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Are fluoropolymers really of low concern for human and environmental health and separate from other PFAS?

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23 Abstract

24 Fluoropolymers are a group of polymers within the class of per- and polyfluoroalkyl substances (PFAS). The objective of this analysis is to evaluate the evidence regarding the environmental 25 26 and human health impacts of fluoropolymers throughout their life cycle(s). Production of some 27 fluoropolymers is intimately linked to the use and emissions of legacy and novel PFAS as 28 polymer processing aids. There are serious concerns regarding the toxicity and adverse effects 29 of these processing aids on humans and the environment. A variety of other PFAS, including 30 monomers and oligomers, are emitted during the production, processing, use and end-of-life 31 treatment of fluoropolymers. There are further concerns regarding the safe disposal of fluoropolymers and their associated products at the end of their life cycle. While recycling and 32 reuse of fluoropolymers is performed on some industrial waste, there are only limited options 33 34 for their recycling from consumer products. The evidence reviewed in this analysis does not find a scientific rationale for concluding that fluoropolymers are of low concern for 35 environmental and human health. Given fluoropolymers' extreme persistence, emissions 36 37 associated with their production, use, and disposal, and high likelihood for human exposure to PFAS, their production and uses should be curtailed except in cases of essential use. 38

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41 Introduction

The class of per- and polyfluoroalkyl substances (PFAS) consists of polymers and non-polymers.¹
Most regulatory and academic attention so far has focused on the non-polymeric PFAS, either
perfluorinated or polyfluorinated alkyl substances. Within the groups of polymeric PFAS, there
are fluoropolymers, side-chain fluorinated polymers, and poly- or perfluoropolyethers.

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47	As defined by Buck et al. (2011), "fluoropolymers" represent a distinct subset of fluorinated
48	polymers, based on a carbon-only polymer backbone with F atoms directly attached to it, e.g.,
49	polytetrafluoroethylene (PTFE). ¹ In this analysis, we focus on fluoropolymers, but do not assess
50	concerns about other fluorine-containing polymers, namely side-chain fluorinated polymers,
51	and poly- or perfluoropolyethers. The group of fluoropolymers is dominated by PTFE; combined
52	with fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE) and
53	tetrafluoroethylene-copolymers; they account for around 75% of the fluoropolymer market. ²
54	Other important fluoropolymers include polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF)
55	and fluoroelastomers. One additional fluoropolymer that is discussed in this policy analysis is
56	the functionalized fluoropolymer Nafion [®] (produced by Chemours), which is a
57	tetrafluoroethylene-based fluoropolymer-copolymer incorporating perfluorovinyl ether groups
58	terminated with sulfonate groups. A review by Gardiner (2015) includes a more complete
59	overview of the different types of fluoropolymers. ³ The fluoropolymer industry produced
60	320 300 tonnes of fluorinated plastic materials in 2018 ⁴ , and production is steadily increasing. ³
61	By 2018 the global fluoropolymer industry was expected to be at \$10 billion per annum. ³
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Here we evaluate the evidence regarding the environmental and health impacts of
fluoropolymers. Our analysis was prompted by a recent suggestion that fluoropolymers should
be considered as polymers of low concern (PLC).² According to the Organization for Economic
Cooperation and Development (OECD), "polymers of low concern are those deemed to have
insignificant environmental and human health impacts".⁵ The PLC status of a material leads to
exemptions for manufacturers from requirements under the legal chemicals management
frameworks in some jurisdictions.⁶

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The PLC concept is currently derived from the characteristics of finished polymers but does not
 cover problems occurring during production and disposal. In recognition of the potential risks
 posed by PFAS-related polymers, the U.S. Environmental Protection Agency has denied PLC
 exemptions for fluorinated side-chain polymers, but has not acted on fluoropolymers per se ⁷.

