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Information Requirements under the Essential-Use Concept: PFAS Case Studies

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1 Information requirements under the essential-use concept: 2 PFAS case studies

3
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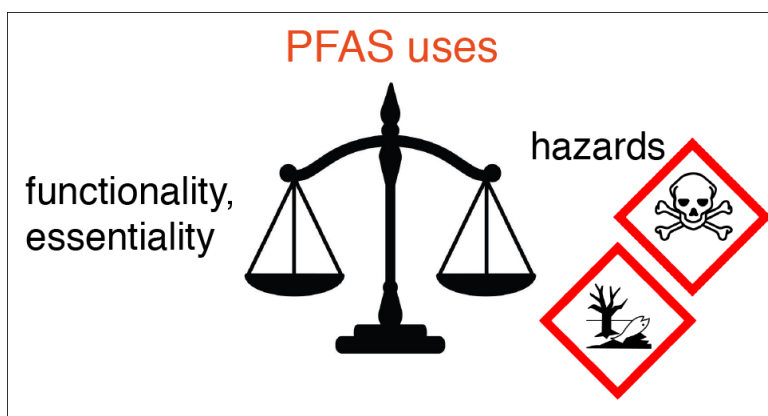
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26 **TOC Art**



27

28 **Abstract**

29 Per- and polyfluoroalkyl substances (PFAS) are a class of substances for which there are widespread
30 concerns about their extreme persistence in combination with toxic effects. It has been argued that
31 PFAS should only be employed in those uses that are necessary for health or safety or are critical for
32 the functioning of society and where no alternatives are available (“essential-use concept”).

33 Implementing the essential-use concept requires a sufficient understanding of the current uses of
34 PFAS and of the availability, suitability and hazardous properties of alternatives. To illustrate the
35 information requirements under the essential-use concept, we investigate seven different PFAS uses,
36 three in consumer products and four industrial applications. We investigate how much information is
37 available on the types and functions of PFAS in these uses, how much information is available on
38 alternatives and their performance and hazardous properties and, finally, whether this information is
39 sufficient as a basis for deciding on the essentiality of a PFAS use. The results show (i) the uses of
40 PFAS are highly diverse and information on alternatives is often limited or lacking; (ii) PFAS in
41 consumer products often are relatively easy to replace; (iii) PFAS uses in industrial processes can be
42 highly complex and a thorough evaluation of the technical function of each PFAS and of the
43 suitability of alternatives is needed; (iv) more coordination of the activities of PFAS manufacturers,
44 manufacturers of alternatives to PFAS, users of these materials, government authorities and other
45 stakeholders is desirable to make the process of phasing out PFAS more transparent and coherent.

46 **Key words:** PFAS, essential-use, chrome plating, fluoropolymer, carpet

47 **Synopsis:** The essential-use concept, which aims to reduce PFAS exposure while avoiding regrettable
48 substitution, is employed in seven different PFAS alternatives case studies.

49 **1 Introduction**

50 Per- and polyfluoroalkyl substances (PFAS) are a class of thousands of substances^{1,2} most of which
51 are either persistent themselves or are transformed into persistent compounds in the environment.
52 Further, the few PFAS studied to date have shown a wide range of biological activity in cell-based,

53 animal, and human epidemiological studies.³ Because of these concerns, it has been argued that
54 PFAS should only be employed in those uses that are necessary for health, safety or are critical for
55 the functioning of society and where no alternatives are available.⁴⁻⁶ This concept of “essential uses”
56 has been incorporated into a working paper on “Elements for an EU strategy for PFAS”⁷ and also in
57 the European Commission’s “Commission Staff Working Document – Poly- and perfluoroalkyl
58 substances (PFAS)”, which is an accompanying document to the Commission’s Chemicals Strategy for
59 Sustainability.⁸

60 Implementing the essential-use concept requires a sufficient understanding of the current uses of
61 PFAS and of the availability, suitability and hazardous properties of alternatives. Cousins et al.
62 (2019a)⁴ analyzed nine different use areas of PFAS and the availability of alternatives. Other research
63 groups and institutions have also looked into alternatives to PFAS in certain use areas⁹⁻¹⁵ and
64 additional information is available on the OECD Portal on PFAS.¹⁷ Glüge et al. (2020)¹⁶ characterized
65 more than 200 uses of more than 1400 individual PFAS. This work has shown that PFAS uses are very
66 diverse and this diversity is a challenge to the implementation of the essential-use concept. In many
67 cases, it is not clear whether the use of PFAS is essential. Accordingly, there is a need for a better
68 understanding of where PFAS are used, what their specific functions in these uses are, and how easy
69 or difficult it is to find alternatives.

