



# Narrowing feedstock exemptions under the Montreal Protocol has multiple environmental benefits

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The Montreal Protocol on Substances that Deplete the Ozone Layer (Montreal Protocol) can be further strengthened to control ozone-depleting substances and hydrofluorocarbons used as feedstocks to provide additional protection of the stratospheric ozone layer and the climate system while also mitigating plastics pollution. The feedstock exemptions were premised on the assumption that feedstocks presented an insignificant threat to the environment; experience has shown that this is incorrect. Through its adjustment procedures, the Montreal Protocol can narrow the scope of feedstock exemptions to reduce inadvertent and unauthorized emissions while continuing to exempt production of feedstocks for time-limited, essential uses. This upstream approach can be an effective and efficient complement to other efforts to reduce plastic pollution. Existing mechanisms in the Montreal Protocol such as the Assessment Panels and national implementation strategies can guide the choice of environmentally superior substitutes for feedstock-derived plastics. This paper provides a framework for policy makers, industries, and civil society to consider how stronger actions under the Montreal Protocol can complement other chemical and environmental treaties.

ozone-depleting substances | ODS and HFC feedstocks | plastics pollution | ocean pollution | Montreal Protocol

The Montreal Protocol on Substances that Deplete the Ozone Layer (Montreal Protocol) (1) protects Earth against the harmful effects of ultraviolet (UV) radiation, which causes skin cancer and cataracts, suppresses the human immune system, damages agricultural crops and ecosystems, and degrades materials such as plastics and paint. It also protects the climate system, because most ozone-depleting substances (ODSs) are potent greenhouse gases (GHGs), and because UV radiation can diminish the terrestrial capacity of plants as carbon sinks (2).

The Montreal Protocol and the underlying Vienna Convention for the Protection of the Ozone Layer are widely regarded as the most effective environmental treaties yet created. Over its 34 y of operation, the

Montreal Protocol has eliminated production of about 98% of the ODSs and put the stratospheric ozone layer on the path to recovery by about 2,065 (3–5). At the same time, phasing out ODSs has avoided GHG emissions that otherwise could have equaled or exceeded the emissions of carbon dioxide (CO<sub>2</sub>) (6). The Protocol has provided additional climate mitigation by preventing UV radiation from damaging terrestrial carbon sinks (2).

Using their existing authority, the parties to the Montreal Protocol have the opportunity to narrow the exemption for feedstocks, which initially were assumed to pose an insignificant threat to the environment (1, 7, 8). Narrowing the feedstock exemption would provide additional protection of the

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stratospheric ozone layer and the climate system by reducing inadvertent and sometimes unauthorized emissions. This will make it easier to identify and prohibit feedstocks that otherwise could be diverted into unauthorized trade and ultimately emitted to the atmosphere.

Furthermore, because ODS and hydrofluorocarbon (HFC) feedstocks are used to make plastics, narrowing their exemptions has the potential to mitigate plastic pollution at the production end, especially if flexible mechanisms under the Montreal Protocol and national implementation strategies help guide the choice of environmentally superior alternatives, as they did for the phase-out of ODSs (see *SI Appendix, Items III and V*). Controlling upstream feedstocks under the Montreal Protocol would complement current downstream efforts to mitigate plastic pollution through reduction, recycling, and clean-up programs and would provide a further economic incentive for innovation to find substitutes for plastics.

In this paper, we begin with an overview of the reaction pathways through which ODS, HFC, and associated feedstocks are made into a variety of plastics. We then illustrate how the Montreal Protocol can reduce inadvertent and unauthorized ODS and HFC feedstock emissions. We also illustrate how the Protocol can reduce the production of some feedstock-derived plastics and replace them with environmentally superior substitutes via industrial innovation. This further evolution of the Montreal Protocol to narrow the scope of feedstock exemption will require continuing international cooperation, consistent with the Montreal Protocol's history.

### ODSs and HFCs Are Key Feedstocks for Making Plastics

Feedstocks are substances that undergo chemical transformation themselves in a process to synthesize other chemicals. In comparison, process agents are also used in industrial chemical processes but, unlike feedstocks, do not undergo chemical transformation themselves during the process. The manufacture, use, and disposal of feedstocks and process agents result in harmful emissions at every stage of the process. The degradation of plastics contributes to additional hazardous pollution.

Complex and multistep chemical pathways are involved in the use of ODSs, HFCs, and associated chemicals as feedstocks to produce plastics via polymerization. Chemical pathways are selected for economic reasons, including access to raw materials and energy, working around process patents controlled by rival companies, or coproducing other chemicals to minimize costs and maximize profits. The pathways of polymerization reviewed here suggest that controlling the ODSs, HFCs, and associated feedstocks under the Montreal Protocol can be part of an effective approach to reducing plastics. A list of the names, formulae, structures of chemicals discussed, and their status of regulation under the Montreal Protocol is provided in *SI Appendix, Item IV*.

Table 1 illustrates reaction pathways from basic feedstocks (column 1 in Table 1) to ODS and HFC feedstocks (column 2 in Table 1) that are controlled by the Montreal Protocol. Table 2 (along with *SI Appendix, Item I*) illustrates the myriad chemical pathways (column 3 in Table 2) of chlorofluoro-containing feedstocks (principally, ODSs and HFCs, column 1 in Table 2) being synthesized to polymeric end products (column 2 in Table 2). The end products (many with applications as plastics) are widely used in industry and daily lives and in some cases cause environmental pollution unrelated to stratospheric ozone depletion and climate warming. For example, production of fluoropolymers

can generate emissions of per- and polyfluoroalkyl substances (PFAS), some of which are used as polymer processing aids. There are serious concerns about the toxic and other harmful impacts of PFAS on human health and the environment (9).

Consider hydrochlorofluorocarbon-22 (HCFC-22), an ODS feedstock made from chloroform, as illustrated in Table 1. As shown in Table 2, HCFC-22 is in turn used as a feedstock for the production of tetrafluoroethylene (TFE), which is a building block for the polymer polytetrafluoroethylene (PTFE), popularly known as Teflon, that is widely used in automotive, textile, construction, and other sectors. According to a recent survey (10), PTFE represented the largest fraction (~65%) of all fluoropolymer production in 2012, with its production predicted to double by 2022. Although of no known chronic toxicity or carcinogenicity, when heated to temperatures between 250 and 600 °C PTFE degrades and releases hazardous substances such as trifluoroacetic acid (9, 11). Also, polymer processing aids such as perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) can be released during the manufacturing process. Both PFOA and PFNA are persistent, bioaccumulative, and toxic substances, with negative impacts on human health (9). TFE also reacts via polymerization to produce other synthetic materials (see *SI Appendix, Item I*); for example, nitroso rubbers are formed through TFE's reactions with perfluoronitrosoalkanes. Rubber, similar to plastics, can cause environmental pollution, especially after photodegradation (12).

Another indicative example of environmentally hazardous use is HCFC-142b, which can be produced from the associated feedstock of 1,1,1-trichloroethane (also known as T-111), as illustrated in Table 1. As shown in Table 2, HCFC-142b is in turn used for production of vinylidene fluoride (VDF), which is the building block for polyvinylidene fluoride (PVDF) as well as a variety of copolymers such as poly(VDF-co-CTFE) (see *SI Appendix, Item I*). PVDF, a nonreactive thermoplastic fluoropolymer, is a specialty plastic used in chemical, electronic, and energy-related applications. PVDF represented the second-largest fraction (~10%) of fluoropolymer production in 2012, following PTFE (10). Like PTFE, it poses threats to human health (9) via its harmful emissions during manufacturing and persistence in the environment.

Further, many chlorofluoro-containing unsaturated chemicals may interlink with a variety of chemicals such as ethylene, vinyl ethers, vinylidene fluoride, and bromofluoroalkenes and with aromatics such as styrene and its derivatives to form copolymers, many of which end up as plastics or other functional materials. A collection of such copolymerization pathways and products are shown in *SI Appendix, Item I*. For example, TFE manufactured from HCFC-22 (see Table 2) may form several types of heterogeneous copolymers from polymerizing with different monomers such as propylene or ethylene (see *SI Appendix, Item I*). According to a recent survey (13), four types of polymers listed in *SI Appendix, Item I*—PTFE, FEP, ETFE, and PFA and similar polymers—accounted for roughly 70 to 75% of the world's fluoropolymer consumption in 2015.