More recently, in 2019, the Industry-led European Centre for Ecotoxicology and Toxicology of 76 77 Chemicals (ECETOC) developed the Conceptual Framework for Polymer Risk Assessment (CF4Polymers).⁸ The CF4Polymers framework provides basic guiding principles to be considered 78 in assessing potential ecological and human health hazards and risks posed by polymer 79 products. Unlike the PLC concept, CF4Polymers also considers specific life cycle stages of 80 81 polymer products and their associated routes of exposure. The CF4Polymers polymer risk assessment thus appears sufficiently flexible to allow consideration of all potential chemical 82 83 hazards at each life stage of a fluoropolymer. However, the authors of the CF4Polymers framework support the PLC approach as a means of streamlining the polymer risk assessment. 84

They specifically support the findings of Henry et al.² and state that they are "...unaware of scientific evidence to justify generally assigning fluoropolymers the same level of regulatory concern as other PFAS".⁸

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89	A fluoropolymer as a finished product could technically meet the definitions of a PLC, but still
90	pose significant concerns to human health and the environment due to emissions occurring
91	during the life cycle (Figure 1). A well-known case where this occurs is the release of processing
92	aids during the manufacture of some fluoropolymers. The pollution caused by emissions of low-
93	molecular-weight PFAS used as polymer processing aids (i.e., emulsifiers, dispersants and
94	surfactants at large) for the manufacture of some types of fluoropolymers has received
95	considerable attention. ^{9–11}
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97	Fluoropolymers are very diverse in how they are produced (as granulates, fine powders or
98	aqueous dispersions, through emulsion or suspension polymerization, with different grades),
99	shipped, and used, which renders generic judgements on their behavior and characteristics
100	difficult. For example, some fluoropolymers do not require PFAS-based processing aids in their
101	manufacture (e.g. granular PTFE), whereas other fluoropolymers (e.g. fine powder PTFE and
102	PVDF) are manufactured using PFAS-based processing aids.

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In this paper, we identify concerns for environmental and human health resulting from
 emissions during fluoropolymer production, processing and disposal. We first review the link

between some types of fluoropolymers and PFAS emissions and then turn to more generalconcerns associated with (fluoro)polymers.

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History of pollution from fluoropolymer production is closely tied to use of PFAS as
 polymer processing aids

Low-molecular-weight PFAS have been used for decades as emulsifiers in the polymerization of 111 some types of fluoropolymer products. The resulting long-term exposure of production 112 113 workers, the environment, and nearby neighborhoods to high levels of PFAS polymer 114 processing aids by fluoropolymer manufacturers is now well documented and has driven much of the initial action on PFAS control.^{12–19} 115 Historically, the most widely used polymer processing aids were the ammonium salts of 116 perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA).^{20,21} The majority of PFOA 117 and PFNA now in the global environment is a result of the historical use of salts of these 118 substances as processing aids.^{20,22} As a consequence of human and environmental health 119 concerns, under the US EPA 2010/15 Stewardship Program, eight major manufacturers phased 120 out PFOA/PFNA in their fluoropolymer production.²³ Many other manufacturers, though, still 121

122 utilize PFOA as a processing aid; PFOA emissions have, for example, now widely polluted the

123 Chinese environment and likely also the Arctic through ocean transport.²⁴

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2. Substitute fluoropolymer processing aids raise similar concerns

128	Fluoropolymer producers in industrialized countries have moved to substitute PFOA and PFNA
129	in polymer production with structurally similar alternatives such as per- and
130	polyfluoroalkylether carboxylic acids (PFECAs). ^{21,25} These PFECAs are not technically classified as
131	"long-chain" perfluoroalkyl acids (PFAAs) like PFOA and PFNA, but they have similar physical
132	and chemical properties (including surfactancy and resistance to degradation) when compared
133	with the original emulsifiers. ²⁶
134	One example is the substitution of PFOA by the ammonium salt of hexafluoropropylene oxide
135	dimer acid (HFPO-DA, CAS 62037-80-3, or GenX) (Figure 2a) for PTFE production. When
136	released into the environment, GenX, due to similarly high persistence and mobility as its
137	predecessor PFOA, accumulates in surface water, groundwater, and soil. ^{27,28} GenX has also
138	been observed in surface water and drinking water in areas where it is produced, e.g., in North
139	Carolina ²⁹ and the Netherlands. ¹² GenX does not bioaccumulate in animals to the same extent
140	as PFOA ³⁰ , but has been added to the EU's Candidate List of Substances of Very High Concern
141	(SVHC) due to an equivalent level of concern about its very high persistence, mobility in water,
142	potential for long-range transport, accumulation in plants and observed effects on human
143	health and the environment. ³¹
144	In another example, (the ammonium salt of) PFNA has been substituted with another PFECA
145	(CAS 329238-24-6) (Figure 2b) ²⁶ , which has since been detected in the surface water near a
146	fluoropolymer production facility in Italy ³² and in the surface and groundwater near a similar