70 To address this need, we investigate here a set of seven different PFAS uses, three in consumer
71 products and four industrial applications. We investigate how much information is available on the
72 types and functions of PFAS in these uses and, if needed, how much information is available on
73 alternatives, their performance and hazardous properties and, finally, whether this information is
74 sufficient as a basis for deciding on the essentiality of a PFAS use. On this basis, we aim to make a
75 contribution to a broader understanding of the information requirements of the essential-use
76 concept and to illustrate the type of questions that are brought up for decision makers by the
77 essential-use concept.

78 2 Methods

79 2.1 Selection of case studies

80 The intention of the case studies selected is to cover a range of different PFAS uses from relatively
81 simple to more complex cases for which there is at least some information on alternatives available
82 in the public domain. By looking into PFAS uses in consumer products and in industrial processes, the
83 diversity of PFAS uses is reflected and different types of assessment tasks and decision-making
84 situations are illustrated. In addition, several of the case studies are in areas where PFAS have caused
85 serious contamination problems, e.g. fluoropolymer¹⁷⁻²⁰ or semiconductor production.^{21,22}

86 Given the large number of PFAS and PFAS uses,¹⁶ the seven case studies are a limited selection.
87 Nevertheless, they show an interesting and relevant range of assessment tasks that may be typical
88 for future applications of the essential-use concept. In particular, the industrial uses may deserve
89 more discussion and further analysis.

90 The three case studies of PFAS uses in consumer products are on PFAS in bicycle lubricants, carpets,
91 and cleaning products. The four industrial uses of PFAS are in fluoropolymer production, in the
92 semiconductor industry, in chrome plating, and in chemical-driven oil production. For each case
93 study, an extensive search of the available literature was conducted, including peer-reviewed journal
94 articles, monographs, industry reports, product descriptions, and patents. In addition, we contacted
95 PFAS manufacturers and downstream users and received additional input from technical experts for
96 most of the case studies, in particular for bicycle lubricants, chrome plating, fluoropolymer
97 production, and PFAS uses in the semiconductor industry. Details of the contacted businesses are
98 provided in the Supporting Information (SI-1, Table S4).

99 2.2 Assessment of alternatives

100 Alternatives for each of the PFAS uses in the seven case studies were mainly found through literature
101 searches. Confirmation of the information was obtained through discussions with providers of
102 alternatives. Alternatives for which chemical identification information (CAS number or SMILES code)

103 was found are listed in the accompanying MS Excel document “Gluege_et_al_SI-2.xlsx” (SI-2). In
104 some cases, the chemical identity of alternatives was declared as confidential business information
105 and not shared.

106 Where the chemical identity of the alternatives could be determined, their human-health and
107 environmental hazards were compared with those of the PFAS currently used. Data on the hazards
108 were taken from three sources: the ECHA Classification & Labelling (C&L) Inventory, the ECHA REACH
109 registration database, and the EPI Suite™ estimation tool,²³ where appropriate. Where a charged
110 organic substance was identified, a neutral form of the substance was run through EPI Suite™. This
111 may introduce error into the calculation. Data were collected or generated for the following hazards:
112 carcinogenicity, mutagenicity, reproductive toxicity (human health) and persistence,
113 bioaccumulation, ecotoxicity, and mobility (environment). The data collected are provided in the SI-
114 2.

