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

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22

23 **Abstract**

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

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41

42 **1. Introduction**

43 The class of per- and polyfluoroalkyl substances (PFAS) consists of polymers and non-polymers.¹

44 Most regulatory and academic attention so far has focused on the non-polymeric PFAS, either
45 perfluorinated or polyfluorinated alkyl substances. Within the groups of polymeric PFAS, there
46 are fluoropolymers, side-chain fluorinated polymers, and poly- or perfluoropolyethers.

47

48 As defined by Buck et al. (2011), “fluoropolymers” represent a distinct subset of fluorinated
49 polymers, based on a carbon-only polymer backbone with F atoms directly attached to it, e.g.,
50 polytetrafluoroethylene (PTFE); though some fluoropolymers also have Cl or O directly attached
51 to the backbone.¹ In this analysis, we focus on fluoropolymers, but do not assess concerns
52 about other fluorinated polymers, namely side-chain fluorinated polymers, and poly- or
53 perfluoropolyethers. Previous studies have already documented that side-chain fluorinated
54 polymers can decompose and release non-polymeric PFAS to the environment²; otherwise they
55 present similar challenges as discussed for fluoropolymers below.

56

57 The group of fluoropolymers is dominated by PTFE; combined with fluorinated ethylene
58 propylene (FEP), perfluoroalkoxy alkanes (PFA), ethylene tetrafluoroethylene (ETFE) and other
59 tetrafluoroethylene-copolymers; they account for around 75% of the fluoropolymer market.³

60 Other important fluoropolymers include polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF)
61 and fluoroelastomers. One additional fluoropolymer that is discussed in this policy analysis is
62 the functionalized fluoropolymer Nafion® (produced by Chemours), which is a
63 tetrafluoroethylene-based fluoropolymer-copolymer incorporating perfluorovinyl ether groups

64 terminated with sulfonate groups. A review by Gardiner (2015) includes a more complete
65 overview of the different types of fluoropolymers.⁴ Industry produced 320 300 tonnes of
66 fluoropolymers in 2018⁵, and production is steadily increasing.⁴ By 2018 the global
67 fluoropolymer industry was expected to be at \$10 billion per annum.⁴

68

69 Here we evaluate the evidence regarding the environmental and health impacts of
70 fluoropolymers. Our analysis was prompted by a recent suggestion that fluoropolymers should
71 be considered as polymers of low concern (PLC).³ According to the Organization for Economic
72 Cooperation and Development (OECD), “polymers of low concern are those deemed to have
73 insignificant environmental and human health impacts”.⁶ The PLC status of a material leads to
74 exemptions for manufacturers from requirements under the legal chemicals management
75 frameworks in some jurisdictions.⁷ In recognition of the potential risks posed by PFAS-related
76 polymers, the U.S. Environmental Protection Agency has denied PLC exemptions for side-chain
77 fluorinated polymers, but has not acted on fluoropolymers per se⁸.

78

79 We here distinguish between fluoropolymer substances, fluoropolymer products and
80 fluoropolymers in finished articles. A fluoropolymer substance such as PTFE, FEP, PFA is a
81 material of known chemical structure. A fluoropolymer product is the actual material produced
82 and sold by a chemical manufacturer (e.g. Chemours, Solvay, Daikin, Asahi Glass, etc.), comes in
83 different grades (e.g. Teflon-granulate, Teflon-fine powder, etc.) and may contain impurities
84 from the production process. These fluoropolymer products are sold to manufacturers of
85 finished articles (e.g. PTFE tape, waterproof clothing with a PTFE membrane, PTFE-coated

86 cookware, etc.) who incorporate the fluoropolymer products in their finished articles. The
87 distinction is important, as there are many different processes of making fluoropolymer
88 products. For example, some fluoropolymers do not require PFAS-based processing aids in their
89 manufacture by suspension polymerization (e.g. granular PTFE), whereas other fluoropolymers
90 (e.g. fine powder PTFE and PVDF) are manufactured using PFAS-based processing aids during
91 emulsion polymerization. Fluoropolymers are also diverse in how they are produced (as
92 granulates, fine powders or aqueous dispersions, through emulsion or suspension
93 polymerization, with different grades), shipped, and used, which renders generic judgements
94 on their behavior and characteristics difficult.