147 PVDF facility in West Deptford, New Jersey (US).³³ Another replacement polymer processing

aid, cC604, is the ammonium salt of [perfluoro{acetic acid, 2-[(5-methoxy-1)] (Figure 2c). cC604
has been detected in surface and groundwater in the Veneto region in Italy.³⁴ Also, ammonium
4,8-dioxa-3H-perfluorononanoate (CAS 958445-44-8, ADONA) (Figure 2d) is a PFECA processing
aid that has been detected in the Rhine River in Germany³⁵ and in the blood of individuals living
near a fluorochemical production facility in this area.³⁶

153 These examples demonstrate the similar concern between legacy and replacement

154 fluoropolymer processing aids mentioned above in terms of environmental exposure,

155 bioaccumulation and toxicity.^{37,38} Many more PFAS with similar structures have been patented

156 for possible use as fluoropolymer processing aids.^{39–41} Thus, even if individual processing aids

are banned, many other PFAS are available with the same functionality and similar concerns

158 with respect to persistence and human health effects. 3M claimed that modern containment

technologies recapture approximately 98% of polymer processing aids such as PFOA and others

⁴², but it is not clear if the remaining 2% are not of concern. Moreover, independent data are

161 not available to support their claim.

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3. Monomer, oligomer and synthesis by-product emissions during the production of fluoropolymers

Fluoropolymers are made of one or several types of monomers. During the synthesis, incomplete polymerization will result in residual monomers and oligomers, and smaller 'polymers' with up to about 100 monomer units. These and other synthesis by-products are not bound to the polymers and may be released to air upon heating during manufacturing and processing (including sintering) and to water through wastewater streams.^{9,13} For example, a series of polyfluoroalkyl carboxylic acids were discovered near Decatur, AL (US), each differing by 1,1difluoroethene, CF₂H₂, which was used as a building block for production of PVDF at that site.¹³ Many ultrashort-chain fluorinated by-products are highly volatile, and therefore difficult to remove in filters or liquid scrubber baths. An example is trifluoromethane (CHF₃), which has a boiling point of -82.1 °C and belongs to the group of hydrofluorocarbon (HFC) gases (HFC-23); it has a 100-year global warming potential of 12400 relative to CO₂.⁴³

Various PFAS oligomers were recently detected in the stack emission samples collected from a fluorochemical production site.⁴⁴ A wide range of byproducts of the functionalized fluoropolymer Nafion has been observed in the environment and found to bioaccumulate in fish⁴⁵, which could be the result of manufacturing discharges¹⁰, or losses resulting from Nafion use over time.⁴⁶ It is noted that Nafion does probably not meet the PLC criteria because its sulfonic functional group can be degraded and lost.

Little is known about emissions of airborne fluoropolymer particles and oligomers, another potential source of PFAS in the atmosphere. Henry et al. (2018) specified the particle size in fluoropolymer powders to vary between 50 and 250 μm, larger than the harmful particle sizes of PM10 and PM2.5 (10 and 2.5 μm) in terms of harms caused by inhalation.² However, fluoropolymer particles vary in size, and may contain and transport residual monomers/oligomers long distances from their emission sources.