Table 2 and *SI Appendix, Item I* indicate that roughly 70 to 80% (by type) of polymer products are used as plastics, especially thermoplastics, with the remainder used mostly as elastomers. These tables also show that ODSs, HFCs, and associated feedstocks have a myriad of pathways for entering and remaining in the environment as pollutants, especially as plastics, but also as rubbers and other materials. Indeed, fluoropolymers' extreme persistence, potentially harmful emissions associated

**Table 1. Indicative description of basic feedstocks and their reaction pathways to ODSs and HFCs (controlled under Montreal Protocol), which are used as feedstocks to make plastics**

Basic feedstocks to make ODS and HFC feedstocks	ODS and HFC feedstocks	Reaction pathways from basic feedstocks to ODS and HFC feedstocks	Polymerization from ODS and HFC feedstocks to plastics (see Table 2 and SI Appendix, Item I for reaction details)	Refs.
Methylene chloride	HFC-32	<p>Pathway 1</p> $\text{CH}_2\text{Cl}_2 + 2\text{HF} \xrightarrow[\text{70}^\circ\text{C} - \text{90}^\circ\text{C}]{\text{SbCl}_5} \text{CH}_2\text{F}_2 + 2\text{HCl}$ <p>11 - 12 kg/cm<sup>2</sup>g</p> <p>Pathway 2</p> $\text{CH}_2\text{Cl}_2 + 2\text{KF} \xrightarrow[\text{150}^\circ\text{C} - \text{240}^\circ\text{C}]{\text{X}(\text{CF}_2)_n\text{O}(\text{CF}_2)_2\text{SO}_2\text{Y}} \text{CH}_2\text{F}_2 + 2\text{KCl}$ <p>(X = H, Cl or F, Y = Cl or F, n = 4 ~ 8)</p>	Methylene chloride is produced together in plants with chloroform (below), a principal feedstock for HCFC-22.	(77, 78)
Chloroform	HCFC-22, HFC-125	<p>HCFC-22*</p> $\text{CHCl}_3 + \text{HF} \xrightarrow[\text{80}^\circ\text{C}]{\text{SbF}_3} \text{CHClF}_2 + \text{byproducts}$ <p>HCFC-22 to tetrafluoroethylene (TFE)</p> $\text{CHClF}_2 \xrightarrow[\text{1 atm}]{\text{750}^\circ\text{C} - \text{950}^\circ\text{C}} \text{CF}_2=\text{CF}_2 + \text{byproducts}$ <p>TFE to HFC-125</p> $\text{CF}_2=\text{CF}_2 + \text{organic nitrogenous base hydrofluoride} \xrightarrow[\text{7-20 bar}]{\text{120}^\circ\text{C} - \text{145}^\circ\text{C}} \text{CF}_3\text{CF}_2\text{H}$	HCFC-22 to TFE, then to polytetrafluoroethylene, or PTFE.	(79, 80)
Carbon tetrachloride (CTC)	CFC-11, CFC-12, HFC-245fa	<p>CFC-11, CFC-12</p> $\text{CCl}_4 + \text{HF} \xrightarrow[\text{ca. 100}^\circ\text{C}]{\text{antimony fluorides}} \text{CF}_2\text{Cl}_2 + \text{CFCl}_3 + \text{HCl}$ <p>2 bar - 5 bar</p> <p>HFC-245fa</p> $\text{CCl}_4 + \text{CH}_2=\text{CHCl} \xrightarrow[\text{50}^\circ\text{C} - \text{150}^\circ\text{C}]{\text{telomerization catalyst}} \text{CCl}_3\text{CH}_2\text{CHCl}_2$ <p>fluorination catalyst</p> $\text{CCl}_3\text{CH}_2\text{CHCl}_2 + 5\text{HF} \xrightarrow[\text{1500 - 2500 KPa}]{\text{115}^\circ\text{C} - \text{155}^\circ\text{C}} \text{CHF}_2\text{CH}_2\text{CF}_3 + 5\text{HCl}$		(81, 82)
Trichloroethylene	HFC-134a	$\text{CHCl}=\text{CCl}_2 + 3\text{HF} \xrightarrow[\text{260}^\circ\text{C}]{\text{CrF}_3/\gamma - \text{AlF}_3} \text{CF}_3\text{CH}_2\text{Cl} + 2\text{HCl}$ $\text{CF}_3\text{CH}_2\text{Cl} + \text{HF} \xrightarrow[\text{350}^\circ\text{C}]{\text{CrF}_3/\gamma - \text{AlF}_3} \text{CF}_3\text{CH}_2\text{F} + \text{HCl}$		(83)
Perchloroethylene	HFC-125, CFC-113, CFC-113a, CFC-114a, HFC-134a, HCFC-124	<p>PCE to HFC-125</p> $\text{CCl}_2=\text{CCl}_2 + 5\text{HF} \xrightarrow[\text{4 bar - 10 bar}]{\text{chromium-containing catalyst}} \text{CF}_3\text{CHF}_2 + 4\text{HCl} + \text{highly fluorinated byproducts}$ <p>PCE to CFC-113</p> $\text{CCl}_2=\text{CCl}_2 + 3\text{HF} + \text{Cl}_2 \xrightarrow[\text{CFC-113 to CFC-113a}]{\text{240}^\circ\text{C} - \text{375}^\circ\text{C}, \text{noncrystalline ZrF}_4} \text{CCl}_2\text{FCClF}_2 + 3\text{HCl}$ <p>CFCl<sub>2</sub>CF<sub>2</sub>Cl</p> $\text{CFCl}_2\text{CF}_2\text{Cl} \xrightarrow[\text{1 atm - 10 bar}]{\text{100}^\circ\text{C} - \text{160}^\circ\text{C}, \text{AlF}_3} \text{CF}_3\text{CCl}_3 + \text{byproducts}$ <p>CFC-113 to CFC-114a</p> $\text{CF}_2\text{ClCCl}_2\text{F} + \text{HF}/\text{Cl}_2 \xrightarrow[\text{450}^\circ\text{C}]{\text{AlF}_3} \text{CF}_3\text{CCl}_2\text{F}$ <p>CFC-114a to HFC-134a and HCFC-124</p> <p>Pathway 1</p> $\text{CF}_3\text{CCl}_2\text{F} + \text{Et}_3\text{SiH} \xrightarrow[\text{100}^\circ\text{C}]{\text{initiator: benzoyl peroxide}} \text{CF}_3\text{CH}_2\text{F} + \text{CHClFCF}_3$ <p>(minor) (major)</p> <p>Pathway 2</p> $\text{CF}_3\text{CCl}_2\text{F} + \text{CH}_3\text{Cl} \xrightarrow[\text{600}^\circ\text{C}]{\text{Ba/Cs}/\gamma\text{-Al}_2\text{O}_3} \text{CF}_3\text{CH}_2\text{F} + \text{CHClFCF}_3$ <p>(minor) (major)</p>	CFC-113 to CTFE, then to polychlorotrifluoroethylene, or PCTFE	(84-87)
Ethylene dichloride or vinyl chloride (VC)	1,1,1-Trichloroethane (also known as T111)	<p>Ethylene dichloride to VC</p> $\text{CH}_2\text{ClCH}_2\text{Cl} \xrightarrow[\text{25 bar - 35 bar}]{\text{500}^\circ\text{C} - \text{600}^\circ\text{C}, \text{initiator: CCl}_4} \text{CH}_2=\text{CHCl} + \text{HCl}$ <p>Vinyl chloride to T111</p> $\text{CH}_2=\text{CHCl} + \text{HCl} \xrightarrow{\text{FeCl}_3} \text{CH}_3\text{CHCl}_2$ $\text{CH}_3\text{CHCl}_2 + \text{Cl}_2 \xrightarrow[\text{3 bar - 5 bar}]{\text{370}^\circ\text{C} - \text{400}^\circ\text{C}, \text{SiO}_2} \text{CH}_3\text{CCl}_3 + \text{HCl}$	Ethylene dichloride is the principal feedstock for VC.	(81)
VC	HFC-152a	$\text{CH}_2=\text{CHCl} + 2\text{HF} \xrightarrow[\text{0.5 - 20kg/cm}^2]{\text{catalyst}, \text{150}^\circ\text{C} - \text{300}^\circ\text{C}} \text{CHF}_2\text{CH}_3 + \text{HCl} + \text{byproducts}$ <p>The catalyst is a vanadium derivative impregnated on activated carbon.</p>	VC to polyvinyl chloride (PVC)	(88)
1,1,1-trichloroethane	HCFC-141b, HCFC-142b, HFC-143a	$\text{CH}_3\text{CCl}_3 + \text{HF} + \text{CH}_2=\text{CF}_2 \xrightarrow[\text{5 - 20 bar}]{\text{60}^\circ\text{C} - \text{120}^\circ\text{C}, \text{antimony compounds}} \text{CCl}_3\text{FCH}_3 + \text{CH}_3\text{CClF}_2 + \text{CH}_3\text{CF}_3 + \text{byproducts}$ <p>Without the catalyst, HCFC-141b and HFC-143a will be the main products. With the catalyst, HCFC-142b and HFC-143a will be the main products.</p>	HCFC-142b, HFC-143a to vinylidene fluoride (VDF), then to polyvinylidene fluoride, or PVDF	(89)