95
96 Recently, polymers have been under increased regulatory scrutiny. In 2019, the industry-led
97 European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) developed a
98 Conceptual Framework for Polymer Risk Assessment (“CF4Polymers”)⁹ and, in 2020, the
99 European Commission contracted a study to propose criteria for the identification of polymers
100 requiring registration (PRR) under REACH (“the Wood report”).¹⁰ CF4Polymers provides guiding
101 elements to be considered in assessing potential ecological and human health hazards and risks
102 posed by polymer substances. Unlike the PLC concept, CF4Polymers also considers specific life
103 cycle stages of polymer products and their associated routes of exposure. CF4Polymers thus
104 appears sufficiently flexible to allow consideration of potential chemical hazards at each life
105 stage of a fluoropolymer. However, the authors of the CF4Polymers framework support the PLC
106 approach as a means of streamlining polymer risk assessments. They specifically support the
107 findings of Henry et al.³ and state that they are “... unaware of scientific evidence to justify

108 generally assigning fluoropolymers the same level of regulatory concern as other PFAS”.⁹ The
109 Wood Report notes that side-chain fluorinated polymers “can potentially lead to the formation
110 of PFAS substances as a result of degradation”, but considers fluoropolymers as PLC, following
111 the recommendations of Henry et al.³.

112
113 The PLC concept is currently derived from the characteristics of substances and articles but
114 does not cover problems occurring during production and disposal. Specific fluoropolymer
115 articles could hence technically meet the definitions of a PLC, but still pose significant concerns
116 to human health and the environment due to emissions occurring during the life cycle (Figure
117 1). A well-known case where this occurs is the release of processing aids during the
118 manufacture of some fluoropolymers (such as PTFE, FEP, PFA, PVDF and some
119 fluoroelastomers). The pollution caused by emissions of low-molecular-weight PFAS used as
120 polymer processing aids (i.e., emulsifiers, dispersants and surfactants at large) for the
121 manufacture of some types of fluoropolymers has received considerable attention.^{11–13}

122
123 In this article, we identify concerns for environmental and human health resulting from
124 emissions during fluoropolymer production, processing and disposal. We first review the link
125 between some types of fluoropolymers and PFAS emissions and then turn to more general
126 concerns associated with (fluoro)polymers.

127
128 **2. History of pollution from fluoropolymer production is closely tied to use of PFAS as**
129 **polymer processing aids**

130 Low-molecular-weight PFAS have been used for decades as emulsifiers in the polymerization of
131 some types of fluoropolymer substances. The resulting long-term exposure of production
132 workers, the environment, and nearby neighborhoods to high levels of PFAS polymer
133 processing aids by fluoropolymer manufacturers is now well documented and has driven much
134 of the initial action on PFAS control.^{14–21}

135 Historically, the most widely used polymer processing aids were the ammonium salts of
136 perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA).^{22,23} The majority of PFOA
137 and PFNA now in the global environment is a result of the historical use of salts of these
138 substances as processing aids.^{22,24} As a consequence of human and environmental health
139 concerns, under the US EPA 2010/15 Stewardship Program, eight major manufacturers phased
140 out PFOA/PFNA in their fluoropolymer production.²⁵ Many other manufacturers, though, still
141 utilize PFOA as a processing aid; PFOA emissions have, for example, now widely polluted the
142 Asian (especially Chinese) environment.²⁶ These Asian emissions are being discharged into the
143 atmosphere, rivers and oceans in large quantities and are causing additional global-scale
144 pollution.²⁶

145

146 **3. Substitute fluoropolymer processing aids raise similar concerns**

147 Fluoropolymer producers in industrialized countries have moved to substitute PFOA and PFNA
148 in polymer production with structurally similar alternatives such as per- and
149 polyfluoroalkylether carboxylic acids (PFECAs).^{23,27,28} These PFECAs are not technically classified
150 as “long-chain” perfluoroalkyl acids (PFAAs) like PFOA and PFNA, but they have similar physical

151 and chemical properties (including surfactancy and resistance to degradation) when compared
152 with the original emulsifiers.²⁸

153 One example is the substitution by Chemours of the ammonium salt of PFOA with the
154 ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA, CAS 62037-80-3, or GenX)
155 (Figure 2a) for PTFE production. When released into the environment, the ammonium salt of
156 HFPO-DA dissociates to HFPO-DA, which due to similarly high persistence and mobility as its
157 predecessor PFOA, accumulates in surface water, groundwater, and soil.^{29,30} HFPO-DA has also
158 been observed in surface water and drinking water in areas where it is produced, e.g., in North
159 Carolina³¹ and the Netherlands.¹⁴ HFPO-DA does not bioaccumulate in animals to the same
160 extent as PFOA³², but has been added to the EU's Candidate List of Substances of Very High
161 Concern (SVHC) due to an equivalent level of concern about its very high persistence, mobility
162 in water, potential for long-range transport, accumulation in plants and observed effects on
163 human health and the environment.³³

