However, there is currently insufficient data available on production volumes and HFC-23

[4] There was only a limited amount of information available on likely HFC-23 generation rates from these processes at the time of writing this report so there is a reasonable degree of uncertainty for estimates of current global HFC-23 generation rates from these chemical pathways and processes.

[5] See MCTOC 2022 Assessment Report, section 2.3.2, Emissions of HFC-23 and PFC-c-318 from the manufacturing process used to produce tetrafluoroethylene and hexafluoropropylene from HCFC-22 for a discussion of HFC-23 generation.

generation rates in these processes to make anything other than rough estimates of possible HFC-23 generation for these processes.

Another potential chemical pathway is the fluorination of polyethylene by fluorine gas. While there is no direct published evidence, HFC-23 generation could be considered theoretically feasible in this process, particularly as it has been reported that short-chain perfluorinated carboxylic acids can be formed depending on conditions[6]. This chemical pathway is not considered further in this report.

2.5 Estimated global HFC-23 generation for chemical pathways that may generate HFC-23 as a by-product

Section 3 responds to decision XXXIV/7, paragraph b, which, among other things, requests the compilation of information on the amount of HFC-23 generation from facilities that manufacture Annex C, Group I, or Annex F substances, the reporting of which is required under Article 7 of the Montreal Protocol.

For additional context and understanding of the potential relative contributions to HFC-23 by-product generation, this section provides indicative estimations of relative global HFC-23 generation by relevant chemical pathways. These estimations can be made by considering the various processes identified to generate HFC-23 by-product (Sections 2.1 to 2.4), known chemical pathways and their global production rates (either reported to the Ozone Secretariat or estimated), the data compiled in Section 3, and estimated HFC-23 generation rates based on available data and/or expert opinion. MCTOC's assessment based on available data and expert opinion is shown in the matrix representation in Figure 2.1 and in Tables 2.1 and 2.2.

Figure 2.1 and Table 2.1 present estimations based on sufficient available data on HFC-23 by-product generation, even if the data are limited. Estimates include chemical pathways used to produce Annex C HCFCs, Annex F HFCs, and substances other than Annex C HCFCs and Annex F HFCs where HFC-23 by-product generation is more than around 10 tonnes per year globally.

Table 2.2 presents order of magnitude estimations of HFC-23 by-product generation for chemical pathways that can be used to produce controlled substances, including Annex C HCFCs, Annex F HFCs, and CFCs, where insufficient HFC-23 generation data are available. These estimates are based on MCTOC expert opinion.

It should be noted that there is currently a lot of uncertainty, including in the matrix representation in Figure 2.1, as there are little or no specific HFC-23 generation data available for many of the chemical pathways. What little HFC-23 generation data are available can be found in, for example:

- Patents, which may not reflect actual operating experience at scale or report anything other than an indication of the presence of HFC-23
- Reported HFC-23 emissions data, for which there typically is no indication of associated abatement or mitigation of any HFC-23 generation, or
- Occasional plant HFC-23 generation data, which may not be representative of the true global mean HFC-23 generation rate for the chemical pathway.

[6] See, for example, Amy A. Rand and Scott A. Mabury, Perfluorinated Carboxylic Acids in Directly Fluorinated High-Density Polyethylene Material, *Environmental Science & Technology,* 2011, **45**(19), 8053–8059. DOI: 10.1021/es1043968.

The process that has the most complete set of HFC-23 generation data[7], HCFC-22 production from chloroform, is also understood to be the major source of HFC-23 generation.

A more refined estimate of HFC-23 generation for chemical pathways would be possible through better data availability[8], which could alter the matrix in Figure 2.1 and Tables 2.1 and 2.2, and the current conclusions.

[7] The HFC-23 generation data from HCFC-22 production are available for numerous plants (e.g., through their UNFCCC CDM reports (https://cdm.unfccc.int/Projects/projsearch.html) and other national reporting programs) and has been widely discussed for many years leading to a broadly consensual view on the range and mean HFC-23 generation rates (Section 3.1). Annual HCFC-22 production has also been reported under the Montreal Protocol for many years (Ozone.unep.org).

[8] As plants producing controlled substances are typically covered by national environmental regulations and will seek to optimise their economic viability, it is likely that more data are gathered on HFC-23 generation than is currently available.

Figure 2.1 Matrix of estimated relative global HFC-23 generation for currently identified chemical pathways that may generate HFC-23 as a by-product (> ~10 tonnes per year globally), predicted based on reported global production and estimated mean HFC-23 generation rate

		Global production				
		<1000 tonnes of product per year	1,000–10,000 tonnes of product per year	10,000–100,000 tonnes of product per year	100,000–1 million tonnes of product per year	>1 million tonnes of product per year
HFC-23 mean generation rate from production	1–10 wt% 10–100 kg of HFC-23 generation per tonne of production					**1**
	0.1–1 wt% 1–10 kg of HFC-23 generation per tonne of production					
	0.01–0.1 wt% 0.1–1 kg of HFC-23 generation per tonne of production				**2, A, B**	
	0–0.01 wt% 0–100 grams of HFC-23 generation per tonne of production	<100 kg per year			**3**	

Note: The numbers in Figure 2.1 matrix refer to the reference numbers in Table 2.1 below

	Less than 100 tonnes of HFC-23 generated globally per year
	More than 10,000 tonnes of HFC-23 generated per year

Table 2.1 Reference table for the matrix of chemical pathways, for which generation of HFC-23 by-product (> ~10 tonnes per year globally) is estimated in Figure 2.1

Reference number	Substance produced	Chemical pathway	Estimated global production tonnage band for each chemical pathway (tonnes per year)	Estimated likely mean HFC-23 generation per tonne of process production globally[9] (weight %)	Availability of HFC-23 generation data
Pathways directly to controlled substances					
1	HCFC-22	Chloroform to HCFC-22, including co-production of HFC-23 and HCFC-21	>1 million	1–10[a]	Good
2	HFC-32	Dichloromethane to HFC-32	100,000–1 million	0.01–0.1[b]	Poor
3	HFC-125	Perchloroethylene to HFC-125, including co-production of HCFC-124 and HCFC-123	100,000–1 million	0.01–0.001[c]	Very poor
Pathways not directly to controlled substances					
A	TFE	HCFC-22 to TFE	100,000–1 million	0.01–0.1[d]	Poor
B	HFP	HCFC-22 to HFP	100,000–1 million	0.01–0.1[d]	Very poor

Supporting references and comments

a. MCTOC 2022Assessment Report, page 40; significant quantity of plant HFC-23 generation data, e.g., UNFCCC CDM projects (some dated).

b. MCTOC 2022 Assessment Report, page 44, US EPA, 2021, Stratospheric Protection Division, Office of Air and Radiation (OAR) Report, *Facilities with HFC-23 Emission*, April 2021[10]; limited quantity of actual plant HFC-23 generation and reported HFC-23 emission data.

c. TEAP 2023 Progress Report, page 41, US EPA, 2021, Stratospheric Protection Division, Office of Air and Radiation (OAR) Report, *Facilities with HFC-23 Emission*, April 2021; limited plant data. Annual global HFC-23 generation by this chemical pathway could credibly be below 10 tonnes per year.

d. MCTOC 2022 Assessment Report, page 41; and example environmental permit of TFE production plant[11].

[9] This is based on reported emissions or analysis from operating plants and or sites, it should be noted that for many pathways the quantity and quality of available data are limited and are subject to confirmation through further acquisition of data.

[10] http://www.regulations.gov/document/EPA-HQ-OAR-2021-0044-0046.

[11] EPR/BU5453IY/V004.

2.5.1 Order of magnitude estimation of HFC-23 by-product generation for chemical pathways to produce controlled substances where insufficient HFC-23 generation data are available

Table 2.2 presents estimates based on expert opinion of annual HFC-23 by-product generation for chemical pathways used to produce Annex C HCFCs, Annex F HFCs, and CFCs (outside the scope of this decision), where there is greater than 10,000 tonnes per year of global production and where little or no specific HFC-23 generation data are available.