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4. Leaching of low-molecular-weight PFAS from fluoropolymers during processing and use

191	Linked to the use of PFAS as production processing aids (see above), there are concerns
192	regarding the remaining low molecular weight PFAS in fluoropolymers after production. For
193	example, Henry et al. (2018) argued that fluoropolymers are not toxic, based on a dataset that
194	was restricted only to a few fluoropolymer finished products, typically > 100,000 Da. ²
195	Concentrations of leachable components reported for those specific fluoropolymer products,
196	particularly a PTFE fine powder, were labeled "very low" at 1 ppm (i.e., 1 mg/kg) ² , though
197	earlier studies reported concentrations of 1-10 ppm in PTFE fine powder and much higher in
198	PTFE aqueous dispersion (see SI in Wang et al. (2014) ²²). Similar levels of PFAAs (0.3-24 ppm)
199	were found in personal care products that contained PTFE fine particles (Assuming the
200	cosmetics contained 1% PTFE, the range of leachables is 0.3 -24 ppm; if the total organofluorine
201	measurements represented PTFE fine powder, then the range of PFAA-leachables is 15-1,000
202	ppm). ⁴⁷
203	Processing aids and other PFAS residuals, impurities and synthesis by-products are also known
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	to leach from fluoropolymer products, for example in chromatographic instrumentation,
205	to leach from fluoropolymer products, for example in chromatographic instrumentation, causing a consistent background signal in analytical chemistry at the ppt level. ^{48,49} Residuals of
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	causing a consistent background signal in analytical chemistry at the ppt level. ^{48,49} Residuals of
206	causing a consistent background signal in analytical chemistry at the ppt level. ^{48,49} Residuals of 1 ppm may have significant toxicological relevance, given the recently proposed drinking water

and drive off volatiles.² Such aggressive treatment raises the question of how these residuals
and volatiles are captured and their releases controlled, or if production by-products become
air or water emissions with potential for human exposure. There is evidence that the drying
step (sintering) of fluoropolymers has led to substantial emissions to air of processing aids at
sites of PTFE production (West Virginia (US) and the Netherlands) and use sites in the US (North
Bennington, VT; Merrimack, NH, Hoosick Falls, NY).^{52–54}

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5. Toxicity of fluoropolymer processing aids, monomers and oligomers

Legacy processing aids (i.e., PFOA, PFNA) used to manufacture fluoropolymers are linked to a 218 219 wide range of health effects in experimental animal models (causative) and humans 220 (associative), including certain types of cancer, immunotoxicity, reproductive and developmental toxicity, liver toxicity, and thyroid disease. ⁵⁵ HFPO-DA shows a similar toxic 221 potency in rodents as PFOA ³⁸, but its pharmacokinetics in humans are still uncertain. Few 222 223 reports have been published regarding the potential toxicity of other replacement PFECAs, such as ADONA 56,57 or the PFECA CAS 329238-24-6 58, but these replacement chemicals are as 224 environmentally persistent as the original polymer processing aids.³⁷ The production of many 225 226 fluoropolymers still requires the use of PFAS as surfactants or as monomers, which causes 227 releases to the environment during manufacture, and thus may pose a risk to human health and the environment. For example, the so-called "Teflon-flu" or "Polymer fume fever" has been 228 ascribed to workers exposure to PTFE oligomers during production/manufacturing ⁵⁹. 229

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6. Penetration of cell membranes by macromolecules

While not specific to fluoropolymers, PLC status is partially based on a mass-based cutoff for 232 233 cellular uptake (MW of > 1000 Da or 10,000 Da, depending on reactive functional groups). This 234 was summarized by Henry et al. (2018), who advocated for PLC status of some fluoropolymers by suggesting "Polymers are too large to penetrate cell membranes".² This position is not 235 236 currently supported by the scientific literature related to the bioavailability of similarly sized 237 micro- and nanoplastics of fluorine-free polymers. Nearly a decade ago, Jiang et al. (2011) 238 showed that polystyrene nanoparticles of about 100 nm diameter are easily able to enter stem cells. ⁶⁰ Similarly, Pitt et al. (2018) reported that 42 nm polystyrene nanoparticles were present 239 240 in tissue and organs of maternally and co-parentally exposed F1 embryos/larvae, proving membrane crossing capabilities of polymer nanoparticles. ⁶¹ Polymer nanoparticles with 241 molecular weights between 12,000 and 21,000 Da have been used to deliver chemotherapeutic 242 243 drugs to cancer cells ⁶², and those on the order of tens of nanometers in size have been found to enter cells and eventually even cell nuclei. ^{63,64} Furthermore, Geiser et al. (2003) showed that 244 inhaled spherical microparticles of Teflon were able to migrate into the surface lining layer of 245 hamster alveoli, where interactions with lung cells could occur. ⁶⁵ Many fluoropolymers are 246 marketed in the form of suspensions with sub-micron fluoropolymer particle sizes (see, e.g. 247 248 https://www.teflon.com/en/products/dispersions), thus, release of bioavailable fluoropolymer 249 particles is plausible. Based on such emerging evidence from environmental and medical research on diverse macromolecules ⁶⁶, a blanket statement that polymers cannot enter cells is 250 251 factually inaccurate.