164 In another example, PFNA or, more specifically, its ammonium salt, has been substituted with
165 salts of another PFECA (CAS 329238-24-6) (Figure 2b).²⁸ The dissociated PFECA has since been
166 detected in the surface water near a fluoropolymer production facility in Italy³⁴ and in the soil³⁵,
167 surface and groundwater near a similar PVDF facility in West Deptford, New Jersey (US).³⁶

168 Another replacement polymer processing aid, cC604, is the ammonium salt of [perfluoro{acetic
169 acid, 2-[(5-methoxy-1)]} (Figure 2c). cC604 has been detected in surface and groundwater in the
170 Veneto region in Italy.³⁷ Also, ammonium 4,8-dioxa-3H-perfluorononanoate (CAS 958445-44-8,
171 ADONA) (Figure 2d) is a PFECA processing aid that has been detected in the Rhine River in

172 Germany³⁸ and in the blood of individuals living near a fluorochemical production facility in this
173 area.³⁹

174 These examples demonstrate the similar concern between legacy and replacement
175 fluoropolymer processing aids mentioned above in terms of environmental exposure,
176 bioaccumulation and toxicity (see also section 6 below).^{40,41} Many more PFAS with similar
177 structures have been patented for possible use as fluoropolymer processing aids.⁴²⁻⁴⁴ Thus,
178 even if individual processing aids are banned, many other PFAS are available with the same
179 functionality and similar concerns with respect to persistence and human health effects. 3M
180 claimed that modern containment technologies recapture approximately 98% of polymer
181 processing aids such as PFOA and others ⁴⁵, but losses of 2% are still of concern given their
182 persistence and related properties. Moreover, independent data are not available to support
183 this claim.

184

185 **4. Monomer, oligomer and synthesis by-product emissions during the production of** 186 **fluoropolymers**

187 Fluoropolymers are made of one or several types of monomers. During the synthesis, incomplete
188 polymerization will result in residual monomers and oligomers, and smaller 'polymers' with up
189 to about 100 monomer units. These and other synthesis by-products are not bound to the
190 polymers and may be released to air upon heating during manufacturing and processing
191 (including sintering) and to water through wastewater streams.^{11,15} For example, a series of
192 polyfluoroalkyl carboxylic acids were discovered near Decatur, AL (US), each differing by one 1,1-

193 difluoroethene, CF_2CH_2 , unit, which was used as a building block for production of PVDF at that
194 site.¹⁵ Chemours discovered more than 250 unknown, potentially unique, PFAS in their
195 wastewater in North Carolina.⁴⁶ Many ultrashort-chain fluorinated by-products are highly
196 volatile, and therefore difficult to remove in filters or liquid scrubber baths. An example is
197 trifluoromethane (CHF_3), which has a boiling point of $-82.1\text{ }^\circ\text{C}$ and belongs to the group of
198 hydrofluorocarbon (HFC) gases (HFC-23); it has a 100-year global warming potential of 12400
199 relative to CO_2 .⁴⁷

200 Little is known about emissions of airborne fluoropolymer particles and oligomers, another
201 potential source of PFAS in the atmosphere. Henry et al. (2018) specified the particle size in
202 fluoropolymer powders to vary between 50 and 250 μm , larger than the harmful particle sizes of
203 PM_{10} and $\text{PM}_{2.5}$ (10 and 2.5 μm) in terms of harms caused by inhalation.³ However,
204 fluoropolymer particles vary in size⁴⁸, and may contain and transport residual
205 monomers/oligomers long distances from their emission sources.

206 Various PFAS oligomers were recently detected in the stack emission samples collected from a
207 fluorochemical production site.⁴⁹ A wide range of byproducts of the functionalized fluoropolymer
208 Nafion has been observed in the environment, fish⁵⁰ and birds⁵¹ downstream of this facility.
209 Moreover, a recent study involving the residents of Wilmington, North Carolina found that the
210 majority have Nafion Byproduct 2 (99%) and other related PFAS in their blood serum as a result
211 of consuming contaminated drinking water in this region⁵². These Nafion-related compounds
212 could be the result of manufacturing discharges¹², or losses resulting from Nafion use over
213 time.^{53,54} It is noted that Nafion probably does not meet the PLC criteria because it has a reactive
214 functional group that can be lost under its harsh use conditions.