\*HFC-23 (with a high GWP) is a by-product during the manufacture of HCFC-22.

**Table 2. Indicative reaction pathways of ODS and HFC feedstocks to polymers (with applications as plastics) built on a singular type of monomers**

ODS and HFC feedstocks	End products functioning as plastics	Reaction pathways	Polymer's main application	Refs.
HCFC-22	PTFE	<p>HCFC-22 to tetrafluoroethylene (TFE):</p> $\text{CHClF}_2 \xrightarrow[1 \text{ atm}]{750^\circ\text{C} - 950^\circ\text{C}} \text{CF}_2=\text{CF}_2 + \text{byproducts}$ <p>TFE to PTFE:</p> $\text{CF}_2=\text{CF}_2 \xrightarrow[20 \text{ atm}]{\text{initiator: ammonium persulfate}, 80^\circ\text{C}} \left( \begin{array}{c} \text{F} & \text{F} \\   &   \\ \text{---C} & \text{---C---} \\   &   \\ \text{F} & \text{F} \end{array} \right)_n$	Thermoplastic	(79, 90)
HCFC-142b, HFC-143a	Polyvinylidene fluoride, or PVDF	<p>HCFC-142b to vinylidene fluoride (VDF):</p> <p>Pathway 1</p> <p>N-doped ordered mesoporous carbons</p> $\text{CH}_3\text{CClF}_2 \xrightarrow{400^\circ\text{C}} \text{CH}_2=\text{CF}_2 + \text{HCl}$ <p>Pathway 2</p> <p>high temperature</p> $\text{CH}_3\text{CClF}_2 \xrightarrow{\text{high temperature}} \text{CH}_2=\text{CF}_2 + \text{HCl}$ <p>(The specified temperature is different among published papers.)</p> <p>HFC-143a to VDF</p> $\text{CH}_3\text{CF}_3 \xrightarrow{750^\circ\text{C} - 910^\circ\text{C}} \text{CH}_2=\text{CF}_2 + \text{byproducts}$ <p>VDF to PVDF</p> <p>Pathway 1 (Emulsion)</p> $\text{CH}_2=\text{CF}_2 \xrightarrow[27\text{bar} - 55\text{bar}]{\text{initiator: organic peroxide or persulfate}, 60^\circ\text{C} - 125^\circ\text{C}} \left( \begin{array}{c} \text{H} & \text{F} \\   &   \\ \text{---C} & \text{---C---} \\   &   \\ \text{H} & \text{F} \end{array} \right)_n$ <p>Pathway 2 (Suspension)</p> $\text{CH}_2=\text{CF}_2 \xrightarrow[70\text{bar} - 100\text{bar}]{\text{initiator: organic peroxide or persulfate}, 20^\circ\text{C} - 60^\circ\text{C}} \left( \begin{array}{c} \text{H} & \text{F} \\   &   \\ \text{---C} & \text{---C---} \\   &   \\ \text{H} & \text{F} \end{array} \right)_n$	Thermoplastic	(91-94)
CFC-113	PCTFE	<p>CFC-113 to chlorotrifluoroethylene (CTFE)</p> <p>Pathway 1:</p> $\text{CClF}_2\text{CCl}_2\text{F} \xrightarrow{500^\circ\text{C} - 600^\circ\text{C}} \text{CF}_2=\text{CClF} + \text{Cl}_2$ <p>Pathway 2:</p> $\text{CClF}_2\text{CCl}_2\text{F} \xrightarrow[50^\circ\text{C} - 100^\circ\text{C}]{\text{Zn/MeOH}} \text{CF}_2=\text{CClF} + \text{ZnCl}_2$ <p>CTFE to PCTFE</p> $\text{CF}_2=\text{CClF} \xrightarrow[4\text{bar} - 20\text{bar}]{\text{initiator: potassium persulfate}, 10^\circ\text{C} - 70^\circ\text{C}} \left( \begin{array}{c} \text{F} & \text{F} \\   &   \\ \text{---C} & \text{---C---} \\   &   \\ \text{F} & \text{Cl} \end{array} \right)_n$	Thermoplastic	(95, 96)
VC*	Polyvinyl chloride, or PVC	$\text{CH}_2=\text{CHCl} \xrightarrow[10 \text{ atm}]{\text{initiator: AIBN}, 65^\circ\text{C}} \left( \begin{array}{c} \text{H} & \text{H} \\   &   \\ \text{---C} & \text{---C---} \\   &   \\ \text{H} & \text{Cl} \end{array} \right)_n$	Thermoplastic	(97)
HFC-152a	Polyvinyl fluoride, or PVF	<p>HFC-152a to vinyl fluoride (VF)</p> $\text{CH}_3\text{CHF}_2 \xrightarrow[\text{atmospheric pressure}]{\text{MgF}_2/\beta\text{-AlF}_3 \text{ or } \text{ZnF}_2/\beta\text{-AlF}_3, 250^\circ\text{C} - 325^\circ\text{C}} \text{CH}_2=\text{CHF} + \text{HF}$ <p>VF to PVF</p> $\text{CH}_2=\text{CHF} \xrightarrow[25\text{atm} - 100\text{atm}]{\text{initiator: AIBN}, 25^\circ\text{C} - 100^\circ\text{C}} \left( \begin{array}{c} \text{H} & \text{H} \\   &   \\ \text{---C} & \text{---C---} \\   &   \\ \text{H} & \text{F} \end{array} \right)_n$	Thermoplastic	(98, 99)

\*Vinyl chloride is not currently controlled under Montreal Protocol but may be considered (along with its principal feedstock, ethylene dichloride) as "associated feedstocks" under the proposed framework for reducing plastics production by restricting feedstocks.

with their production, use, and disposal, and a high likelihood of human exposure to PFAS justify curtailing the production and use of plastics made from ODS and HFC feedstocks except for time-limited essential uses (9, 14).

Estimating the percentage of ODS and HFC feedstock-derived plastics in total plastics production is subject to large uncertainty (15) and warrants further analysis. Based on publicly disclosed data and chemical pathways, our preliminary estimate is that narrowing the scope of the exemptions for ODS and HFC feedstocks has the potential to reduce up to

6% of the total plastics production. This percentage would increase if other feedstocks and chemical pathways get included in this "feedstock-induced plastics reduction" approach. For example, if the Montreal Protocol were amended to control vinyl chloride (and its associated feedstock ethylene dichloride), which is mostly made into polyvinyl chloride (PVC), total plastic production could be reduced by up to 20% (see *SI Appendix, Item II*).