115 When a brand name is mentioned in this work, this does not constitute endorsement of the brand or
116 its product. The chemical identity of the PFAS in the different uses was taken from Glüge et al.
117 (2020).¹⁶ Where multiple substances had been identified as alternatives for a use, those with the
118 most severe hazards were selected for comparison with an example PFAS (worst-case comparison).

119 In addition to cases where an alternative is a direct replacement of PFAS by other chemicals with the
120 same technical function, there are also cases where the design of the product or technical process
121 can be modified such that the technical need for PFAS no longer exists. Depending on the chemicals
122 used in the modified products or processes (if any), an alternative assessment may or may not be
123 needed.

124 2.3 Essentiality categories

125 Where possible, we applied the categories of “non-essential”, “substitutable”, and “essential” uses,
126 as defined by Cousins et al. (2019a),⁴ to the PFAS identified in the seven case studies. We did not
127 judge whether or not a product or process is essential for health, safety or the functioning of society.

128 Instead, the classification is based on whether the function provided by PFAS is needed in a specific
129 product or process and on the availability of suitable alternatives. Products or processes where PFAS
130 are not needed at all are classified as “non-essential”. Products or processes where PFAS can be
131 replaced by other substances or processes are classified as “substitutable”. Cases where PFAS cannot
132 (yet) be replaced are classified as essential. A further discussion and development of criteria for
133 essential uses is not part of this work.

134 3 Case studies on alternatives to PFAS

135 3.1 Bicycle lubricants

136 **Uses:** Polytetrafluoroethylene (PTFE) is added to different kinds of bicycle lubricants including dry
137 lubes, wet lubes and wax lubes. Dry lubes are designed for riding in dry conditions and are often
138 made by mixing ca. 10% lubricant (synthetic oils and additives) and 90% carrier fluid (solvent). Wet
139 lubes contain larger quantities of higher-viscosity synthetic oils and additives such as PTFE and are
140 intended for riding in wet conditions.²⁴ There are also lubricants based on paraffin wax mixed with
141 additives such as PTFE and a carrier fluid. PTFE may be used within a range of 5–25% by weight in
142 dry lubes to reduce friction and wear.²⁵ Wet lubricants seem to contain less PTFE; the safety data
143 sheet of a wet PTFE lubricant reveals a PTFE content of 1–3% by weight.²⁶ Another aspect is that a
144 PTFE content of less than 1% may be added just for marketing purposes.²⁷ For a substantial effect on
145 performance, at least 4–5% PTFE is needed.²⁷

146 **Availability of alternatives and alternative assessment:** There are lubricants on the market that do
147 not contain PTFE and perform well according to tests and user experiences.^{28–30} The providers of
148 alternative lubricants state that their lubricants are “plant based” and decompose rapidly,³¹ but no
149 information about biodegradability test results is provided. However, it can be assumed that,
150 compared to the extreme persistence of PTFE, the persistence of these alternatives is much lower.

151 **Conclusion:** Although PFAS in bicycle lubricants may increase lubricating performance, they are
152 technically not needed to keep chains lubricated. In addition, PFAS-free products have always been
153 available on the market. In conclusion, the use of PFAS in bicycle lubricants is non-essential.

154 3.2 Carpets

155 **Uses:** PFAS have been used in carpets to impart water and oil repellency, stain resistance, and soil
156 release to synthetic carpet face fibers.³² The reason is that nylon and other synthetic fibers are both
157 oleophilic and hydrophobic and, thus, have a great affinity for soils. Soil removal on untreated nylon
158 is therefore more difficult than on treated nylon.

159 **Availability of alternatives:** One carpet manufacturer, Interface, changed the formulation of the
160 nylon used in face fibers so that the fibers themselves are stain-resistant.³³ The yarn producer,
161 Aquafil, offers stain-free fibers based on the nylon-6 fiber “Econyl StayClean”.³⁴ This fiber is made
162 from nylon waste that was depolymerised and recycled.³⁵ No PFAS are added to the recycled fiber.
163 Another yarn manufacturer, Universal Fibers, describes the use of a “sulfonated nylon copolymer”
164 for a PFAS-free stain protection.³² In this case PFAS are not needed because the modified nylon fiber
165 is stain-resistant itself. The carpet manufacturer, Tarkett, on the other hand, treats its “Tandus
166 Centiva”-branded products with fluorine-free soil protection products,³⁶ which means that in the
167 topical treatment PFAS are replaced by other chemicals.