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

Linked to the use of PFAS as production processing aids (see above), there are concerns regarding the remaining low molecular weight PFAS in fluoropolymers after production. For example, Henry et al. (2018) argued that fluoropolymers are not toxic, based on a dataset that was restricted only to a few fluoropolymer substances, typically > 100,000 Da.³ Concentrations of leachable components reported for those specific fluoropolymer products, particularly a PTFE fine powder, were labeled “very low” at 1 ppm (i.e., 1 mg/kg)³, though earlier studies reported concentrations of 1-10 ppm in PTFE fine powder and much higher in PTFE aqueous dispersion (see SI in Wang et al. (2014)²⁴). Similar levels of PFAAs (0.3-24 ppm) were found in personal care articles that contained PTFE fine particles (Assuming the cosmetics contained 1% PTFE, the range of leachables is 0.3 -24 ppm; if the total organofluorine measurements represented PTFE fine powder, then the range of PFAA-leachables is 15-1,000 ppm).⁵⁵ Residuals of 1 ppm may have significant toxicological relevance, given the recently proposed drinking water guidelines for some PFAS set at 10-100 ng/L in different countries.^{56,57} The levels of leachables (e.g. processing aids, synthesis by-products and oligomers) in individual fluoropolymer substances and products depend on the production process and subsequent treatment processes; a comprehensive global overview is currently lacking.

Fluoropolymer-coated food contact materials (e.g. metal cookware), if not been properly pre-treated, could lead to the leaching of non-polymeric PFAS residuals into food during the use

236 phase. Processing aids are known to leach from fluoropolymer articles, for example in
237 chromatographic instrumentation, causing a consistent background signal in analytical
238 chemistry at the ppt level^{58,59}

239 Further, Henry et al. (2018) state that the low residual levels found in the finished PTFE
240 products that they tested are due in large part to “aggressive” steps taken to wash out residuals
241 and drive off volatiles.³ Such aggressive treatment raises the question of how these residuals
242 and volatiles are captured and their releases controlled, or if production by-products become
243 air or water emissions with potential for human exposure. There is evidence that the drying
244 step (sintering) of fluoropolymers has led to substantial emissions to air of processing aids at
245 sites of PTFE production (West Virginia (US)²⁹ and the Netherlands) and use sites in the US
246 (North Bennington, VT; Merrimack, NH, Hoosick Falls, NY).^{60–62}

247

248 **6. Toxicity of fluoropolymer processing aids, monomers and oligomers**

249 Legacy processing aids (i.e., PFOA, PFNA) used to manufacture fluoropolymers are linked to a
250 wide range of health effects in experimental animal models (causative) and humans
251 (associative), including certain types of cancer, immunotoxicity, reproductive and
252 developmental toxicity, liver toxicity, and thyroid disease.⁶³ The production of many
253 fluoropolymers still requires the use of PFAS as surfactants or as monomers, which causes
254 releases to the environment during manufacture, and thus may pose a risk to human health
255 and the environment (see also point 9 below). A replacement processing aid, HFPO-DA, shows a
256 similar toxic potency in rodents as PFOA⁴¹, but its pharmacokinetics in humans is less certain⁶⁴.

257 Few reviews have been published regarding the potential toxicity of other replacement PFECAs,
258 such as ADONA ^{65,66} or the PFECA CAS 329238-24-6 ⁶⁷, but these replacement chemicals need to
259 have similar properties to work, and are as environmentally persistent as the original polymer
260 processing aids.⁴⁰

261

262 **7. Penetration of cell membranes by macromolecules**

263 While not specific to fluoropolymers, the PLC status is partially based on a mass-based cutoff
264 for cellular uptake (MW of > 1000 Da or 10,000 Da, depending on reactive functional groups).
265 This was summarized by Henry et al. (2018), who advocated for PLC status of some
266 fluoropolymers by suggesting “Polymers are too large to penetrate cell membranes”.³ This
267 position is not currently supported by the scientific literature related to the bioavailability of
268 similarly sized micro- and nanoplastics of fluorine-free polymers. Nearly a decade ago, Jiang et
269 al. (2011) showed that polystyrene nanoparticles of about 100 nm diameter are easily able to
270 enter stem cells.⁶⁸ Similarly, Pitt et al. (2018) reported that 42 nm polystyrene nanoparticles
271 were present in tissue and organs of maternally and co-parentally exposed F1 embryos/larvae,
272 proving membrane crossing capabilities of polymer nanoparticles.⁶⁹ Polymer nanoparticles
273 with molecular weights between 12,000 and 21,000 Da have been used to deliver
274 chemotherapeutic drugs to cancer cells⁷⁰, and those on the order of tens of nanometers in size
275 have been found to enter cells and eventually even cell nuclei.^{71,72} Furthermore, Geiser et al.
276 (2003) showed that inhaled spherical microparticles of Teflon were able to migrate into the
277 surface lining layer of hamster alveoli, where interactions with lung cells could occur.⁷³ Many
278 fluoropolymer substances are marketed in the form of suspensions with sub-micron