The regulation of additional feedstocks by amending the Montreal Protocol could potentially play a significant role in

**Table 3. Indicative feedstocks controlled under the Montreal Protocol but exempted from phase-out**

Feedstock	Ozone-depletion potential (ODP)*	Global warming potential (GWP <sub>100-y</sub> )	Identified GHG by-products
Bromochloromethane		4.7	
CFC-11	1	4,660	
CFC-12	0.73–0.81	10,200	
CFC-113	0.98	5,820	
CTC†	0.89	1,730	
HCFC-22	0.024–0.034	1,760	HFC-23 (GWP <sub>100-y</sub> = 12,690)
HCFC-142b	0.057	1,980	
HCFC-225ca	0.025	127	
HCFC-225cb	0.033	525	
HFC-143a	0	4,800	
Halon 1301	15.2–19.0	6,290	

\*All ODPs are from the 2018 Report of the Scientific Assessment of Ozone Depletion (5); all GWPs are from the IPCC Fifth Assessment Report (18).

†CTC is used 1) historically for solvent, fire extinguishing and other purposes; 2) to produce HFCs such as HFC-236fa, HFC-245fa and HFC-365mfc, which are scheduled for phasedown under the Kigali Amendment to the Montreal Protocol; 3) to produce HFOs developed as low-GWP replacements for HFCs; 4) to produce perchloroethylene and specialty chemicals such as cypermethrin acid chloride (DV acid chloride, a feedstock for cypermethrin, permethrin, betacypermethrin, and some other products); and 5) for limited analytical and laboratory uses under the Montreal Protocol Essential Use Exemption. Historically, CTC was used to produce CFCs for use in aerosol products, foams, solvents, and other applications as shown in Table 1 (56, 100, 101).

reducing plastics, rubber, and related pollution of the atmospheric, terrestrial, and aquatic environments. As a starting point, narrowing the scope of the exemptions for ODS and HFC feedstocks shown in Tables 2 and 3 and *SI Appendix, Item 1*, as well as their associated feedstocks shown in Table 1 (for example, methylene chloride and chloroform, associated feedstocks for HCFC-22, as well as ethylene dichloride, an associated feedstock for vinyl chloride), would make the production of such plastics less technically or economically feasible. Following the practice that preceded adoption of previous adjustments and amendments, detailed assessments by the Montreal Protocol Technology and Economic Assessment Panel (TEAP), Scientific Assessment Panel (SAP), and Environmental Effects Assessment Panel (EEAP) should guide the process of narrowing the scope of the feedstock exemptions and identifying feasible alternatives.

### Chemical Feedstocks and Resulting Plastics Harm Human Health and the Environment

Emissions of ODSs deplete stratospheric ozone and thereby increase UV radiation, which causes skin cancer and cataracts, weakens human immune systems, damages agricultural and natural ecosystems, and degrades materials such as plastics and paint (3, 16). Most ODSs also contribute to climate change (see, for example, Table 3 for the global warming potential [GWP]<sub>100-y</sub>). Unconstrained, increasing ODS consumption could have contributed the equivalent of 24 to 76 billion metric tons of CO<sub>2</sub>-eq per year to climate warming by 2010 (6). Moreover, the increased UV radiation without the Montreal Protocol would have diminished the capacity of terrestrial carbon sinks, adding an estimated 115 to 235 ppm of CO<sub>2</sub> to the atmosphere by the end of the century (2).

The increased UV radiation also would have damaged plants and animals at the base of the marine food chain (17, 18). In

addition, climate warming is increasing the length and severity of heat waves, disrupting food webs, and diminishing fisheries (19). Finally, when ODSs, HFCs, and associated feedstocks are turned into plastics they can end up polluting the land as well as freshwater and marine environments. In particular, Earth's oceans are threatened from anthropogenic industrial, commercial, and consumer activities, including chemical pollution, overfishing, acidification, deep-sea mining, and plastic and other waste (20).

The world generated more than 6,000 million metric tons (Mt) of plastic waste up to 2015; less than 10% of it was recycled and more than 75% ended up in landfills, with the remaining 15% disposed as unabated pollution. Geographically, plastic debris has been found in all major ocean basins (21). The flow of plastics into the ocean was estimated at 9 to 14 Mt in 2016 and is projected to grow to about 29 Mt by 2040 (22, 23). Plastics discarded on the landscape after a relatively short period of use mostly make their way by water or wind to the ocean, where they can entangle and get ingested by marine life (24). Recycling does not always eliminate pollution, as plastic can be recycled only once or twice (15).

The climate impact will be even greater if microplastics in the oceans reduce the ability of phytoplankton to fix carbon through photosynthesis (25). As plastics degrade, microplastics (0.1 to 5 μm in size) and nanoplastics (<100 nm in size) accumulate in aquatic and terrestrial organisms, with unknown long-term consequences to agricultural and maricultural productivity and food safety (26–32). Plastics fragment into persistent pieces that are susceptible to wind entrainment. The dispersed plastics and the micro- and/or nanoplastics are ubiquitous in the ocean, from the digestive tracts of marine animals to the seafloor. Microplastics are also found in the atmosphere and rainwater, with uncertain consequences (33–35). Because of their small size, micro- and nanoplastics are extremely difficult to clean up from the open ocean and atmosphere, further supporting the advantage of addressing the problem upstream by phasing down the feedstocks used to make the plastics (22).

In addition, plastics degraded by UV light and abrasion may contain high levels of toxic pollutants such as polychlorinated biphenyls (PCBs), nonylphenol (NP), dichlorodiphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), and bisphenol A (BPA). Several of these toxic pollutants are strongly resistant to environmental degradation through chemical, biological, and photolytic processes and are controlled under the Stockholm Convention on Persistent Organic Pollutants (POPs) (36, 37). Furthermore, some PFAS pollutants, including PFOA used as a polymer processing aid during plastics manufacturing (9), are also controlled under the Stockholm Convention on POPs.

### The Montreal Protocol's Success Shows It Can Reduce Feedstocks and Associated Harm

As a "start and strengthen" treaty, the Montreal Protocol has consistently increased its ambition, including speeding up its ODS phase-out schedules as well as broadening its scope to include new chemicals through five amendments (adding new controlled substances) and six adjustments (accelerating controlled substance phase-out) (38). This evolution includes broadening the treaty's scope from the original focus on protecting the stratospheric ozone layer with climate mitigation as a collateral benefit to explicitly focusing on climate mitigation. The latter started with the accelerated phase-out of HCFCs in 2007, which was done specifically for climate protection as well as

ozone protection (39), followed by the 2016 Kigali Amendment to phase-down HFCs, potent GHGs that only have a *de minimis* impact on stratospheric ozone.

The Montreal Protocol exercises its control of harmful chemicals upstream at the source of production, rather than downstream after use. The success of this approach is shown by the successful phase-out—with exemptions for feedstocks and process agents—of worldwide production and consumption of about 98% of the ODSs, including CFCs, HCFCs, CTC, halons, methyl bromide, and methyl chloroform, which has put the stratospheric ozone layer on the path to recovery by midcentury (3, 4, 17, 40). The Montreal Protocol has also provided significant climate cobenefits: Without the Protocol, in 2010 the ODS emissions would have reached 15 to 18 gigatonnes (Gt) carbon dioxide equivalent (CO<sub>2</sub>-eq) per year (6). The Kigali Amendment to phase down HFCs will avoid 2.8 to 4.1 Gt of CO<sub>2</sub>-eq.y<sup>-1</sup> emissions by 2050 and 5.6 to 8.7 Gt of CO<sub>2</sub>-eq.y<sup>-1</sup> emissions by 2100 (5). A faster HFC phasedown would potentially avoid up to 0.5°C warming by 2100 (5, 41, 42). In conjunction with the Kigali Amendment, parties to the Montreal Protocol also have taken a series of decisions to encourage improvement in the energy efficiency of cooling equipment during the transition away from HFC refrigerants (42). The combined strategies can avoid cumulative emissions from 2030 to 2050 of 130 to 260 Gt of CO<sub>2</sub>-eq and cumulative emissions of 210 to 460 Gt of CO<sub>2</sub>-eq from 2030 to 2060 (42). Moreover, by protecting the stratospheric ozone layer, the Montreal Protocol prevented damage to terrestrial carbon sinks, which by the end of the 21st century would have added an additional 115 to 235 ppm CO<sub>2</sub> to the atmosphere and led to additional 0.5 to 1.0°C warming of global mean surface temperature (2).