168
169 Some PFAS-free carpets can also be found under the “Blue Angel” certificate. The certificates Blue
170 Angel,³⁷ Nordic Swan and Cradle-to-Cradle³⁸ ban halogenated organic compounds (including all PFAS)
171 from their labeled products. GUT (Association for Environmentally Friendly Carpets) lists 33 single
172 PFAS that are not allowed in products with their certificate³⁹ and Oeko-Tex 100 bans PFOA-related
173 substances.⁴⁰ In response to our information request, Blue Angel replied that PFAS-free polyamide
174 carpets have been registered by the Condor Group.⁴¹

175 **Alternatives assessment:** Limited information about alternatives is publicly available.³² Some
176 information on chemical synthesis processes and ingredients can be found in patents, as listed in the
177 SI-1. However, no information is available on the specific properties of the materials or on any results
178 from toxicity or degradability tests. According to the manufacturers contacted, this is confidential
179 business information.

180 **Conclusion:** It is possible and economically feasible to produce synthetic carpets without PFAS-based
181 impregnation. PFAS in carpets are therefore substitutable. More information on the alternatives
182 should be made publicly available so that their impacts can be evaluated transparently.

183 3.3 Cleaning products

184 **Uses:** PFAS lower the surface tension and improve wetting and rinse-off in a variety of industrial and
185 household cleaning products. Examples are car wash products, floor cleaning products and floor
186 polish, carpet spot cleaner, cleaning solutions for optical devices, and dishwashing liquids in which,
187 e.g., PFOA has been detected.^{42,43}

188
189 **Availability of alternatives:** Alternative household cleaning products are based on ingredients that
190 are biodegradable, in some cases readily biodegradable. These products are available on the market.
191 Examples for surfactants other than PFAS used in dish soap include for example sodium lauryl sulfate
192 and lauryl glucoside.⁴⁴ Surfactants used in laundry detergent are for example C12-16 pareth-7,
193 potassium cocoate, decyl glucoside⁴⁵ or sophorolipids.⁴⁶ Examples for floor polish and carpet spot
194 cleaner are provided in the SI-1.

195
196 **Alternative assessment:** The list of ingredients of a dish soap (Ecover Zero dish soap)⁴⁴ was used for
197 the assessment of alternatives. No indication of carcinogenic, mutagenic, or reproductive hazards
198 was found for any of the ingredients. The environmental hazards were also lower: all substances in
199 the dishwashing liquid have a calculated persistence of 4–37 days, with biodegradation studies
200 available and in agreement with the estimated values for most of the substances. Regarding

201 bioaccumulation, all logarithmic octanol-water partition coefficients ($\log K_{ow}$) are below 3 and all
202 bioconcentration factors (BCFs) are below 20. Not all ingredients are listed in the REACH database,
203 but data on the BCF for those available agreed with the estimated values. The use of these
204 substances represents therefore a reduced human-health and environmental hazard when compared
205 to the PFAS used in cleaning products. However, for some surfactants used in floor polish and carpet
206 spot cleaner, the data in the C&L inventory indicate that they are toxic to aquatic organisms.

207

208 **Conclusion:** PFAS in household cleaning products are not technically needed; many alternatives are
209 available and PFAS uses are non-essential. For industrial cleaning products, it would be necessary to
210 look at each case individually in order to evaluate what level of performance is needed, and why, and
211 if alternatives to PFAS are available.

212

213 3.4 Chrome plating

214 **Uses:** PFAS are used in chrome plating as wetting agents in the pre-treatment (etching) of plastic and
215 as mist suppressing agents in the electroplating process. In electroplating (often referred to as
216 chrome plating), fluorosurfactants reduce the exposure to toxic hexavalent chromium aerosols from
217 the plating baths by (i) reducing the size of the bubbles formed and (ii) forming a barrier over the
218 electrolyte solution. More information about PFAS uses in both processes is provided in the SI-1.