It is recognized, however, that the global production of fluoropolymers (though not insignificant
at 320 000 tons in 2018⁴, and increasing³) is relatively low in volume compared to global
production of plastics (300 million tons in 2018⁶⁷) and therefore nano-sized fluoropolymers may
not make a large contribution to the total exposure to, and toxicity, of nano-plastics.
Furthermore, the exposure and toxicity of nano-plastics is an area of ongoing research with
many unknowns.⁶⁸

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7. Persistence and disposal of fluoropolymers

Fluoropolymers are extremely persistent⁴², which, in the same way as for other polymers, can lead to a wide array of issues, particularly with respect to disposal of fluoropolymer-containing wastes and products.⁶⁹ Current concern over microplastics present in the oceans provides an example of why manufacture of polymers likely to be released into the environment should ideally be curtailed ⁷⁰, or move to easily recyclable materials.⁷¹ Hence, production of persistent polymers, such as the highly persistent fluoropolymers, should occur only in currently essential use categories.

At the industrial scale, recycling of clean PTFE waste or scraps generated during production is already happening, often by converting these into PTFE micropowder (so-called fluoroadditives) and then using them to reduce wear rate and friction. ⁷² This has the unintended consequence of spreading fluoropolymers into more uses, and complicating any efforts of controlling and reducing their losses from the technosphere. More recently, a pilot-scale industrial high-

temperature recycling process (vacuum pyrolysis) to regenerate gas-phase monomers from

273 end-of-life industrial-scale fluoropolymer products has been established. ⁷³

274 On the other hand, the recycling of fluoropolymers in consumer products is not well established, 275 as those fluoropolymers are typically contaminated by other substances and fillers, which makes 276 recycling difficult. ^{73,74} Fluoropolymers applied to metal products (e.g., nonstick frying pans) 277 might end up in metal recycling streams, leading to their uncontrolled breakdown in metal 278 smelters at high temperatures.

Commercial bakeries regularly remove fluoropolymer coatings from their baking forms after 12-24 months of use either via burning or blasting, with unknown emissions of PFASs and fluoropolymer particles to air, water and soil, and then have the forms re-coated. In Sweden alone, for example, every year some 20 000 baking pans are 'recoated' with a total baking surface of 500 000 m². Stripping the old coating is performed by either 'burning off' at 450 °C for 4-5 h to 'break down' the coating followed by grit blasting or by water blasting at 1500 bar; it is unclear whether emissions are controlled.⁷⁵

Landfilling of fluoropolymers leads to contamination of leachates with PFAS and can contribute to releases of plastics and microplastics. Even with an exceptional chemical and thermal stability, fluoropolymer particles will be disintegrated into microplastics by weathering and physical stress, which enables further dispersion and increased bioavailability. ^{76,77} Storage in abandoned mines and oil extraction fields is an option not routinely explored (except when court-ordered, see below), but is costly and logistically complicated.

The remaining option for the disposal of fluoropolymers is incineration; its effectiveness to destroy PFAS and the tendency for formation of fluorinated or mixed halogenated organic byproducts is not well understood ⁷⁸. Fluorinated compounds are more difficult to destroy than other organic compounds.