Many researchers have described why the Montreal Protocol has been successful and which environmental issues are most amenable to the Montreal Protocol approach (16, 43–51). The Montreal Protocol is successful in part because of innovative operating concepts and a structure that allows it to be ambitious and rigorously enforced, yet flexible with respect to critical industry needs and responsive to new scientific findings and technology advances. This includes “start and strengthen,” that is, starting with a politically acceptable phase-down schedule then strengthening to a complete phase-out by accelerating the initial schedule. Essential-use exemptions allow parties to err on the side of stringency without the consequences of noncompliance by allowing time-limited use of ODSs considered essential for society until alternatives are commercialized. Over time, the essential-use exemptions have been progressively narrowed. Narrowing the scope of feedstock exemptions is consistent with this Montreal Protocol approach, where requirements are strengthened in response to new scientific findings and technological advances.

The Protocol also has achieved success because of the dedicated Multilateral Fund (MLF), which provides financial support to qualifying developing countries for the agreed incremental costs of transitioning to acceptable alternatives, as well as for institutional strengthening and training of National Ozone Units to facilitate compliance with Montreal Protocol deadlines and monitoring and reporting requirements. The Montreal Protocol also guides technology toward environmentally superior alternatives with its SAP, EEAP, TEAP, and MLF. National governments implement the Montreal Protocol’s mandatory controls with regulations, as elaborated in *SI Appendix, Items III and V*.

In addition, the Montreal Protocol has a history of successful coordination with other treaties and United Nations (UN) organizations on topics of overlapping concern and authority. Examples include coordination with the International Plant Protection Convention during the methyl bromide phase-out; coordination with the International Civil Aviation Organization, the International Maritime Organization, and the Montreal Convention for the Unification of Certain Rules for International Carriage by Air when negotiating elimination of halons used in aviation and marine fire protection; and coordination with the UN Framework Convention on Climate Change on HFCs and perfluorocarbons.

In limiting feedstocks and potentially helping to reduce plastics pollution, the Montreal Protocol will need to continue such coordination to understand the jurisdictions of other treaties and coordinate with efforts by other organizations, including the UN Environment Programme. In an intensifying effort to reduce plastics pollution, the UN Environment Assembly (UNEA) has organized experts to review 1) the present situation of marine plastic litter and microplastic; 2) the potential national, regional, and international response options; and 3) the choice of future and continued work at the global level (52, 53). Significantly, a 13 October 2020 draft document (54) includes a focus on upstream controls, as is proposed here under the Montreal Protocol. Efforts to develop a coherent global strategy on marine litter and plastic pollution have advanced, with Ecuador, Germany, Ghana, and Vietnam organizing a Ministerial Conference in September 2021 to inform action at the resumed UNEA fifth session scheduled for February 2022.\* Furthermore, a coalition of businesses, including 5 of the top 10 global plastic polluters, have signed a manifesto calling on the UN to develop an international treaty on plastic pollution rules (55).

### The Montreal Protocol Parties Have the Authority to Control ODS and HFC Feedstocks

Montreal Protocol Parties have authority over ODSs and HFCs and can exercise this authority to narrow the use of these chemicals as feedstocks (1, 7, 8). Early in the history of the Montreal Protocol, parties were acting on the assumption that feedstocks were converted to other chemicals in their entirety and were not emitted or diverted to unauthorized trade (56, 57). When experience showed that significant amounts of chemicals were emitted from the use of feedstocks, thereby damaging stratospheric ozone and warming the climate, the parties took a number of actions to reduce manufacturing emissions (58–60) (see *SI Appendix, Item III and Tables A1–A7*), including requiring data reporting and assessment panel investigations (1, 59–62).

Parties also exercised their authority to provide limited exemptions for feedstocks. This included agreeing, first by adjustment and then by amendment, to modify the definition of “production” to exempt controlled substances entirely used as feedstocks from calculations of controlled substances produced and consumed (1, 3, 63). Further, the parties agreed to an adjustment that exempts “insignificant quantities of controlled substances originating from inadvertent, unauthorized or coincidental production during a manufacturing process, from unreacted feedstock, or from their use as process agents which are present in chemical substances as trace impurities, or that are emitted during product manufacture or

\*See the Ministerial Conference on Marine Litter and Plastic Pollution, held virtually and in Geneva, Switzerland from 1 to 2 September 2021. See also the Online Session of the Fifth Session of the UN Environment Assembly (UNEA-5.1), held virtually from Nairobi, Kenya on 22 and 23 February 2021. The resumed session (UNEA-5.2) will take place in Nairobi, Kenya on 28 February to 2 March 2022.

handling from the definition of controlled substances" (58, 60). The parties later observed that this adjustment refers to feedstock emissions, rather than feedstock use or consumption (64).

With feedstocks erroneously assumed to be converted into nonemissive or otherwise environmentally safe uses, the continuing production of feedstocks exempted by the Montreal Protocol contributes to an unauthorized market of chemicals that are then unlawfully used as refrigerants and foam blowing agents (65, 66). For example, the Protocol's SAP has long been concerned that global atmospheric emissions of carbon tetrachloride (CTC) are far greater than is explained by legal production. The chlorofluorocarbon CFC-11, for which CTC is an associated feedstock, illustrates the problem of unlawful feedstock production and consumption. In 2018, scientists determined that the global atmospheric emissions of CFC-11 were much greater than could be explained by known production and product life-cycle profiles (67). As illustrated in Table 1, CFC-11 is manufactured from CTC and is typically coproduced with CFC-12. The warning of possible unauthorized CTC, CFC-11, and CFC-12 production inspired an intense search by scientists and environmental authorities for the sources (68).

In 2019, scientists monitoring regional ODS concentrations suggested that increases in emissions of CFC-11 arising primarily around China's northeastern provinces accounted for at least 40 to 60% of the global rise in CFC-11 emissions (69). In 2020, using innovative statistical methods, scientists confirmed elevated emissions of CFC-11, CFC-12, and CFC-113 (70). In addition, as early as 2010 other scientists confirmed high levels of the unwanted HFC-23 (with a very high GWP<sub>100-y</sub>; see Table 3), a by-product of HCFC-22 production, which manufacturers had pledged to minimize (71–73). Reducing feedstock uses would reduce unlawful ODS and HFC production because there would be fewer facilities capable of producing these substances, which could then be more carefully monitored.

Just as the parties amended their treaty in 1990 to exempt feedstocks, they have the power to modify or eliminate such exemptions. For feedstock chemicals already under the jurisdiction of the Montreal Protocol, the parties should be able to narrow exemptions using their adjustment procedures. Adjustments take effect automatically for all parties after 6 mo, except parties who affirmatively opt out. Other feedstock chemicals can be added by amendment. The parties can still exempt critical uses of feedstocks, for example, in the production of substances that are necessary for rapidly replacing high-GWP HFCs under the Kigali Amendment, as well as the use of HCFC-22 to produce PTFE for medical applications, until suitable alternatives are available.

It is not yet possible to accurately quantify the feedstock emissions (both absolute quantities and relative percentages) that can be avoided by narrowing the feedstock exemptions under the Montreal Protocol, primarily because of inaccurate and incomplete reporting of feedstock production and use. However, recent atmospheric monitoring suggests that the benefits of narrowing feedstock exemptions can be substantial. For example, 309 Tg CO<sub>2</sub>-eq of HFC-23 emissions were added to the atmosphere between 2015 and 2017, roughly equivalent to

the total GHG emissions of Spain in 2017 (71). Also, global emissions of high-GWP CFC-11, CFC-12, CFC-113, and HFC-23 (see Table 3) have all been elevated in the past few years beyond levels explained by legal production and *de minimis* feedstock emissions (67, 70, 71). As Solomon et al. pointed out, "so far, the added CFC-11 has not been enough to significantly delay the closing of the ozone hole, but continuing additions of CFC-11 beyond 2030 would impede successful healing of the ozone hole by a decade or more" (40).