279 fluoropolymer particle sizes (see, e.g. <https://www.teflon.com/en/products/dispersions>), thus,
280 release of bioavailable fluoropolymer particles is plausible. Based on such emerging evidence
281 from environmental and medical research on diverse macromolecules ⁷⁴, a blanket statement
282 that polymers cannot enter cells is factually inaccurate.

283 It is recognized that the global production of fluoropolymers (though not insignificant at
284 320,000 tonnes in 2018⁵, and increasing⁴) is relatively low in volume (at ~ 0.1%) compared to
285 global production of plastics (300 million tonnes in 2018⁷⁵). However, detection of PTFE
286 microparticles in Mediterranean fish and remote Arctic Ocean sediment samples demonstrates
287 their global presence, albeit representing a small fraction of all detected microplastics.^{76,77} We
288 note that the occurrence, exposure to, and toxicity of nano-plastics is an area of ongoing
289 research with many unknowns.⁷⁸

290

291 **8. Persistence and disposal of fluoropolymers**

292 Fluoropolymers are extremely persistent under environmental conditions⁴⁵, which, in the same
293 way as for other polymers, can lead to a wide array of issues, particularly with respect to
294 disposal of fluoropolymer-containing wastes and products.⁷⁹ Current concern over microplastics
295 present in the oceans provides an example of why manufacture of polymers likely to be
296 released into the environment should ideally be curtailed ⁸⁰. Hence, production of persistent
297 polymers, such as the highly persistent fluoropolymers, should occur only in time-limited
298 essential use categories, i.e., critical for the safety, health and functioning of society.

299 At the industrial scale, recycling of clean PTFE waste or scraps generated during production is
300 already happening, often by converting these into PTFE micropowder (so-called fluoroadditives)
301 and then using them to reduce wear rate and friction.⁸¹ This has the unintended consequence
302 of spreading fluoropolymers into more uses, and complicating any efforts of controlling and
303 reducing their losses from the technosphere. More recently, a pilot-scale industrial high-
304 temperature recycling process (vacuum pyrolysis) to regenerate gas-phase monomers from
305 end-of-life industrial-scale fluoropolymer products has been established.⁸²

306 On the other hand, the recycling of fluoropolymers in consumer articles is not well established,
307 as those fluoropolymers are typically contaminated by other substances and fillers, which makes
308 recycling difficult.^{82,83} Fluoropolymers applied to metal articles (e.g., nonstick frying pans) might
309 end up in metal recycling streams, leading to their uncontrolled breakdown in metal smelters at
310 high temperatures.

311 Commercial bakeries regularly remove fluoropolymer coatings from their baking forms after 12-
312 24 months of use either via burning or blasting, with unknown emissions of PFASs and
313 fluoropolymer particles to air, water and soil, and then have the forms re-coated. In Sweden
314 alone, for example, every year some 20 000 baking pans are 'recoated' with a total baking surface
315 of 500 000 m². Stripping the old coating is performed by either 'burning off' at 450 °C for 4-5 h to
316 'break down' the coating followed by grit blasting or by water blasting at 1500 bar; it is unclear
317 whether emissions are controlled.⁸⁴

318 Landfilling of fluoropolymers leads to contamination of leachates with PFAS and can contribute
319 to releases of plastics and microplastics. Even with an exceptional chemical and thermal stability,

320 fluoropolymer particles will be disintegrated into microplastics by weathering and physical stress,
321 which enables further dispersion and increased bioavailability.^{85,86} Storage in abandoned mines
322 and oil extraction fields is an option not routinely explored (except when court-ordered, see
323 below), but is costly and logistically complicated.