These estimates have been included to support understanding of the likely order of magnitude of HFC-23 by-product generation from these chemical pathways.

Chemical pathways to produce HCFC-142b, HFC-143a, HFC-152a, HFC-227ea, HFC-245fa, CFC-113, and CFC-114, with annual production of greater than 10,000 tonnes per year, are each considered likely to have HFC-23 by-product generation of less than 1 tonne per year globally. The chemical pathway to produce HFC-134a from trichloroethylene, with annual production 100,000–1 million tonnes per year, is considered likely to have HFC-23 by-product generation of less than 10 tonnes per year globally.

Chemical pathways, with annual production of controlled substances of less than 10,000 tonnes per year each, are considered likely to have insignificant total global HFC-23 by-product generation and are not considered further in this report.

HCFC-21 is also produced for feedstock use at less than 10,000 tonnes per year; however, it is usually produced as a by-product from HCFC-22 production and any over fluorination to form HFC-23 can be considered associated with the production of HCFC-22 (the reaction pathway is HCFC-21 to HCFC-22 to HFC-23). If HCFC-21 is produced on dedicated HCFC-21 production plants, without HCFC-22 co-production, the magnitude of the HFC-23 generation rate would be expected to be lower.

It should also be noted that, when required as a product, HFC-23 is neither destroyed nor vented; rather, it is collected for use as a feedstock or for emissive uses, which are discussed in sections 3.3.3, 3.3.4, and 3.3.7.

Table 2.2 Table of expert opinion estimates of annual global HFC-23 generation for chemicals pathways producing >10,000 tonnes per year globally of controlled substances where little or no HFC-23 generation data are currently available

Controlled substance produced	Chemical pathway	Estimated global production tonnage band for each chemical pathway (tonnes per year)	Availability of HFC-23 generation data[12]	Estimate of annual HFC-23 generation (tonnes per year)
HCFC-142b	Vinylidene chloride/Trichloroethane	100,000–1 million	Insufficient data available.	<1
HFC-134a	Trichloroethylene to HFC-134a, including co-production of HCFC-133a	100,000–1 million	Limited evidence of trace HFC-23 being generated[a]	<10
HFC-143a	Trichloroethane	100,000–1 million	Insufficient data available. Lack of emission reporting and patent reference to HFC-23 generation could indicate only trace HFC-23 being generated	<1
CFC-113	Perchloroethylene to CFC-113	100,000–1 million		<1
HFC-152a	Vinyl chloride to HFC-152a	10,000–100,000	Insufficient data available. Lack of emission reporting and patent reference to HFC-23 generation could indicate only trace HFC-23 being generated, coupled with lower global production.	<1
HFC-227ea	HFP to HFC-227ea[13]	10,000–100,000		<1
HFC-245fa	Pentachloropropane	10,000–100,000		<1
CFC-114	Perchloroethylene to CFC-114	10,000–100,000		<1

Supporting references and comments

a. Limited plant data indicate very low levels of HFC-23 detected[14], with similar reactor chemistry to HFC-125; HFC-23 generation is likely to be small because emissions are not typically reported.

[12] This is based on reported emissions or analysis, or lack thereof, from operating plants and or sites. It should be noted that for many pathways the quantity of data is limited and subject to confirmation through further acquisition of data if the data become available. For some of these chemical pathways, the rate of HFC-23 generation may be so low (practically zero) as to be undetected in routine analysis.

[13] Note this pathway is only the HFP to HFC-227ea element; the chloroform to HCFC-22 and HCFC-22 to HFP elements are included in Table 2.1.

[14] One unpublished example, which analysed the components from the degassing tower after the HFC-134a reactors, found ~10ppm HFC-23, confirming HFC-23 generation in trace quantities.

2.5.2 HFC-23 by-production due to the electrochemical production of fluorocarbons

It has been reported that electrochemical production of fluorocarbons can produce HFC-23 by-product[15]. A site undertaking the electrochemical production of fluorocarbons has reported annual HFC-23 emissions in excess of 40 tonnes (Section 3). Therefore, it could be expected that because the electrochemical production of fluorochemicals generates more than 10 tonnes per year of HFC-23 by-product, these chemical pathways should be included in the matrix or the tables. However, as information on the substances produced, their HFC-23 generation rates, and the estimated global production tonnages are not generally available to MCTOC, HFC-23 by-product generation during electrochemical production of fluorocarbons is not included in the matrix or tables.

2.5.3 HFC-23 generation rates during the production of HFOs

HFOs are not Annex C HCFCs or Annex F HFCs, and, as also for TFE and HFP, are outside the scope of decision XXXIX/7.

HFO production is not included in Tables 2.1 and 2.2 because insufficient data are currently available. However, it is reported that some chemical pathways and processes used to produce HFO-1234yf go through HCFC-22, HFP and/or TFE intermediates[16]. If the quantity of HCFC-22 is reported as feedstock to the Ozone Secretariat, then its associated HFC-23 by-product generation would be accounted for in the respective feedstock related HFC-23 generation. If the HCFC-22 is not reported as feedstock (unlikely), then additional HFC-23 by-product generation not currently accounted for may be taking place.

2.5.4 HFC-23 generation rates through fluoropolymer destruction

There is the possibility that HFC-23 can be generated during the destruction of fluoropolymers[17]. There is currently no data relating to HFC-23 generation rates from real-life destruction of fluoropolymers.

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[15] MCTOC 2022 Assessment Report, page 45.

[16] MCTOC 2022 Assessment Report, page 38.

[17] Huber, S., Moe, M.K., Schmidbauer, N., Hansen, G.H., Herzke, D., *Emissions from incineration of fluoropolymer materials. A literature survey*, The Norwegian Pollution Control Authority (SFT), NILU OR 12/2009, 2009, https://www.nilu.com/publication/24739/. Accessed August 2023.

3 Compilation of information on the amount of HFC-23 generation and emissions from facilities that manufacture Annex C, Group I, or Annex F substances

This section responds to decision XXXIV/7, paragraph b, that requests the compilation of information on the amount of HFC-23 generation and emissions from facilities that manufacture Annex C, Group I, or Annex F substances, the reporting of which is required under Article 7 of the Montreal Protocol.

Generation is defined here as the total HFC-23 produced as a by-product, without taking into account abatement of emissions.

Emissions are defined here as the total HFC-23 emitted from a facility that either generates HFC-23 as a by-product or uses HFC-23 as a feedstock. Although HFC-23 may be emitted via different routes, the dominant emission pathway is direct emissions to atmosphere (see Section 1.4).

There are three main sources of information for the amounts of HFC-23 generation:

- A global estimate of the generation of HFC-23 using a default HFC-23 emission factor, assuming no abatement methods, and the global production of HCFC-22. There is limited information on the generation of HFC-23 from other processes.
- HFC-23 generation reported by parties, which is an optional report, under Article 7 of the Montreal Protocol.
- Data submitted to the Executive Committee (ExCom) as part of project proposals to enable compliance with the HFC-23 by-product control obligations of the Kigali Amendment. Data for individual production units are also available. The May 2023 TEAP Decision XXXIV/2 Replenishment Task Force Report summarises the information[18].

In addition, some data are available from UNFCCC submissions by Annex 1 countries. Generation rates for individual facilities are reported historically for CDM projects. There is limited information for generation rates for other sources of HFC-23.

There are three main sources of information for the amounts of HFC-23 emissions:

- Annual emissions derived from atmospheric monitoring as reported by the Science Assessment Panel (SAP), including the SAP 2022 Assessment Report, known as top-down emissions.
- Annual emissions reported by parties either to UNFCCC for Annex 1 countries, and/or as required under Article 7 of the Montreal Protocol. In practice, most available emission reports are for the emissions of HFC-23 from HCFC-22 production. Reported emissions are described as bottom-up emissions.
- Data submitted to ExCom as part of project proposals to enable compliance with the HFC-23 by-product control obligations of the Kigali Amendment. Data for individual production units are also available. The May 2023 TEAP Decision XXXIV/2 Replenishment Task Force Report summarises the information[19].