296 Tetrafluoromethane and perfluoroethane have been identified as very stable combustion 297 byproducts from the incineration of fluorine-containing waste, but given the extra stability of 298 perfluorinated radicals, larger molecules might also be formed as a result of incomplete 299 combustion.^{78,79} PTFE can produce PFCAs (including trifluoroacetic acid (TFA)) and other 300 fluorinated compounds when heated above about 250 °C and up to 600 °C (relevant for uncontrolled burning).^{80–83} Myers et al. (2014) identified multiple thermal decomposition 301 302 products of polychlorotrifluoroethylene (PCTFE), a common fluoropolymer, including 29 perhalogenated carboxylic acid congener classes and 21 chlorine/fluorine substituted polycyclic 303 304 aromatic hydrocarbon congener classes.⁸⁴ It is currently unclear whether typical municipal solid waste incinerators can safely destroy 305 fluoropolymers without emissions of harmful PFAS and other problematic substances. 306 Combustion within an optimized waste incinerator (870 °C, 4 s residence time of 0.3% PTFE by 307 weight), as opposed to the less strict 850 °C and 2 s required in the EU for municipal solid waste 308 incinerators ⁸⁵ yielded inconclusive results with respect to stack emissions of PFAS.⁸⁶ PFOA was 309 regularly detected in the exhaust, but the study was marred by elevated blanks. The authors 310 311 were only able to account for 56-78% of the fluorine mass balance during incineration, meaning

that a wide variety of other PFAS could have been released.⁸⁶ In any case, municipal waste

incinerators can only tolerate limited amounts of fluoropolymers due to the corrosive nature of
 the hydrogen fluoride released during the fluoropolymers' thermal decomposition. 42

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8. Can fluoropolymers be considered separately from the use of PFAS as processing
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aids?

For current manufacturing processes, it has not been clearly demonstrated that those 318 fluoropolymer products that are made using emulsion polymerization (in contrast to 319 320 suspension polymerization) can be produced without the use and emissions of PFAS as processing aids. For example, after discovery of widespread PFAS contamination of the Cape 321 322 Fear watershed resulting from the production of fluoropolymers, a "Zero" emission policy to water was mandated in North Carolina.¹¹ This includes the capture of PFAS-containing liquid 323 processing waste, which is now moved out of the state for deep well injection, merely 324 325 relocating the environmental concern. Emulsion polymerization processes with much reduced PFAS use,⁸⁷ or without the use of PFAS,^{41,88} as processing aids have been developed, but a 326 327 phase-out of all PFAS as fluoropolymer processing aids has not yet been implemented.

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9. Are fluoropolymers polymers of low or high concern?

The concerns we present above suggest that there is no sufficient evidence to consider fluoropolymers as being of low concern for environmental and human health. The group of fluoropolymers is too diverse to warrant a blanket exemption from additional regulatory

review. Their extreme persistence and the emissions associated with their production, use, and
 disposal result in a high likelihood for human exposure as long as uses are not restricted.
 Concluding that some fluoropolymers are of low concern for environmental and human health
 can only be achieved by narrowly focusing on their use phase as was done by Henry et al
 (2018).²

338 Ideally, the assessment and management of fluoropolymers would consider the complete life cycle including associated emissions during production and disposal, as described above (see 339 340 also Figure 1). The ECETOC CF4Polymers framework was an improvement over the OECD PLC 341 criteria by introducing life cycle considerations in polymer risk assessment and it is 342 recommended that these approaches are applied rather than focusing narrowly on the use 343 phase. Monitoring emissions of harmful volatile and particulate PFAS at manufacturing and incineration sites is urgently needed. Furthermore, mapping of all industrial activities that 344 345 produce, process and dispose/incinerate fluoropolymers would allow for targeted monitoring of potentially contaminated sites and protection of potentially exposed communities. 346

Further, there is no scientific basis to separate and subsequently remove fluoropolymers from discussions of other PFAS as a class or in terms of their impacts on human or environmental health. The conclusion that all fluoropolymers are of low concern, simply based on tests on limited finished products of four types of fluoropolymers,² ignores major emissions linked to their production, and large uncertainties regarding their safe end-of-life treatment.