## Conclusion

The Montreal Protocol provides a proven upstream approach that has the potential to limit inadvertent emissions of ODS and HFC feedstocks as well as unauthorized production while also curtailing a significant fraction of plastics production made from these feedstocks. Reducing plastic pollution comprehensively also requires multiple strategies, including bans on single-use products, better collection and presorting, reuse, and recycling, and faster development of environmentally superior alternatives.

The Protocol is a successful and flexible policy instrument that is sensitive to business and national economic concerns. It also fully implements the principle of common but differentiated responsibilities and respective capabilities. The Montreal Protocol's success in protecting the ozone layer is well-documented (2, 5, 74), as is its success in protecting the climate (3, 17, 68, 73, 75, 76). Agreeing to narrow the feedstock exemptions under the Montreal Protocol would be consistent with the evolutionary "start-and-strengthen" history of the treaty and would provide significant benefits, including reduced ozone depletion, reduced climate warming, reduced plastics pollution, and reduced hazards to chemical workers and surrounding communities. Understanding of this previously missing link between ODS and HFC feedstocks and plastics manufacturing can motivate parties to further strengthen the Montreal Protocol to better protect the environment and human health.

As next steps, parties to the Montreal Protocol could 1) provide more detailed and accurate reporting of feedstock production, 2) ask the SAP to estimate the atmospheric impact of narrowing the feedstock exemptions, and 3) ask the TEAP to identify and catalog substitutes for plastics currently made with ODS and HFC feedstocks. With guidance from the MLF and the TEAP, national governments can continue to guide the choice of replacements that are affordable as well as technically and environmentally superior.

**Data Availability.** All study data are included in the article and/or *SI Appendix*.

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- 1 United Nations, Montreal Protocol on Substances that Deplete the Ozone Layer. <https://ozone.unep.org/treaties/montreal-protocol-substances-deplete-ozone-layer/text>. Accessed 4 November 2021.
- 2 P. J. Young et al., The Montreal Protocol protects the terrestrial carbon sink. *Nature* **596**, 384–388 (2021).
- 3 R. J. Salawitch, et al., "Twenty questions and answers about the ozone layer: 2018 Update" (World Meteorological Organization, United Nations Environment, National Oceanic and Atmospheric Administration, National Aeronautics and Space Administration, and European Commission, 2019).
- 4 UNEP OzoneAction, About Montreal Protocol. <https://www.unep.org/ozonaction/who-we-are/about-montreal-protocol>. Accessed 4 November 2021.

- 5 SAP, "Scientific assessment of ozone depletion: 2018" (World Meteorological Organization, United Nations Environment, National Oceanic and Atmospheric Administration, National Aeronautics and Space Administration, and European Commission, 2019).
- 6 G. J. M. Velders, S. O. Andersen, J. S. Daniel, D. W. Fahey, M. McFarland, The importance of the Montreal Protocol in protecting climate. *Proc. Natl. Acad. Sci. U.S.A.* **104**, 4814–4819 (2007).
- 7 United Nations, Vienna Convention for the Protection of the Ozone Layer. [https://treaties.un.org/doc/Treaties/1988/09/19880922%2003-14%20AM/Ch\\_XXVII\\_02p.pdf](https://treaties.un.org/doc/Treaties/1988/09/19880922%2003-14%20AM/Ch_XXVII_02p.pdf). Accessed 4 November 2021.
- 8 UNEP, "Briefing note: Legal aspects in the context of HFC management under the Montreal Protocol" (United Nations Environment Programme, 2016).
- 9 R. Lohmann *et al.*, Are fluoropolymers really of low concern for human and environmental health and separate from other PFAS? *Environ. Sci. Technol.* **54**, 12820–12828 (2020).
- 10 B. Ameduri, Fluoropolymers: The right material for the right applications. *Chemistry* **24**, 18830–18841 (2018).
- 11 K. R. Solomon *et al.*, Sources, fates, toxicity, and risks of trifluoroacetic acid and its salts: Relevance to substances regulated under the Montreal and Kyoto Protocols. *J. Toxicol. Environ. Health B Crit. Rev.* **19**, 289–304 (2016).
- 12 Crow Polymer Science, Thermal-oxidative degradation of rubber. <https://polymerdatabase.com/polymer%20chemistry/Thermal%20Degradation.html>. Accessed 4 November 2021.
- 13 B. J. Henry *et al.*, A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers. *Integr. Environ. Assess. Manag.* **14**, 316–334 (2018).
- 14 M. I. Gomis, R. Vestergren, D. Borg, I. T. Cousins, Comparing the toxic potency in vivo of long-chain perfluoroalkyl acids and fluorinated alternatives. *Environ. Int.* **113**, 1–9 (2018).
- 15 R. Geyer, J. R. Jambeck, K. L. Law, Production, use, and fate of all plastics ever made. *Sci. Adv.* **3**, e1700782 (2017).
- 16 S. O. Andersen, K. M. Sarma, *Protecting the Ozone Layer: The United Nations History* (Earthscan Press, 2002).
- 17 SAP, "Scientific assessment of ozone depletion: 2010" (World Meteorological Organization, United Nations Environment, National Oceanic and Atmospheric Administration, National Aeronautics and Space Administration, and European Commission, 2011).
- 18 IPCC, *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge University Press, 2014).
- 19 C. Laufkötter, J. Zscheischler, T. L. Frölicher, High-impact marine heatwaves attributable to human-induced global warming. *Science* **369**, 1621–1625 (2020).
- 20 O. Hoegh-Guldberg, "Reviving the Ocean Economy: The Case for Action—2015" (World Wildlife Fund, 2015).
- 21 D. K. A. Barnes, F. Galgani, R. C. Thompson, M. Barlaz, Accumulation and fragmentation of plastic debris in global environments. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* **364**, 1985–1998 (2009).
- 22 J. R. Jambeck *et al.*, Marine pollution. Plastic waste inputs from land into the ocean. *Science* **347**, 768–771 (2015).
- 23 Pew Charitable Trusts & SYSTEMIQ, "Breaking the plastic wave: A comprehensive assessment of pathways towards stopping ocean plastic pollution" (Pew Charitable Trusts & SYSTEMIQ, 2020).
- 24 L. M. Rios, C. Moore, P. R. Jones, Persistent organic pollutants carried by synthetic polymers in the ocean environment. *Mar. Pollut. Bull.* **54**, 1230–1237 (2007).
- 25 L. A. Hamilton, *et al.*, "Plastic & climate: The hidden costs of a plastic planet" (Center for International Environmental Law, Environmental Integrity Project, FracTracker Alliance, Global Alliance for Incinerator Alternatives, and 5Gyres, 2019).
- 26 X.-D. Sun *et al.*, Differentially charged nanoplastics demonstrate distinct accumulation in *Arabidopsis thaliana*. *Nat. Nanotechnol.* **15**, 755–760 (2020).
- 27 A. L. Dawson *et al.*, Turning microplastics into nanoplastics through digestive fragmentation by Antarctic krill. *Nat. Commun.* **9**, 1001 (2018).
- 28 A. A. de Souza Machado, W. Kloas, C. Zarfl, S. Hempel, M. C. Rillig, Microplastics as an emerging threat to terrestrial ecosystems. *Glob. Change Biol.* **24**, 1405–1416 (2018).
- 29 N. Weithmann *et al.*, Organic fertilizer as a vehicle for the entry of microplastic into the environment. *Sci. Adv.* **4**, eaap8060 (2018).
- 30 T. S. Galloway, M. Cole, C. Lewis, Interactions of microplastic debris throughout the marine ecosystem. *Nat. Ecol. Evol.* **1**, 0116 (2017).
- 31 M. E. Hodson, C. A. Duffus-Hodson, A. Clark, M. T. Prendergast-Miller, K. L. Thorpe, Plastic bag derived-microplastics as a vector for metal exposure in terrestrial invertebrates. *Environ. Sci. Technol.* **51**, 4714–4721 (2017).
- 32 E. Huerta Lwanga *et al.*, Microplastics in the terrestrial ecosystem: Implications for *Lumbricus terrestris* (oligochaeta, lumbricidae). *Environ. Sci. Technol.* **50**, 2685–2691 (2016).
- 33 J. Brahney, M. Hallerud, E. Heim, M. Hahnenberger, S. Sukumaran, Plastic rain in protected areas of the United States. *Science* **368**, 1257–1260 (2020).
- 34 Y. Zhang *et al.*, Atmospheric microplastics: A review on current status and perspectives. *Earth Sci. Rev.* **203**, 103118 (2020).
- 35 S. Allen *et al.*, Atmospheric transport and deposition of microplastics in a remote mountain catchment. *Nat. Geosci.* **12**, 339–344 (2019).
- 36 United Nations, Stockholm Convention on Persistent Organic Pollutants (POPs). [www.pops.int/TheConvention/Amendments/Overview/tabid/7908/Default.aspx](http://www.pops.int/TheConvention/Amendments/Overview/tabid/7908/Default.aspx). Accessed 4 November 2021.
- 37 D. Taufik, M. J. Reinders, K. Molenveld, M. C. Onwezen, The paradox between the environmental appeal of bio-based plastic packaging for consumers and their disposal behaviour. *Sci. Total Environ.* **705**, 135820 (2020).
- 38 UNEP, Handbook for the Montreal Protocol on Substances that Deplete the Ozone Layer, (United Nations Environment Programme, ed. 14, 2020). <https://ozone.unep.org/sites/default/files/Handbooks/MP-Handbook-2020-English.pdf>.
- 39 D. Kaniaru, R. Shende, D. Zaelke, Landmark agreement to strengthen Montreal Protocol provides powerful climate mitigation. *Sustain. Dev. Law Policy* **8**, 46–51 (2008).
- 40 S. Solomon, J. Alcamo, A. R. Ravishankara, Unfinished business after five decades of ozone-layer science and policy. *Nat. Commun.* **11**, 4272 (2020).
- 41 Y. Xu, D. Zaelke, G. J. M. Velders, V. Ramanathan, The role of HFCs in mitigating 21st century climate change. *Atmos. Chem. Phys.* **13**, 6083–6089 (2013).
- 42 G. Dreyfus *et al.*, "Assessment of climate and development benefits of efficient and climate-friendly cooling" (Climate & Clean Air Coalition and Institute for Governance & Sustainable Development, 2020).
- 43 M. Molina *et al.*, Reducing abrupt climate change risk using the Montreal Protocol and other regulatory actions to complement cuts in CO<sub>2</sub> emissions. *Proc. Natl. Acad. Sci. U.S.A.* **106**, 20616–20621 (2009).
- 44 S. O. Andersen, M. Gonzalez, *Global Success in Avoiding the Intangible Threat of Stratospheric Ozone Depletion* (American Society for Environmental History, Chicago, IL, 2013).
- 45 K. M. Sarma, S. O. Andersen, D. Zaelke, "Ozone layer, international protection" in *Max Planck Encyclopedias of International Law* (Max Planck Institute for Comparative Public Law and International Law, 2012).
- 46 D. Zaelke, S. O. Andersen, N. Borgford-Parnell, Strengthening ambition for climate mitigation: The role of the Montreal Protocol in reducing short-lived climate pollutants: The role of the Montreal Protocol. *Rev. Eur. Community Int. Environ. Law* **21**, 231–242 (2012).
- 47 S. Carvalho, S. O. Andersen, D. Brack, N. J. Sherman, "Alternatives to high-GWP hydrofluorocarbons" (Institute for Governance & Sustainable Development and OzonAction, 2014).
- 48 S. O. Andersen, D. Brack, J. Depledge, "A global response to HFCs through fair and effective ozone and climate policies" (The Royal Institute of International Affairs, 2014).
- 49 D. Zaelke, N. Borgford-Parnell, The importance of phasing down hydrofluorocarbons and other short-lived climate pollutants. *J. Environ. Stud. Sci.* **5**, 169–175 (2015).
- 50 S. Gao, Managing short-lived climate forcers in curbing climate change: An atmospheric chemistry synopsis. *J. Environ. Stud. Sci.* **5**, 130–137 (2015).
- 51 D. Hunter, J. Salzman, D. Zaelke, *International Environmental Law and Policy* (Foundation Press, ed. 6, 2021).