324 The remaining option for the disposal of fluoropolymers is incineration; its effectiveness to
325 destroy PFAS and the tendency for formation of fluorinated or mixed halogenated organic
326 byproducts is not well understood.⁸⁷

327 Tetrafluoromethane and perfluoroethane have been identified as very stable combustion
328 byproducts from the incineration of fluorine-containing waste, but given the extra stability of
329 perfluorinated radicals, larger molecules might also be formed as a result of incomplete
330 combustion.^{87,88} PTFE can produce PFCAs (including trifluoroacetic acid (TFA)) and other
331 fluorinated compounds when heated to temperatures between 250 °C and 600 °C (relevant for
332 uncontrolled burning).⁸⁹⁻⁹¹ Myers et al. (2014) identified multiple thermal decomposition
333 products of polychlorotrifluoroethylene (PCTFE), a common fluoropolymer, including 29
334 perhalogenated carboxylic acid groups and 21 chlorine/fluorine-substituted polycyclic aromatic
335 hydrocarbon groups, such as mixed halogenated benzenes and naphthalenes.⁹²

336 It is currently unclear whether typical municipal solid waste incinerators can safely destroy
337 fluoropolymers without emissions of harmful PFAS and other problematic substances.⁸⁷ There
338 is evidence that PFOA itself is not thermally stable at elevated temperatures⁹³ or produced in
339 high-temperature (> 1000 °C) incineration of fluorotelomer based articles.^{94,95} Combustion
340 within an optimized waste incinerator (870 °C, 4 s residence time of 0.3% PTFE by weight), as

341 opposed to the less strict 850 °C and 2 s required in the EU for municipal solid waste
342 incinerators⁹⁶ yielded inconclusive results with respect to stack emissions of PFAS.⁹⁷ PFOA was
343 regularly detected in the exhaust, but the study was marred by elevated blanks. The authors
344 were only able to account for 56-78% of the fluorine mass balance during incineration, meaning
345 that a wide variety of other PFAS could have been released.⁹⁷ In any case, municipal waste
346 incinerators can only tolerate limited amounts of fluoropolymers due to the corrosive nature of
347 the hydrogen fluoride released during the fluoropolymers' thermal decomposition.⁴⁵

348

349 **9. Can fluoropolymers be considered separately from the use of PFAS as processing**
350 **aids?**

351 For current manufacturing processes, it has not been clearly demonstrated that those
352 fluoropolymer products that are made using emulsion polymerization (in contrast to
353 suspension polymerization) can be produced without the use and emissions of PFAS as
354 processing aids. For example, after discovery of widespread PFAS contamination of the Cape
355 Fear watershed resulting from the use as various PFAS, including HFPO-DA, as processing aids in
356 the production of fluoropolymers, a "Zero" emission policy to water was mandated in North
357 Carolina.¹³ This includes the capture of PFAS-containing liquid processing waste, which is now
358 moved out of the state for deep well injection⁹⁸, merely relocating the environmental concern
359 and creating the possibility of spills and leaking. In Dordrecht (Netherlands), regulations exist
360 for air emissions (which are now restricted to 450 kg/y), direct (surface water) emissions
361 (recently restricted to 5 kg/yr) and indirect emission to a local WWTP (recently restricted to 140

362 kg/yr, was 2 tonnes/yr in 2018 and 6 tonnes/yr in 2017).¹⁴ A report to the Nordic Council
363 compiled additional production and release estimates for various per- and
364 polyfluoroalkylethers.⁹⁹ Emulsion polymerization processes with much reduced PFAS use,¹⁰⁰ or
365 without the use of PFAS,^{44,101} as processing aids have been developed, but it is unclear whether
366 they will be implemented industry-wide. A phase-out of all PFAS as fluoropolymer processing
367 aids would be a vast improvement, but would not address the current problems associated with
368 impurities, as well as a lack of recycling and disposal.

369

370 **10. Are fluoropolymers polymers of low or high concern?**

371 The concerns we present above suggest that there is no sufficient evidence to consider
372 fluoropolymers as being of low concern for environmental and human health. The group of
373 fluoropolymers is too diverse to warrant a blanket exemption from additional regulatory
374 review. Their extreme persistence and the emissions associated with their production, use, and
375 disposal result in a high likelihood for human exposure as long as uses are not restricted.
376 Concluding that some specific fluoropolymer substances are of low concern for environmental
377 and human health can only be achieved by narrowly focusing on their use phase as was done by
378 Henry et al (2018).³

379 Ideally, the assessment and management of fluoropolymer products would consider the
380 complete life cycle including associated emissions during production and disposal, as described
381 above (see also Figure 1). The ECETOC CF4Polymers was an improvement over the early OECD
382 PLC criteria by introducing life cycle considerations in polymer risk assessment and it is

383 recommended that these approaches are applied rather than focusing narrowly on the use
384 phase. Monitoring emissions of harmful volatile and particulate PFAS at manufacturing and
385 incineration sites is urgently needed. Furthermore, mapping of all industrial activities that
386 produce, process and dispose/incinerate fluoropolymers would allow for targeted monitoring
387 of potentially contaminated sites and protection of potentially exposed communities.