[18] May 2023 TEAP Decision XXXIV/2 Replenishment Task Force Report, Chapter 4, HFC Production sector and HFC-23 by-product emission mitigation.

[19] Ibid.

3.1 Compilation of information on the amount of HFC-23 generation from facilities that manufacture Annex C HCFCs or Annex F HFCs

3.1.1 Estimate of the amount of HFC-23 generation from HCFC-22 production using default emission factors

The 2019 Refinement to the 2006 Intergovernmental Panel on Climate Change (IPCC) Guidelines for National Greenhouse Gas Inventories, Chapter 3 provides default emission factors for HFC-23 emissions from HCFC-22 production, assuming no abatement methods, which means HFC-23 emission factors equals HFC-23 generation factors.

Table 3.1 2019 Refinement to 2006 IPCC Guidelines for National Greenhouse Gas Inventories, HFC-23 Default Emissions Factors

3.28 (UPDATED) HFC-23 DEFAULT EMISSION FACTORS	
Technology	**Emission Factor (kg HFC-23/kg HCFC-22 produced)** *equals generation factors*
Old, unoptimised plants (e.g., 1940s to 1990/1995)	0.04
Plants of recent design, not specifically optimised	0.03
Global average emissions (1978–1995) (*see note)*	0.02
For comparison: – *Optimised large plant requiring measurement of HFC-23 (Tier 3)* – *Plant with effective capture and destruction of HFC-23 (Tier 3)*	 *Down to 0.015* *Down to zero*

Note: The global average is calculated from the change in atmospheric concentration of HFC-23. It does not discriminate between plant emissions, which range from nothing to greater than 4 percent of the HCFC-22 production.

Assuming the global HFC-23 generation factor is in the range 1.5% to 3%, allows the estimation of HFC-23 generation from total HCFC-22 production. This indicates that HFC-23 by-product generation from HCFC-22 production is expected to be in the range of about 15,000 to 30,000 tonnes per year.

Table 3.2 Estimate of the amount of HFC-23 generation from HCFC-22 production using default factors

	2019	**2020**	**2021**
Total HCFC-22 production	1,018,687	946,190	1,060,940
HFC-23 generation at 1.5%	15,280	14,193	15,914
HFC-23 generation at 3.0%	30,561	28,386	31,828

3.1.2 Compilation of data on the amount of HFC-23 generation reported by parties

Data on HFC-23 generation reported by parties is an optional report under Article 7 of the Montreal Protocol. HFC-23 generation data are not reported for all parties that are known to produce HCFC-22. Some parties would not have been expected to report optionally for each of these years (2019, 2020, 2021) because of when parties ratified the Kigali Amendment and associated obligations.

Annex 1 countries annually provide to the UNFCCC publicly available National Inventory Reports (NIRs) and detailed data in Common Reporting Format tables (CRF). For some countries, the amounts of HFC-23 generation can be inferred from HFC-23 emissions and recovery[20].

The available data for 2020 and 2021 from both Article 7 and UNFCCC for quantities of HFC-23 generated are from about 80% of the reported global HCFC-22 production. For both these years, the calculated HFC-23 by-product generation rate is about 2.4% for the relevant reported HCFC-22 production. For 2019, much less data are available and is not considered representative. Most of the HFC-23 by-product generation rates reported for 2020 and 2021 are in the range 1.5–3%, with some just outside this range and one country's data at about 5%. Overall, this is broadly consistent with the HFC-23 generation rate indicated previously in MCTOC 2022 Assessment Report[21], *"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.*"

Applying the HFC-23 by-product generation rate of 2.4% to the total reported HCFC-22 production provides an indication of the total HFC-23 by-product generation, estimated at about 25,000 tonnes in 2021.

Table 3.3 Estimate of the amount of HFC-23 generation from HCFC-22 production using reported Article 7 data

	2019	2020	2021
Total HCFC-22 production	1,018,687	946,190	1,060,940
HFC-23 generation at 2.4%	24,448	22,709	25,463

3.1.3 Compilation of data on the amount of HFC-23 generation reported to ExCom

The May 2023 RFT Report summarises the HFC emissions data for five parties (Argentina, China, India, the Democratic People's Republic of Korea and Mexico) that have reported 2021 data for HFC-23 production and emissions under the Kigali Amendment.

In 2018, Argentina reported the production of 1,192 tonnes of HCFC-22. ExCom 82/69 estimated the proportion of HFC-23 as about 3.3% of the HCFC-22 produced. Table 3.4[22] provides data for 2018 on 11 HCFC-22 production plants in China that applied for government subsidies, with production of HCFC-22 of 598,098 tonnes.

[20] The Russian Federation in CRF Table 2(II)BHs-1 has emission and recovery data for HFC-23 from HCFC-22 production. It also has HCFC-22 production quantities (the activity data). From this data, the emission rate can be assumed to be a generation rate, based on the calculated emission rate.

[21] MCTOC 2022 Assessment Report, Section 2.3.1, HFC-23 by-production from HCFC-22 production, page 40.

[22] Reproduced from May 2023 TEAP Decision XXXIV/2 Replenishment Task Force Report, Chapter 4 HFC Production sector and HFC-23 by-product emission mitigation, Table 4-1.

Table 3.4 Amounts of HCFC-22 and HFC-23 produced as well as HFC-23 incinerated in plants that received subsidies in 2018 in China (Table 4-1, May 2023 RTF Report)

Producer	HCFC-22 production (tonnes)	HFC-23 production (tonnes)	% of HFC-23 formed	Incinerated HFC-23 (tonnes)
Dongyue Chemical Co (Shandong)	207,043.5	4,244.93	2.05	4,244.88
Quhua Co (Zhejiang)	91,298.0	2,072.23	2.27	2,065.15
Meilan (Jiangsu)	101,469.9	2,803.39	2.76	2,803.18
3F Changsu (Jiangsu)	39,312.3	1,135.27	2.89	1,134.82
ZhongHao ChenGuang (Sichuan)	34,868.6	890.6	2.55	884.79
Linhai Limin Chemical (Zhejiang)	25,750.2	525.3	2.04	524.8
Arkema Changshu (Jiangsu)	37,942.7	724.7	1.91	722.38
Sanmei Chemical (Zhejiang)	13,977.2	344.88	2.47	340.01
Jinhua Yonghe (Zhejiang)	24,185.0	496.37	2.05	450.55
Lanxi Juhua (Zhejiang)	25,551.5	704.38	2.76	424.95
Pengyou Chemical (Zhejiang)	9,459.8	210	2.22	218.24
Average	/		2.32	
Totals	**610,858.70**	**14,152.05**	**/**	**13,813.75**

The Democratic People's Republic of Korea HCFC-22 production facilities have not had a CDM project and have not built destruction facilities. The RTF has assumed that HFC-23 is vented at these two facilities at the level of 3% HCFC-22 production.

In India, 5 HCFC-22 production facilities have implemented a CDM project in the past. Destruction facilities continue to be operated after the expiration of the CDM projects. The September 2021 RTF Report, based on ExCom Document 82/68, estimates a HFC-23 generation rate for India of 2.9% in 2018[23]. For 2021, India reported zero emissions of HFC-23 in 2021 (and HFC-23 production of 607.6 tonnes, although most of this was reported to be destroyed) under Article 7.

In 2018, Mexico reported the production of 7,718 tonnes of HCFC-22, with a 1.96% ratio of HFC-23 generated as a by-product.

In summary, the HFC-23 generation data reported to ExCom are, as expected, similar to the average HFC-23 generation rates from data from Article 7 and UNFCCC submissions.

3.2 Compilation of information on the amount of HFC-23 emissions from facilities that manufacture Annex C HCFCs or Annex F HFCs reported by parties (Montreal Protocol) and Annex 1 countries (UNFCCC)

The HFC-23 emissions data reported under Article 7 are incomplete for 2019, 2020 and 2021 due to the timing of reporting obligations, for example, depending on when parties ratified the Kigali Amendment. The data set for 2021 is the most complete, with HFC-23 emissions data from HCFC-22

[23] September 2021 TEAP Decision XXXI/1 Replenishment Task Force Report, Table 4-2, Amounts of HFC-23 estimated in 2015 and 2018 in A5 Parties.

production reported by 10 parties, including individual European Union member states. The 10 parties reported 1,286.6 tonnes of HFC-23 emissions in 2021. A total of 13 parties are currently reporting HCFC-22 production.