In addition, there is only very limited information on the compositions, grades, etc. of the
 fluoropolymers on the market. Not all fluoropolymers meet the OECD PLC criteria, as suggested

354 by Henry et al. (2018) in the conclusions of their paper; for example, functionalized 355 fluoropolymers do not meet the criteria (e.g. Nafion) due to the presence of reactive functional groups. It would anyway be impossible to verify if all fluoropolymer products were PLC or not 356 with the information available in the public domain. If PLC is part of a regulatory framework, 357 358 PLC assessment should be performed on a product-by-product basis because various grades 359 and commercial products of fluoropolymers may or may not meet the PLC criteria. For example, a PTFE product made in China cannot be assumed to be equivalent to the PTFE products tested 360 361 by Henry et al. (2018).² Our recommendation is to move toward the use of fluoropolymers in 362 closed-loop mass flows in the technosphere and in limited essential-use categories, unless manufacturers and users can eliminate PFAS emissions from all parts of the life cycle of 363 364 fluoropolymers.

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- are those of the authors and do not necessarily represent the views or policies of the European
- 377 Environment Agency or the U.S. Environmental Protection Agency.

- 379 Figure 1: Conceptual diagram of the life cycle emission during fluoropolymer production, product
- 380 manufacturing and disposal.

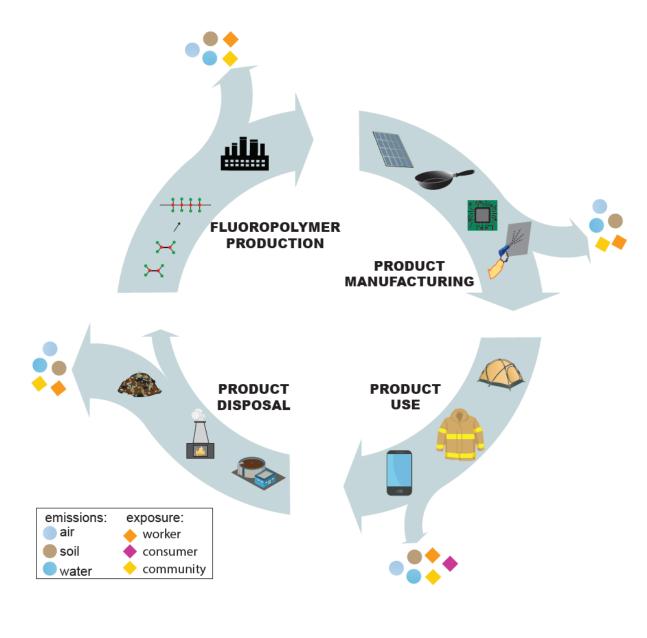
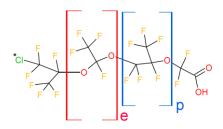


Figure 2: Structures of replacement fluoropolymer processing aids detected in the environment



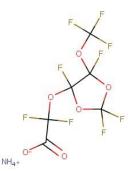
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- a) Ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA, CAS 62037-80-3, or GenX)
- detected in the environments of North Carolina and the Netherlands.



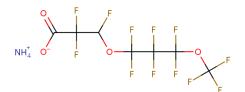
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- b) Functionalized PFPE reported in Wang et al. 2013 (CAS 329238-24-6) now observed in Bormida River
- 392 (Italy) and New Jersey. Note: the e = ethyl group can range from 0 2 units and p = propyl group can
- range from 1 4 units with the ethyl group most likely being closest to the chlorine. Additionally, the
- 394 chlorine can be on the terminal carbon as shown or on the C2 position as $CF_3CF(CI)CF_2$ -O.



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- c) Perfluoro{acetic acid, 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt (CAS No 1190931-27-1)
- 397 (cC604) now observed in ground- and surface water in the Veneto region (Italy).
- 398 <u>https://echa.europa.eu/substance-information/-/substanceinfo/100.207.411</u>



- d) Ammonium 4,8-dioxa-3H-perfluorononanoate (CAS 958445-44-8) (ADONA) detected in the Rhine
- 401 River and serum samples.

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