388 Further, there is no scientific basis to separate and subsequently remove fluoropolymers from
389 discussions of other PFAS as a class or in terms of their impacts on human or environmental
390 health. The conclusion that all fluoropolymers are of low concern, simply based on tests on
391 limited substances of four types of fluoropolymers,³ ignores major emissions linked to their
392 production, and large uncertainties regarding their safe end-of-life treatment.

393 In addition, there is only very limited information on the compositions, grades, etc. of the
394 fluoropolymer products on the market. Not all fluoropolymer products meet the OECD PLC
395 criteria, as suggested by Henry et al. (2018) in the conclusions of their paper; for example,
396 functionalized fluoropolymers do not meet the criteria (e.g. Nafion) due to the presence of
397 reactive functional groups. It would anyway be impossible to verify if all fluoropolymer products
398 were PLC or not with the information available in the public domain. If PLC is part of a
399 regulatory framework, PLC assessment should be performed on a product-by-product basis
400 because various grades and commercial products of fluoropolymers may or may not meet the
401 PLC criteria. For example, a PTFE product made in China cannot be assumed to be equivalent to
402 the PTFE products tested by Henry et al. (2018).³ Our recommendation is to move toward the
403 use of fluoropolymers in closed-loop mass flows in the technosphere and in limited essential-

404 use categories, unless manufacturers and users can eliminate PFAS emissions from all parts of
405 the life cycle of fluoropolymers.

406

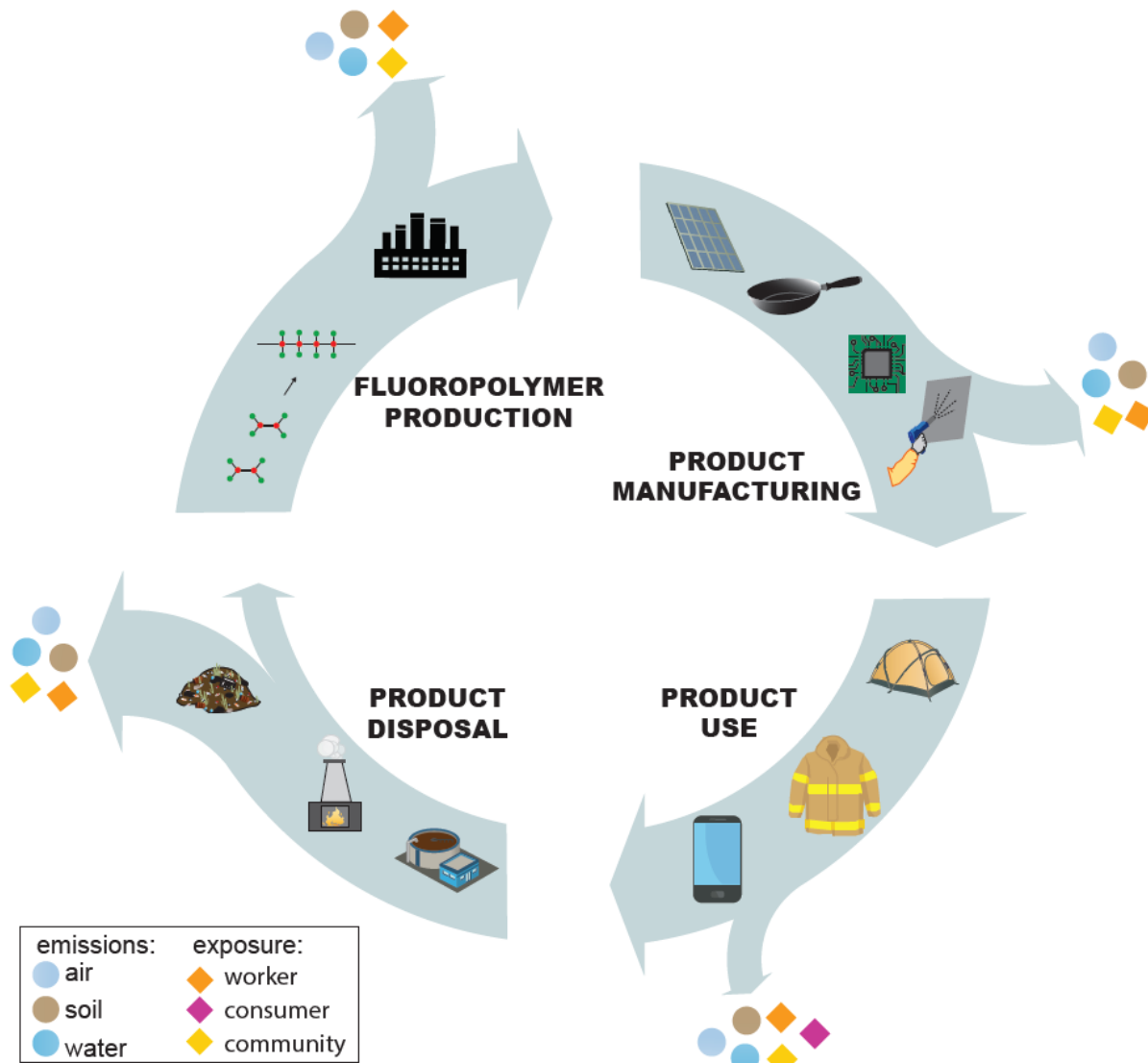
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419