Annex 1 countries provide publicly available National Inventory Reports (NIRs) and detailed data in Common Reporting Format tables (CRF) annually to the UNFCCC[24]. The CRF tables report emissions of HFC-23 as a by-product from fluorochemical production and as fugitive emissions[25]. Some countries also report activity data (HCFC-22 production); however, this can also be classed as confidential or in some instances appears incomplete, when compared to Article 7 data, possibly due to confidentiality requirements. Table 3.5 summarises the HFC-23 emissions data from the Common Reporting Format tables[26].

Table 3.5 HFC-23 emissions data from HCFC-22 and other chemical production reported to UNFCCC (tonnes) (from CRF tables)

HFC-23 emissions from HCFC-22 production (tonnes)	**2020**	**2021**
European Union	9.99	17.81
Japan	9.5	8.9
Russian Federation	1174.16	1105.14
United States of America	141.96	180.26
HFC-23 fugitive emissions from chemical production (tonnes)	**2020**	**2021**
European Union (reported to be from electrochemical fluorination)	48.73	8.05
Japan	NA	NA
Russian Federation	0.12	0.13
United States of America	NA	NA

Allowing for duplicate reports, the combined HFC-23 emissions reported as by-product from HCFC-22 production (UNFCCC and under Article 7) is 2,572 tonnes in 2021. It is possible that some Article 7 data also include HFC-23 emissions from facilities that manufacture other Annex C, Group I, or Annex F substances, however this does not appear to be the case for the European Union[27]. Nevertheless, the reported HFC-23 emissions should include emissions from over 99% of the total HCFC-22 production (feedstock and non-feedstock), from a comparison of the countries that have reported emissions (Article 7 and UNFCCC) and their reported HCFC-22 production as a share of the total reported HCFC-22 production.

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[24] UNFCCC, Greenhouse Gas Inventories, Annex I Countries, National Inventory Submissions 2023, National Inventory Submissions 2023 | UNFCCC

[25] CRF table guidance states "*Fugitive emissions include emissions from fluorinated gas (F-gas) production. Some of the possible activities include the telomerization process used in the production of fluorochemicals fluids and polymers, photo oxidation of tetrafluoroethylene to make fluorochemical fluids, sulphur hexafluoride (SF_6) production, halogen exchange processes to make low-boiling PFCs like C_2F_6 and CF_4, HFC-134a and HFC-245fa, NF_3 manufacturing, and production of uranium hexafluoride, of fluorinated monomers (e.g. tetrafluoroethylene and hexafluoropropylene), and of fluorochemical agrochemicals and/or anaesthetics. Both production and handling losses are to be included.*"

[26] CRF Table2(II) and Table 2(II)BHs-1 contain the relevant data.

[27] The Article 7 emissions data for the European Union member states are virtually identical to the UNFCCC European Union emissions data from HCFC-22 production. This indicates that other HFC-23 emissions reported by the EU to the UNFCCC are from facilities that do not manufacture Annex C, Group I, or Annex F substances.

3.2.1 Compilation of data on amounts of HFC-23 emissions reported to ExCom

Five Article 5 parties (Argentina, China, India, DPRK and Mexico) have reported 2021 data for HFC-23 emissions under the Kigali Amendment. The quantities of HFC-23 emissions reported by the relevant parties in 2021 is: Argentina (33.31 tonnes), China (1,089.95 tonnes), DPRK (8.40 tonnes), India (0.00 tonnes) and Mexico (128.52 tonnes), respectively.[28]

HFC-23 emissions for individual production units in China in Table 3.4 can be calculated from the reported HFC-23 production and destruction data, if no HFC-23 is captured for use as a feedstock or for consumption.

3.2.2 HFC-23 emissions reported from electrochemical fluorination

Some data are available in CRF tables from submissions to UNFCCC by Annex 1 countries for HFC-23 emissions from chemical processes other than as a by-product of HCFC-22 production, and these are shown in Table 3.5. The reported fugitive HFC-23 emissions for the European Union (2020: 48.73 tonnes; 2021: 8.05 tonnes) are indicated to be from electrochemical fluorination processes, according to a European Union member state in its NIR submission to UNFCCC[29]. In the period 2010 to 2020, the average of reported HFC-23 emissions was 62.33 tonnes per year. *"The emissions of category 2B9 (Production of halocarbons) are those of an electrochemical synthesis (electro-fluorination) plant, which emits, or has emitted, PFCs and HFCs, as well as fluorinated greenhouse gases not covered by the Kyoto Protocol. This plant produces a broad range of fluorochemical products, which are used as basic chemicals as well as end products, mainly in the electronics industry. The processes used in this electro-fluorinated plant are unique within Europe (there are however some similar plants in the US). This means that there are no established guidelines for monitoring and reporting."*

3.3 Information on HFC-23 emissions, including from sources other than facilities that manufacture Annex C HCFCs or Annex F HFCs

Sections 3.1 and 3.2 respond to decision XXXIV/7 paragraph b. This section provides additional contextual information on HFC-23 emissions, including from sources other than facilities that manufacture Annex C HCFCs and Annex F HFCs such as feedstock and consumptive uses. While outside the scope of decision XXXIV/7, this additional contextual information was considered useful in understanding the relative importance of HFC-23 emissions from chemical pathways used in the production of Annex C, Group I, or Annex F substances that may generate HFC-23 as a by-product, which is the focus of decision XXXIV/7.

3.3.1 HFC-23 emissions derived from atmospheric monitoring

The SAP 2022 Assessment[30] reports a rise in HFC-23 emissions derived from atmospheric monitoring to 17.2 ± 0.8 Gg yr^{-1} (17,200 tonnes) in 2019, and a similar value of 16.5 ± 0.8 Gg yr^{-1} (16,500 tonnes) in 2020. Up until 2013, global bottom-up emissions, derived from reported data, track (within ± 2 Gg yr^{-1}, 2,000 tonnes) the global emissions derived from atmospheric measurements. Similarly, up until 2013, the ratio of HFC-23 emissions to HCFC-22 production (E23/P22) derived from atmospheric data closely matched that derived from bottom-up estimates. Between 2015 and 2019, as reported abatement increased dramatically in China and India, bottom-up emissions (derived from

[28] The data for Argentina, China, DPRK and Mexico are cited from the Country Programme Data and Prospects for Compliance. UNEP/OzL.Pro/ExCom/91/8.

[29] Belgium NIR submission 2023, section 4.3.2.7, Fluorochemical production (category 2B9), available at National Inventory Submissions 2023 | UNFCCC.

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

reported data) and E23/P22 declined substantially. However, emissions and E23/P22, derived from atmospheric data, increased. By 2019, the difference between top-down and bottom-up emissions and E23/P22 was the largest since atmospheric records began. Stanley et al. (2020)[31] estimated that only 27% of the reported global abatement capacity was achieved in 2018. The SAP reported that a small number of regional top-down studies have provided additional information on the spatial distribution of global HFC-23 emissions. However, none of these studies can explain the discrepancy between bottom-up and top-down global emissions after 2016.

This compares with the combined reported HFC-23 emissions from HCFC-22 production (UNFCCC and under Article 7), as noted above, which is 2,572 tonnes in 2021.

3.3.2 HFC-23 by-product emissions from the production of TFE/HFP

Section 2.4 and 2.5 describe HFC-23 by-product generation from the pyrolysis of HCFC-22 to produce TFE and HFP, which is estimated to generate up to around 1kg of HFC-23 per tonne of HCFC-22 consumed (0.1 wt%). Taking into account estimated global production, HFC-23 generation of between 100 to 1,000 tonnes might be expected, with some uncertainty.