- 52 United Nations Environment Assembly, Marine litter and microplastics (2018). <https://wedocs.unep.org/bitstream/handle/20.500.11822/22773/K1800210%20-%20UNEP-EA-3-RES-7%20-%20Advance.pdf?sequence=15&isAllowed=y>. Accessed 4 November 2021.
- 53 United Nations Environment Assembly, Marine plastic litter and microplastics (2019). <https://documents-dds-ny.un.org/doc/UNDOC/GEN/K19/010/91/PDF/K1901091.pdf>. Accessed 4 November 2021.
- 54 United Nations Environment Assembly, Virtual preparatory meetings of the AHEG. <https://environmentassembly.unenvironment.org/virtual-preparatory-meetings>. Accessed 4 November 2021.
- 55 J. Wallace, Corporations call for international plastic waste rules, *GreenWire* (2020). <https://www.eenews.net/greenwire/2020/10/14/stories/1063716217>. Accessed 4 November 2021.
- 56 M. K. Miller, T. A. Batchelor, "Feedstock uses of ODS: Information paper on feedstock uses of ozone-depleting substances" (Touchdown Consulting, 2012).
- 57 UNEP OzonAction, Training program for national ozone officers, Module 5: Control measures, exempted uses of controlled substances. [https://www.ozonactionmeetings.org/system/files/5.4\\_background\\_exempted\\_uses\\_final\\_1.pdf](https://www.ozonactionmeetings.org/system/files/5.4_background_exempted_uses_final_1.pdf). Accessed 4 November 2021.
- 58 UNEP, Decision IV/12: Clarification of the definition of controlled substances. <https://ozone.unep.org/treaties/montreal-protocol/meetings/fourth-meeting-parties/decisions/decision-iv12-clarification-definition-controlled-substances>. Accessed 4 November 2021.
- 59 UNEP, Decision X/12: Emissions of ozone-depleting substances from feedstock applications. <https://ozone.unep.org/treaties/montreal-protocol/meetings/tenth-meeting-parties/decisions/decision-x12-emissions-ozone-depleting-substances-feedstock-applications>. Accessed 4 November 2021.
- 60 UNEP, Decision XXIV/6: Feedstock uses. <https://ozone.unep.org/treaties/montreal-protocol/meetings/twenty-fourth-meeting-parties/decisions/decision-xxiv6-feedstock-uses>. Accessed 4 November 2021.
- 61 UNEP, Decision IX/28: Revised formats for reporting data under Article 7 of the Protocol. <https://ozone.unep.org/treaties/montreal-protocol/meetings/ninth-meeting-parties/decisions/decision-ix28-revised-formats-reporting-data-under-article-7-protocol?q=treaties/montreal-protocol/meetings/ninth-meeting-parties/decisions/decision-ix28-revised-formats>. Accessed 4 November 2021.
- 62 UNEP, Decision VII/30: Export and import of controlled substances to be used as feedstock. <https://ozone.unep.org/treaties/montreal-protocol/meetings/seventh-meeting-parties/decisions/decision-vii30-export-and-import-controlled-substances-be-used-feedstock>. Accessed 4 November 2021.
- 63 UNEP, Decision I/12B: Clarification of terms and definitions: Controlled substances produced. <https://ozone.unep.org/treaties/montreal-protocol/meetings/first-meeting-parties/decisions/decision-i12b-clarification-terms-and-definitions-controlled-substances-produced>. Accessed 4 November 2021.
- 64 UNEP, Decision XXIII/7: Use of controlled substances as process agents. <https://ozone.unep.org/treaties/montreal-protocol/meetings/twenty-third-meeting-parties/decisions/decision-xxiii7-use-controlled-substances-process-agents?q=treaties/montreal-protocol/meetings/twenty-third-meeting-parties/decisions/decision-xxiii7-use>. Accessed 4 November 2021.
- 65 UNEP, "Illegal trade in ozone depleting substances: Is there a hole in the Montreal Protocol?" OzonAction Newsletter Special Supplement 6 (2001).
- 66 M. K. Miller, T. A. Batchelor, "Future needs in ozone layer protection: An overview of the remaining challenges in ozone layer protection, and their relevance to countries with economies in transition" (Touchdown Consulting, 2009).
- 67 S. A. Montzka et al., An unexpected and persistent increase in global emissions of ozone-depleting CFC-11. *Nature* **557**, 413–417 (2018).
- 68 N. R. P. Harris, S. A. Montzka, P. A. Newman, "Report on the International Symposium on the Unexpected Increase in Emissions of Ozone-Depleting CFC-11" (SPARC newsletter no. 53, 2019).
- 69 M. Rigby et al., Increase in CFC-11 emissions from eastern China based on atmospheric observations. *Nature* **569**, 546–550 (2019).
- 70 M. Lickley et al., Quantifying contributions of chlorofluorocarbon banks to emissions and impacts on the ozone layer and climate. *Nat. Commun.* **11**, 1380 (2020).
- 71 K. M. Stanley et al., Increase in global emissions of HFC-23 despite near-total expected reductions. *Nat. Commun.* **11**, 397 (2020).
- 72 B. R. Miller et al., HFC-23 (CHF<sub>3</sub>) emission trend response to HCFC-22 (CHClF<sub>2</sub>) production and recent HFC-23 emission abatement measures. *Atmos. Chem. Phys.* **10**, 7875–7890 (2010).
- 73 S. O. Andersen, K. M. Sarma, "Making climate change and ozone treaties work together to curb HFC-23 and other "super greenhouse gases" (Natural Resources Defense Council, 2010).
- 74 SAP, "Scientific assessment of ozone depletion: 2013" (World Meteorological Organization, United Nations Environment, National Oceanic and Atmospheric Administration, National Aeronautics and Space Administration, and European Commission, 2014).
- 75 SAP, "Scientific assessment of ozone depletion: 2006" (World Meteorological Organization, United Nations Environment, National Oceanic and Atmospheric Administration, National Aeronautics and Space Administration, and European Commission, 2007).
- 76 M. Molina, D. Zaelke, "A comprehensive approach for reducing anthropogenic climate impacts including risk of abrupt climate changes" in *Proceedings of the Working Group, Scripta Varia.*, P. J. Crutzen, L. Bengtsson, V. Ramanathan, Eds. (Pontifical Academy of Sciences, 2013).
- 77 K. H. Nam, D. C. Na, D. S. Kim, Method for the preparation of difluoromethane (1996). <https://patentimages.storage.googleapis.com/bf/c5/63/5f634c34f7325d/US5495057.pdf>. Accessed 4 November 2021.
- 78 Y. Wu, Y. Lin, Y. Wang, J. Xu, Method for preparation of HFC-32 (1997). <https://patentimages.storage.googleapis.com/0a/d8/e2/8cd12df293a0b4/CN1167102A.pdf>. Accessed 4 November 2021.
- 79 G. J. Puts, P. Crouse, B. M. Ameduri, Polytetrafluoroethylene: Synthesis and characterization of the original extreme polymer. *Chem. Rev.* **119**, 1763–1805 (2019).
- 80 E. Piepho, V. Wilmet, O. Buyle, Pentafluoroethane production method (2006). <https://patentimages.storage.googleapis.com/2d/2c/82/a642240a976bfe/US7067707.pdf>. Accessed 4 November 2021.
- 81 K. Weissmerl, H.-J. Arpe, *Industrial Organic Chemistry* (Wiley, ed. 3, 1997).
- 82 M. VanDerPuy, A. Thenappan, Process for the Manufacture of 1, 1, 3, 3-pentafluoropropane (1996). <https://patentimages.storage.googleapis.com/32/d9/b7/4ffd449b610edc/US5574192.pdf>. Accessed 4 November 2021.
- 83 J. Lu et al., Synthesis of HFC-134a over CrF<sub>3</sub>/AlF<sub>3</sub> catalysts. *Catal. Lett.* **41**, 221–224 (1996).
- 84 H.-M. Deger, W. Krause, D. Schmid, M. Hoeveler, Process for preparing Pentafluoroethane (R 125) (1998). <https://patentimages.storage.googleapis.com/08/26/cd/b2db5e17416416/US5763701.pdf>. Accessed 4 November 2021.
- 85 C. Woolf, Manufacture of 1, 2, 2-trichloro-1, 1, 2-trifluoroethane (1958). <https://patentimages.storage.googleapis.com/88/75/6f/e3febb756a35de/US2850543.pdf>. Accessed 4 November 2021.
- 86 P. Cuzzato, L. Bragante, Process to obtain CFC 113a from CFC 113 (2004). <https://patentimages.storage.googleapis.com/85/07/d1/297991339aeab/US6791001.pdf>. Accessed 4 November 2021.
- 87 A. J. Sicard, R. T. Baker, Fluorocarbon refrigerants and their syntheses: Past to present. *Chem. Rev.* **120**, 9164–9303 (2020).
- 88 G. Martens, M. Godfroid, Manufacture of 1, 1-difluoroethane (1975). <https://patentimages.storage.googleapis.com/ea/e5/4a/7c45474e260633/US3862995.pdf>. Accessed 4 November 2021.
- 89 D. Balthasart, P. Pennetreau, Process for the manufacture of 1, 1, 1-trihaloethanes (1996). <https://patentimages.storage.googleapis.com/80/2d/41/a186ba9498c3d2/US5574191.pdf>. Accessed 4 November 2021.
- 90 B. M. Martin, Process for polymerizing tetrafluoroethylene (1946). <https://patentimages.storage.googleapis.com/59/2e/d4/0933e4a0ff6168/US2393967.pdf>. Accessed 4 November 2021.
- 91 Z. Wang, W. Han, H. Tang, Y. Li, H. Liu, Preparation of N-doped ordered mesoporous carbon and catalytic performance for the pyrolysis of 1-chloro-1,1-difluoroethane to vinylidene fluoride. *Microporous Mesoporous Mater.* **275**, 200–206 (2019).
- 92 B. Ameduri, From vinylidene fluoride (VDF) to the applications of VDF-containing polymers and copolymers: Recent developments and future trends. *Chem. Rev.* **109**, 6632–6686 (2009).