420 **Figure 1: Conceptual diagram of PFAS emissions during fluoropolymer production, product**
421 **manufacturing and disposal.**

422



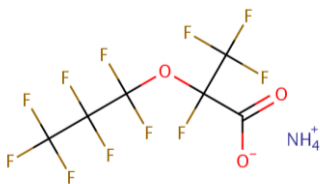
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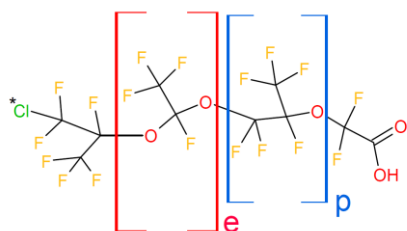
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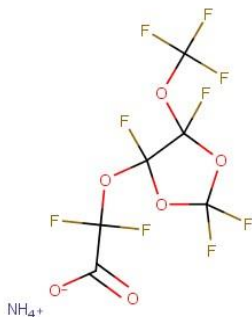
427 **Figure 2: Structures of replacement fluoropolymer processing aids detected in the environment**



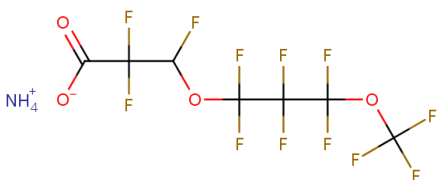
428
 429 a) Ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA, CAS 62037-80-3, or “GenX”)
 430 detected in the environments of North Carolina and the Netherlands.



431
 432 b) Functionalized PFPE reported in Wang et al. 2013 (CAS 329238-24-6) now observed in Bormida River
 433 (Italy) and New Jersey. Note: the e = ethyl group can range from 0 - 2 units and p = propyl group can
 434 range from 1 – 4 units with the ethyl group most likely being closest to the chlorine. Additionally, the
 435 chlorine can be on the terminal carbon as shown or on the C2 position as CF₃CF(Cl)CF₂-O.



436
 437 c) Perfluoro{acetic acid, 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt (CAS No 1190931-27-1)
 438 (cC604) now observed in ground- and surface water in the Veneto region (Italy).
 439 <https://echa.europa.eu/substance-information/-/substanceinfo/100.207.411>



440
 441 d) Ammonium 4,8-dioxa-3H-perfluorononanoate (CAS 958445-44-8) (ADONA) detected in the Rhine
 442 River and serum samples.

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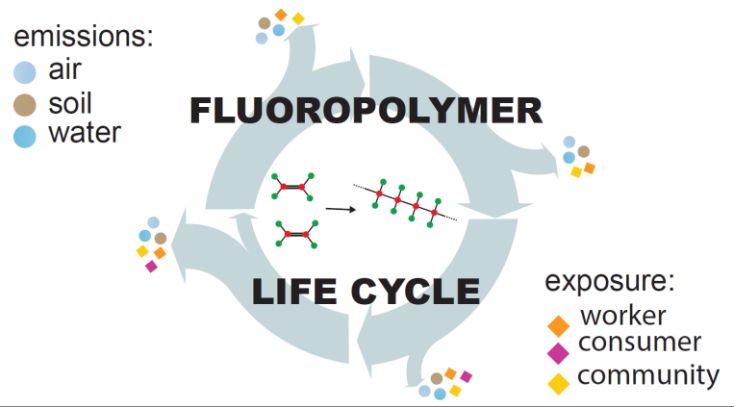
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Graphical TOC



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