As described in the MCTOC 2022 Assessment Report[32], although some TFE/HFP production facilities would have abatement technology, data are not available to enable an accurate estimate of global HFC-23 emissions from TFE/HFP production. As a theoretical upper estimate, HFC-23 emissions could be as high as total global HFC-23 by-product generation, estimated in this report to be in the range 100–1,000 tonnes. The MCTOC 2022 Assessment Report used indicative low to medium HFC-23 by-product generation rates for TFE/HFP production, based on HCFC-22 feedstock use, to estimate HFC-23 by-product emissions, without consideration of their possible abatement, of between 280–1,040 tonnes[33].

3.3.3 Use of HFC-23 as feedstock

A main use of HFC-23 as feedstock is production of halon 1301 (bromotrifluoromethane), which is then used as a feedstock for fipronil and other chemical production[34]. HFC-23 emissions arise from this feedstock use; from the supply of the HFC-23 and from chemical processes where HFC-23 is used as feedstock. Feedstock production for internal use and imports are reported by parties, under Article 7. Some parties have not been required to report HFC data for each of these years (2019, 2020, 2021) due to the timing of reporting obligations, such as when parties ratified the Kigali Amendment.

Although Halon 1301 is produced from HFC-23, other possible routes to produce Halon 1301 have been reported; it is not known if these routes are used commercially[35]. However, HFC-23 is readily available as a by-product from HCFC-22 production, which means that other routes may be less commercially attractive. Over that last 10 years further uses of HFC-23 as feedstock have been

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[31] 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.

[32] MCTOC 2022 Assessment Report, section 2.3.2, page 42.

[33] Reported 2020 HCFC-22 feedstock data are 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.

[34] 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).

[35] See, for example, China patent, CN102516021A, Method for producing bromotrifluoromethane by monochlorodifluoromethane thermal bromination process.

investigated and proposed, but some of these are potentially very low quantities[36,37], have low selectivity or rapid catalyst deactivation[38,39]. An overview of some feedstock uses of HFC-23 was included in a presentation at the China HFC-23 mitigation workshop[40]. 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[41], 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. A demonstration plant in the same HCFC-22 production unit in China has been reported. This feedstock use will eliminate HFC-23 emissions from HCFC-22 production.

$$CHF_3 + CHCl_3 \rightarrow CHClF_2 + CHCl_2F$$

HFC-23 *chloroform* *HCFC-22* *HCFC-21*

In 2021, the available data from Article 7 reporting show that for two parties the reported quantities of HFC-23 produced as feedstock broadly match the reported quantities of halon 1301 produced as feedstock. However, one party reports significant halon 1301 production, but no HFC-23 production or imports of HFC-23 for feedstock use. Another party reports significant HFC-23 production, but no halon 1301 production. These parties might be using other chemical processes, either to produce halon 1301 or not using HFC-23 to produce or isolate halon 1301.

The total reported HFC-23 feedstock production (for own use and imports) in 2021 is 734 tonnes, although the reported data may be incomplete due to timing of reporting obligations. The reported halon 1301 feedstock production (for own use and imports) in 2021 is 1,796 tonnes[42].

3.3.4 HFC-23 emissions from feedstock use

The MCTOC 2022 Assessment Report provides emission factors for production, distribution, and feedstock use[43]. The most likely emission factors for modern-day regulated manufacturing are summarised in Table 3.6. Only emissions from the supply chain and from feedstock conversion are

[36] 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.

[37] 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.

[38] 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 LaF3–BaF2 composites for the coupling of CH4 with CHF3 to VDF, *Catal. Sci. Technol.*, 2019, **9**, 1338. https://doi.org/10.1039/C8CY02376J.

[39] 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 CH4 with CHF3 for the synthesis of VDF over LaOF catalyst, *Greenhouse Gas. Sci. Technol.*, 2018, **8**, 587–602. https://doi.org/10.1002/ghg.1769.

[40] 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.

[41] 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.

[42] The data confidentiality rules applied allow disclosure of these feedstock quantities. Three-party rule: Any value that is published must be the sum of at least three different parties. 5% significance rule: The contributions of some parties to any value may be insignificant, therefore, a value remains confidential if fewer than three parties make up more than 95% of the total.

[43] MCTOC 2022 Assessment Report, Tables 2.6, 2.7, 2.8.

relevant here because the emissions from HFC-23 generated as a by-product from HCFC-22 production are already considered under HCFC-22 production.

Table 3.6 Most likely emission factors for modern-day, regulated manufacturing activities

Production and supply chain emissions – Current Day in Heavily Regulated Sophisticated Plants	
Production emission factor (most likely) *Emission factors from use as feedstock are different and additive (not applicable for by-product)*	*0.9–4%* *Mean ~2.5%*
Distribution emission factors to be used depend on knowledge of applicable supply chain	0.3–1.2%
Feedstock emissions from feedstock conversion plants – Current Day in Heavily Regulated Sophisticated Plants	
Losses from feedstock process including maintenance	0.3– 0.9% Mean 0.6%
Total emission factor from supply chain and feedstock conversion	
	0.6–2.1% Mean ~1.4%

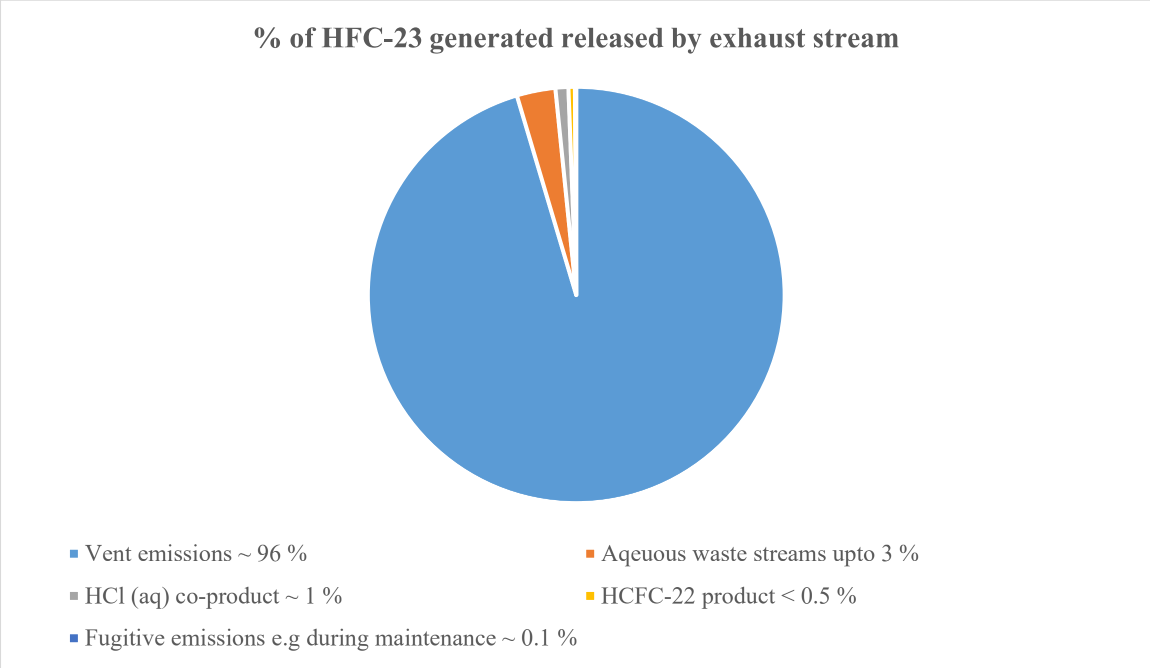
Applying these emission factors to the production and use of reported HFC-23 feedstock in 2021 results in HFC-23 emissions for feedstock use in the range 4 to 15 tonnes with a mean of 10 tonnes.