- 93 F. B. Downing, A. F. Benning, R. C. McHarness, Method for pyrolyzing polyfluoroalkanes (1949). <https://patentimages.storage.googleapis.com/bb/43/3c/d6401afdcd9b1d/US2480560.pdf>. Accessed 4 November 2021.
- 94 J. T. Goldbach et al., "Commercial synthesis and applications of poly(vinylidene fluoride)" in *Fluorinated Polymers: Volume 2: Applications*, B. M. Ameduri, H. Sawada, Eds. (The Royal Society of Chemistry, 2017), chap. 6, pp. 127–157.
- 95 F. Boschet, B. Ameduri, (Co)polymers of chlorotrifluoroethylene: Synthesis, properties, and applications. *Chem. Rev.* **114**, 927–980 (2014).
- 96 J. A. Abusleme, C. Manzoni, Synthesis of perhalogenated thermoplastic (co)polymers of chlorotrifluoroethylene (2004). <https://patentimages.storage.googleapis.com/dd/c1/25/9de3cfca81b6f8/US6706803.pdf>. Accessed 4 November 2021.
- 97 S. R. Sandler, W. Karo, *Polymer Syntheses* (Elsevier, ed. 2, 1994).
- 98 V. N. M. Rao, A. M. Subramanian, Catalytic manufacture of vinyl fluoride (1999). <https://patentimages.storage.googleapis.com/af/b9/c1/1147ddd69d207c/US5880315.pdf>. Accessed 4 November 2021.
- 99 F. L. Johnston, P. D. Cargill, Vinyl fluoride polymerization process (1950). <https://patentimages.storage.googleapis.com/15/a8/98/ba67b716f46010/US2510783.pdf>. Accessed 4 November 2021.
- 100 MLF ExCom, "Report on emission reductions and phase-out of CTC (Decision 55/45)" (Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol, 2009).
- 101 D. Sherry, "Unexpected CFC-11 emissions: The ramifications for CTC: An update on its production—How much is available?" (Montreal Protocol Technology and Economic Assessment Panel, 2019).