3.3.5 HFC-23 emissions as an impurity in other chemicals

Most HFC-23 will be released through the plant vent(s), and/or mitigated, on the site where the HFC-23 is generated. However, there is the possibility of a wide dispersal of the small percentage of HFC-23 generated that is entrained/contained within products and waste streams leaving the process where HFC-23 is generated. For example:

- Products including HCFCs, HFCs and co-produced HCl(aq.) have been found to contain up to ~0.04 wt% of HFC-23.
- HFC-23 contained as an impurity within HCFC or HFC products will likely be released to the atmosphere when the HCFC or HFC product is released, either during use or at end of life.
- HFC-23 contained within co-produced HCl(aq.) will slowly degas to atmosphere when the HCl(aq.) is transferred to a storage system that vents to atmosphere or during use (e.g., in metal pickling vats).
- Aqueous waste streams resulting from contact with process streams containing HFC-23 (e.g., in plant scrubbing systems) will contain a small quantity of HFC-23 (possibly up to 0.1 wt%, although often considerably less) that will eventually enter the atmospheric compartment, either at the waste treatment plant or in the wider environment, e.g., river system into which the treated aqueous effluent is ultimately discharged under regulatory permit.

Figure 3.1 HFC-23 emissions from an HCFC-22 plant by exhaust stream, circa. late 1990s



Note: The example HCFC-22 plant operated with an HFC-23 generation rate of 3–4 wt% HFC-23 per tonne HCFC-22 produced. Current HCFC-22 plants may have different emission rates due to variations and improvements in design and operation.

These small, but potentially widely distributed, HFC-23 emissions associated with the use of the products could manifest themselves as either a more generalised widespread HFC-23 emission or a localised point source HFC-23 emission, possibly both being a considerable distance from the HFC-23 by-product generating plant and not directly relatable to that plant's production timings.

3.3.6 Estimated emissions of HFC-23 from the HCFC-22 bank

Banks are the total amount of substances contained in existing equipment, chemical stockpiles, foams, and other products, not yet released to the atmosphere. The HCFC-22 bank is discussed in the MCTOC 2022 Assessment Report[44]. Emissions of HCFC-22 from the bank are mainly due to leakage and end-of-life emissions from refrigeration and air-conditioning equipment. HFC-23 as an impurity in HCFC-22 refrigerant will also be emitted to atmosphere. HFC-23 emissions can be estimated from its concentration as an impurity in HCFC-22 and the reported emissions of HCFC-22.

HFC-23 impurity in HCFC-22 is typically <150 ppm (see Figure 3.1), and it is assumed that all HCFC-22 contains 100 ppm of HFC-23. SAP 2022 reports annual emissions of HCFC-22, which are shown in Figure 3.2 reproduced from the SAP report. The reported HCFC-22 emissions[45] are: for 2016, 375 ± 53 Gg/yr (AGAGE), 373 ± 51 Gg/yr (NOAA); for 2020, 348 ± 55 Gg/yr (AGAGE), 337 ± 53 Gg/yr (NOAA).

[44] MCTOC 2022 Assessment Report, Section 8.2.3.3, HCFC-22 banks and amounts reaching end-of-life.

[45] World Meteorological Organization (WMO). *Scientific Assessment of Ozone Depletion: 2022*, GAW Report No. 278, 509 pp.; WMO: Geneva, 2022.

Figure 3.2 From SAP 2022, Figure 1-3: Atmospheric observation-based “top-down” global emission estimates (Gg yr^{-1}) for long-lived ozone-depleting substances

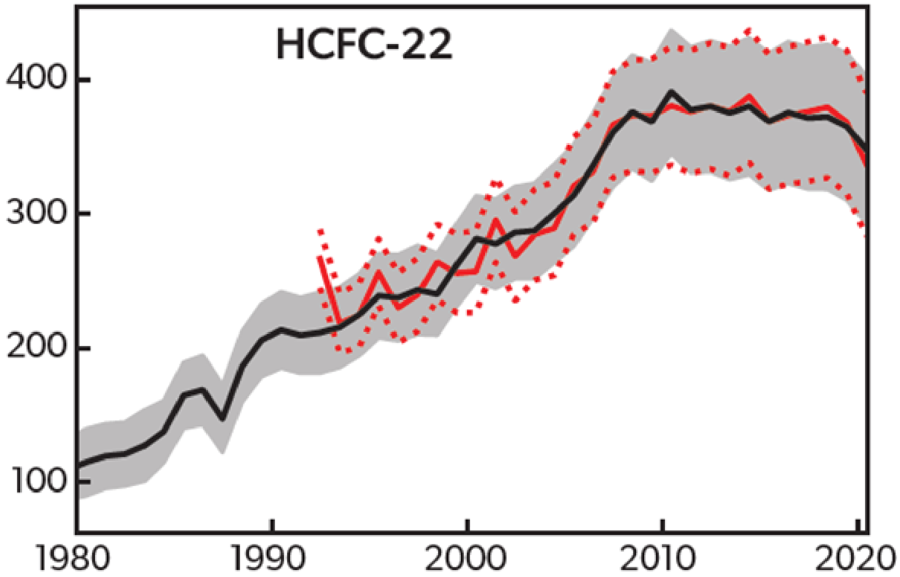


Table 3.7 presents estimated HFC-23 emissions assuming 100 ppm impurity in HCFC-22. Estimated HFC-23 emissions from this source, as an impurity in HCFC-22, are about 40 tonnes per year.

Table 3.7 Estimated emissions of HFC-23 as impurity in HCFC-22, assuming 100 ppm HFC-23 impurity

Year	HCFC-22 emissions per year (kilotonnes)	HFC-23 emissions per year as impurity (tonnes)
2016	375	37.5
2020	348	34.8

3.3.7 Production and consumption of HFC-23 for emissive uses

There are three main industry sector uses of HFC-23 that result in potential emissions:

- Fire suppressant
- Low temperature refrigerant
- Etchant and chamber cleaning in semiconductor and electronics manufacturing

Use as fire suppressant and low temperature refrigerant creates a bank of installed equipment containing HFC-23. Emissions can occur during manufacture (filling), use, and at end-of-life. The use of HFC-23 as an etchant and for chamber cleaning results in emissions of unreacted HFC-23 that can be significantly reduced by implementation of emissions control technologies.

In 2021, the consumption of HFC-23, reporting of which is required under Article 7 of the Montreal Protocol, was about 1,000 tonnes. Consumption data are not available for all parties due to the timing of reporting obligations. Some data are available from other sources relating to the quantities used and emissions for each of these applications.

3.3.8 Emissions of HFC-23 from use as fire suppressant

The 2022 FSTOC Assessment Report states it is not possible to estimate the amount of HFC-23 used in fire protection from atmospheric measurements. HFC-23 is typically limited to use in cold temperature applications. Only limited information on actual amounts of HFC-23 used in fire protection is available and indicates that it is typically small compared to HFC-227ea. FSTOC estimates HFC-23 is about 1% of HFC-227ea use. The model used by FSTOC for HFC-227ea provides estimated fire protection emissions of 5,250 metric tonnes and a global HFC-227ea fire protection bank of 168,000 metric tonnes for the end of 2022[46].

Based on this indicative estimate, and assuming similar emission factors are applicable, HFC-23 fire protection emissions would be about 50 tonnes for the end of 2022, with a fire protection bank of about 1,700 tonnes. These estimates are similar to the data reported in UNFCCC submissions for 2021[47] (Table 3.8), taking into account that there are limited available data as reporting does not apply to non-Annex I countries, for example, China and India.

Table 3.8 HFC-23 consumption, banks and emissions data for fire protection reported to UNFCCC (from CRF tables)

2021	Filled into new manufactured products (tonnes)	In operating systems (average annual bank) (tonnes)	Product life factor % emissions	Disposal loss factor (%)	Emissions (tonnes)		
					From bank	From disposal	Total
USA	9.26	154.77	1.56		2.42		2.42
EU	1	919.6	2.14	8.57	19.64	1.06	20.7
Japan	0	581.88	0.09				0.51
Australia	0.41	5.13	0.05	0.28	0.27	0.32	0.407
Total		**1661.38**					**24.037**

Note: Australia includes recovery of 0.18 tonnes in its total emissions. Canada, Iceland, New Zealand, Norway, Russian Federation, Switzerland, Turkey and UK report no emissions for HFC-23 in 2021 for this application.

3.3.9 Low temperature refrigerant

Due to its very low boiling point (-82°C), HFC-23 is used as a low temperature refrigerant. The 2022 TOC Refrigeration, AC and Heat Pumps Assessment Report (RTOC 2022) discusses the use of HFC-23 in transport refrigeration (super freezers) and pharmaceutical applications[48]. There is only a very small consumption of HFC-23 in RACHP applications. It is only used in ultra-low temperature (ULT) refrigeration equipment (e.g., below -50°C) as the refrigerant in the low temperature stage of cascade refrigeration systems. For these applications HFC-23 can be used as a pure fluid or as a component in blends. One ULT use is small storage cabinets (similar to domestic refrigerators) for medical products that must be stored at ULT, e.g., vaccines, tissue samples etc. These are factory-built sealed systems, so leakage is close to zero, but there could be emissions at end-of-life if refrigerant is not recovered.

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[46] 2022 Fire Suppression Technical Options Committee Assessment Report, Section 6.4.3, HFC-23 Estimates.

[47] National Inventory Submissions 2023 | UNFCCC CRF Table2(II) and Table 2(II)BHs-2 contain the relevant data when available.

[48] 2022 Refrigeration, AC and Heat Pumps TOC Assessment Report, Section 6.2.2, Marine containers, and Section 10.2.2, Cold storage.

Other larger ULT systems, such as climate test chambers, could use these refrigerants and could have higher leakage rates if they are not factory-sealed systems, but there is little information about the size of this market[49]. RTOC 2022 reports that five to ten thousand so-called super freezers exist for the shipment of tuna at -60 °C; these units are a refrigerant cascade with HFC-134a in the high side and HFC-23 in the low side. Conventional containers have a refrigerant charge typically between 4.5 and 7.5 kg[50].

Some emissions data are available for 2021 in UNFCCC submissions[51] (Table 3.9), which suggests that emissions are relatively low from this application compared with emissions of HFC-23 as a by-product.

Table 3.9 HFC-23 consumption, banks and emissions for HFC-23 used as refrigerant reported to UNFCCC (from CRF tables)

2021	Filled into new manufactured products (tonnes)	In operating systems (average annual banks) (tonnes)	Emissions (tonnes)
EU	20.06	149.58	21.06
Russian Federation	27.08	184.5	27.68
Canada		2.61	0.29
Switzerland	0.19	4.27	0.3
Norway	0.08	0.58	0.09
Total		**341.54**	**49.42**

Note: No emissions: Iceland, Japan, New Zealand, Turkey and UK; Data not available: USA[52].

3.3.10 Etchant and chamber cleaning in semiconductor and electronics manufacturing

In the 2019 IPCC Refinement, the default emission factor 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).

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 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.

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%. This is a much smaller

[49] Ray Gluckman, TEAP Senior Expert.

[50] US EPA Transitioning to low-GWP alternatives in transport refrigeration Transitioning to Low-GWP Alternatives in Transport Refrigeration (epa.gov).

[51] National Inventory Submissions 2023 | UNFCCC CRF Table2(II) and Table 2(II)BHs-2 contain the relevant data when available.

[52] Data from one country are not included as the data appears to be erroneous.

growth rate than the growth rate in consumption, indicating an increase in the percentage of HFC-23 destroyed by abatement systems. Therefore, emissions of HFC-23 are about 64 tonnes in 2013 and about 92 tonnes in 2020 using AR4 GWP value for HFC-23 (14,800). Consumption and emissions are expected to have increased in 2021.

Some data are also available for HFC-23 emissions from UNFCCC submissions by Annex 1 countries for this application[53]. The available data are in Table 3.10.

Table 3.10 HFC-23 consumption and emissions data from electronics industry reported to UNFCCC (from CRF tables) (tonnes)

	2020	2021
EU		
Consumption	Incomplete	Incomplete
Emissions	2.63	2.60
USA		
Consumption	52.69	52.83
Emissions	26.59	30.33
Russian Federation		
Consumption	0.6	0.6
Emissions	0.02	0.02
UK		
Consumption	4.39	4.39
Emissions	1.65	1.54

Note: No data are available for Japan in the CRF tables, Turkey reported emissions of 0.01 tonnes in 2021

The use of fluorinated gases as etchant and for chamber cleaning in semiconductor and electronics manufacturing is also discussed in detail in the MCTOC 2022 Assessment Report[54].

HFC-23 is commonly used for selective etching of silicon dioxide (SiO_2) and silicon nitride (SiN)[55]. When HFC-23 (CHF_3) is used as the etching gas and silicon (Si) as the substrate to be etched, in reactive ion etching (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. 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. The rate of unreacted gases depends on the type of gas and process conditions. For HFC-23, the unreacted rate is 0.47. A small fraction of the gas will also be converted into fluorinated by-products; HFC-23 is generated as a by-product from other process gases, such as CF_4 (by-product formation rate: 0.04), C_3F_8 (0.0000012), c-C_4F_8 (0.022), and even NF_3 (0.0068) and SF_6 (0.0014)[56]. If

[53] National Inventory Submissions 2023 | UNFCCC CRF Table2(II) and Table 2(II)BHs-1 contain the relevant data when available.

[54] MCTOC 2022 Assessment Report, Section 5, Semiconductor and other electronics manufacturing.

[55] 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.

[56] 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Chapter 6, p.6.47, Table 6.7. https://www.ipcc-nggip.iges.or.jp/public/2019rf/pdf/3_Volume3/19R_V3_Ch06_Electronics.pdf.

the amount of fluorinated gas used for etching is known, the amount of HFC-23 by-product can be estimated with noted assumptions[57] (Table 3.11).

Table 3.11 Estimation of HFC-23 arising from etching equipment (before abatement)

Used gas	Amount of use[58] (tonnes, 2021)	Reaction type, rate	Outcome HFC-23 from etching equipment (tonnes)[59]
HFC-23	580	Unreacted, 0.47	272.6
CF_4	3,650	By-product, 0.04	146
C_3F_8	NA	By-product, 0.0000012	–
$c\text{-}C_4F_8$	630	By-product, 0.022	13.9
NF_3	21,000	By-product, 0.0068	34.3
SF_6	696	By-product, 0.0014	1.0
		Total	467.7

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.

Best Practice Guidance for Semiconductor PFC Emission Reduction was published in 2017, which is relevant as a reference for reducing HFC-23 emissions. The followings are some examples of the guidance[60,61,62,63]:

- Process recipe optimization— optimizing processes to consume less greenhouse gases.
- Gas replacement— replacing the gas with lower GWP or using more reactive gases in the process.

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57 WSC data were not available for 2021 for HFC-23 consumption; Fuji Keizai Corporation data for 2022 have been used instead. The two datasets (WSC data are reported by semiconductor manufacturers and Fuji Keizai Corp. data are marketing data) do not correlate for earlier years; however, both show an increasing trend. HFC-23 consumption data for 2021 from WSC, when available, are also likely to show an increasing trend from 2020 (720 tonnes) to 2021.

58 Fuji Keizai Corporation, 2022, *Current status and future prospects of the semiconductor materials market in 2022*. For SF_6 only, 2020 consumption data from the WSC are used as a proxy for 2021 consumption. World Semiconductor Council, 2021, *Joint Statement of the 25th Meeting of the World Semiconductor Council (WSC).*

59 To estimate the HFC-23 emissions from NF_3, it was assumed that only 24% of the total shown for NF_3 consumed was used for non-remote plasma clean processes, for which this emission rate is applicable.

60 MCTOC 2022 Assessment Report, Section 5, Semiconductor and other electronics manufacturing.

61 PFAS-Containing Fluorochemicals Used in Semiconductor Manufacturing Plasma-Enabled Etch and Deposition (Semiconductor Industry Association). https://www.semiconductors.org/pfas-containing-fluorochemicals-used-in-semiconductor-manufacturing-plasma-enabled-etch-and-deposition/.

62 World Semiconductor Council, Bes Practice Guidance for Semiconductor PFC Emission reduction. http://www.semiconductorcouncil.org/wp-content/uploads/2017/07/Best-Practice-Guidance-of-PFC-Emission-Reduction.pdf

63 Beu, L., S Raoux, Y.C. Chang, M R Czerniak, F. Illuzzi, T. Kitagawa, D. Ottinger, et al. 2019. Chapter 6 Electronics Industry Emissions, Table 6.16. https://www.ipcc-nggip.iges.or.jp/public/2019rf/pdf/3_Volume3/19R_V3_Ch06_Electronics.pdf

- Point of use abatement— an abatement system is used to reduce emission by destructing unreacted and by-product gas.

For abatement, there are several technologies to be applied:

- Cartridge— dry-bed passive scrubber with active media. The cartridge absorbs HFC and should be exchange before breakthrough.
- Plasma— decompose fluorinated gases to HF and CO_2.
- Combustion— incineration with fuel.
- Combination of the above technology.

Default destruction removal efficiency rate for HFC-23 for electronics industry process is 0.98. There are no available data for installation rate, but assuming 90% of the HFC-23 that is exiting the etching chambers passes through abatement systems, about 61 tonnes of HFC-23 would be emitted to the atmosphere, based on the estimates in Table 3.10.

4 Best practices available to control emissions of HFC-23 by-product

4.1 Technical measures to control emissions of HFC-23 by-product

This section responds to decision XXXIV/7 paragraph c, regarding best practices available to control emissions of HFC-23 by-product from facilities that manufacture Annex C HCFCs or Annex F HFCs.

Best practices available to control emissions of HFC-23 by-product are consistent with those used to control other emissions associated with chemical manufacturing.

These include optimising plant design, equipment, operation, maintenance; instrumentation and monitoring of process and emissions; training and instruction for plant operators; periodic mass balancing; technologies for destruction (i.e., thermal oxidation) or for separation and chemical transformation to treat unwanted co-products or by-products and abate their emissions; and regulatory controls to provide the economic framework to ensure any or all of the above emissions mitigation measures are implemented by operators, and to require emissions and other reporting.

Article 2J requires HFC-23 emissions generated in production facilities that manufacture Annex C, Group I, or Annex F substances to be destroyed to the extent practicable using technology approved by the Parties. Of the best practices available to control emissions, thermal oxidation is used as an end-of-pipe process that destroys unwanted by-products to environmentally acceptable substances. When a process includes an effectively operated HFC-23 mitigation step, e.g., thermal oxidation on the process vents containing HFC-23, emission rates of HFC-23 can be significantly lower than the HFC-23 generation rates because destruction efficiencies can exceed 99%. The capital cost is estimated as ~US$1.25–3.5 million, with annual operating costs ~US$300,000–600,000.

MCTOC elaborated generic best practices available to control emissions in its recent 2022 Assessment Report, Section 2.5, on production emissions and their mitigation, which was reproduced in its recent response to decision XXXIV/5, paragraph b, and is reproduced again below.

4.1.1 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, intermediates, feedstock, or by-products; which of these are being emitted will have an important bearing on how the operation mitigates those emissions.

4.1.2 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
- Periodic plant mass balancing
- Plant tours
- Maintenance procedures including routine leak checking
- Consideration of inherent emissions when selecting equipment, e.g., seal-less 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.

4.1.3 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.

4.1.4 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.

4.1.5 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[64]; 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.

4.2 Measures by parties to control emissions of HFC-23 by-product

This section summarises a sample of various measures implemented or being implemented by parties to control emissions of HFC-23 by-product. This summary is non-exhaustive.

4.2.1 Argentina

As detailed in the May 2023 TEAP RTF Report, Argentina ratified the Kigali Amendment on 22 November 2019 and submitted a project proposal via UNIDO to enable compliance with the HFC-23 by-product control obligations of the Kigali Amendment. At its 87th meeting, ExCom *inter alia* approved in principle funding and support costs, to enable Argentina to comply with the HFC-23 by-product emission control obligations under the Kigali Amendment. At its 91st meeting, ExCom agreed to consider the draft of agreement for funding for control of emissions of HFC-23 generated in the production of HCFC-22.

4.2.2 China

As detailed in the May 2023 TEAP RTF Report, China supports the incineration and conversion of HFC-23 by-product generated by valid HCFC-22 production capacities that were recognised by the then Ministry of Environmental Protection before April 27, 2015, when *Supplementary Circular on Strict Control of New, Reconstruction and Expansion of HCFCs Production Facilities* was issued. From 2014 to 2019, China provided financial subsidies for the operation of HFC-23 destruction facilities of the HCFC-22 manufacturers. Citing information reported in 2020 TEAP RTF Report, 11 HCFC-22 production plants in China applied for government subsidies, with production of HCFC-22 of 598,098 t.

UNEP/OzL.Pro/ExCom/84/74, paragraph 12, states: "*The verification report had included national information on the management of HFC-23 by-product generated in all HCFC-22 feedstock production lines established after 2010. In 2018, 99.8 per cent of the HFC-23 generated at all HCFC-22 production plants, including the integrated facilities, had been incinerated or collected, stored and sold, and 0.22 per cent had been vented.*"

In September 2021, China's Ministry of Ecology and Environment issued the *Circular on Controlling the Emissions of HFC-23 By-products*, which requires the destruction, to the extent practicable, of HFC-23 by-product from HCFC-22 and HFC production facilities using technology approved by the Parties to the Montreal Protocol. Companies are required to install HFC-23 storage facilities or take other measures to avoid potential HFC-23 emissions. The HCFC-22 or HFC production processes must be paused to avoid HFC-23 emissions if HFC-23 destruction and storage are not functioning. Technology innovation is also encouraged to reduce the rate of HFC-23 generation as a by-product and promote resource utilisation of HFC-23 as a feedstock.[65]

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

[65] IGSD, September 15, 2021, *China Takes Steps to Address HFC-23 Emissions in Advance of International Ozone Day*, https://www.igsd.org/china-takes-steps-to-address-hfc-23-emissions-in-advance-of-international-ozone-day/#:~:text=The%20Circular%20enters%20into%20effect%2015%20September%202021.,and%20hydrofluorocarbons%20%28HFCs%29%20as%20of%20its%20effective%20date. Accessed August 2023. Link to *Circular on Controlling the Emissions of HFC-23 By-products*, https://www.mee.gov.cn/xxgk2018/xxgk/xxgk06/202109/t20210915_943345.html.

4.2.3 European Union and United Kingdom

Article 7 of the F-gas regulation (EU 517/2014) imposes requirements on producers to take all necessary precautions to limit emissions of F-gases in their production, transport, and storage. Furthermore, this provision overlaps with the Industrial Emissions Directive (2010/75/EU) and imposed no new requirements.

Article 7 also required producers or importers, if placing on the market F-gases or substances listed in Annex II, to provide evidence of the capture and destruction of any HFC-23 produced as a by-product in the manufacture of F-gases, where relevant.

4.2.4 India

In India, 5 HCFC-22 production facilities have implemented CDM projects in the past. Destruction facilities continue to be operated after the expiration of the CDM projects. In 2016, India made an internal commitment requiring enterprises to mitigate emissions through incineration/destruction of HFC-23 by-product.

4.2.5 Mexico

As detailed in the May 2023 TEAP RTF Report, "*In Mexico, HFC-23 by-product from HCFC-22 production is partially emitted (and/or separated for a specific use) or destroyed. One destruction facility attached to a Quimobásicos plant (CDM project from 2006) was operating in 2015. Mexico ratified the Kigali Amendment on 25 September 2018 and submitted a project proposal via UNIDO to enable compliance with the HFC-23 by-product control obligations of the Kigali Amendment.*" At its 86th meeting, ExCom considered a project proposal[66] and approved funding in principle. At its 87th meeting, ExCom approved an Agreement.

4.2.6 United States

EPA established requirements for all entities producing HFC-23 to control these emissions (40 CFR 84.27). Specifically, EPA requires under 40 CFR 84.27 that no later than October 1, 2022, no more than 0.1 percent of HFC-23 created on a facility line may be emitted (including any HFC-23 emissions during transportation to and destruction at a different facility), as compared to the amount of chemical intentionally produced on the line.

[66] UNEP/OzL.Pro/ExCom/86/96