219 Fluorinated surfactants have been used previously for both decorative chrome plating and hard
220 chrome plating. Hard chrome plating provides resistance against corrosion and abrasion to various
221 items such as hydraulic cylinders and rods or railroad wheel bearings and couplers.⁴⁷ Decorative
222 chrome plating is mainly used for plated parts, for example in the automotive industry (including car
223 and truck bumpers), but also in the sanitary, medicine, cosmetic and furniture sector.^{47,48}

224 **Availability of alternatives:** Tests showed that chromium-(VI) emissions can be reduced substantially
225 by avoiding air convection.⁴⁹ Some companies use closed systems with underpressure and found
226 almost no chromic-acid aerosols. No PFAS are therefore necessary as mist suppressants.⁵⁰

227 Another reason why the use of chromium (VI) is not essential for all types of decorative chrome
228 plating is that trivalent chromium can be used instead.^{47,51} One disadvantage is that trivalent
229 chromium cannot achieve the silvery-bluish color of chromium (VI).^{51,52} However, trivalent chromium
230 is much less toxic than chromium (VI) and mist-suppressing PFAS are therefore not needed in
231 processes with trivalent chromium.^{42,47,53} A different technology for decorative chrome plating
232 includes processes based on physical vapor deposition (PVD), where PFAS are also not needed.⁵²
233 However, the quality of the coating produced by PVD may not be sufficient for materials used for
234 drinking water contact.⁵⁴ Also, as of 2016, PVD-based processes did not fulfill the requirements of the
235 German automotive industry in terms of quality, aesthetic value and functionality of the parts.⁵⁵

236 For hard metal plating, it has been suggested that trivalent chromium could also be used in some
237 applications.⁴⁷ Atotech launched a hard-chrome plating process with trivalent chromium and stated
238 that the process exhibits the same benefits as hexavalent-chromium processes.⁵⁶ This includes high
239 plating speed, bath stability, and high hardness deposits and wear resistance. However, the
240 technology requires a nickel underlayer to meet the corrosion resistance requirements and is
241 therefore not a drop-in replacement. Besides Atotech, Faraday Technology is also working on a
242 trivalent chromium plating process for functional applications. They stated to us that the trivalent
243 chromium plating process has already passed the tests specified for aerospace applications. They are
244 currently further optimizing the process such that the coating microstructure and appearance is
245 equivalent to that of hexavalent-chromium coatings. More information on chrome plating with
246 trivalent chromium is provided in the SI-1.

247 **Alternative assessment:** The use of closed systems with underpressure reduces the reproductive
248 hazard of chromium (VI) from the level of “Repr. 1B/H360D” (may damage the unborn child) to
249 “Repr. 2/H361F” (suspected of damaging fertility). It also reduces the environmental hazard as no
250 PFAS or other hazardous substances are needed in this process.

251 The use of chromium (III) instead of chromium (VI) in electroplating constitutes a shift to a less
252 hazardous substance without the carcinogenic, mutagenic and reproductive toxicity properties of

253 chromium (VI).⁵⁷ Atotech and Faraday Technology (the latter from 2015 on) use no boric acid in their
254 processes, which was for a long time a serious drawback of the chromium (III) process.^{56,58}

255 Processes based on PVD use UV-lacquer and, according to Gerhardt Kunststofftechnik (2016a),⁵²
256 some of the substances in the application in UV-lacquers are listed as Substances of Very High
257 Concern in the EU. However, no further details are available.

258 **Conclusion:** PFAS have been technically important in both decorative and hard chrome plating. For
259 many decorative chrome plating processes, trivalent chromium can be used. For hard chrome
260 plating, there are two ways in which the use of PFAS in the electroplating step may be avoided:
261 either by switching to a closed system in a process still using hexavalent chromium or by switching to
262 trivalent chromium, which removes the need for a mist-suppressing surfactant. The first approach
263 has already been used for 10 years and is feasible, although initially more expensive due to the costs
264 for modifications of the plant. The second approach is not yet used at large scale and might require
265 more research and time for implementation. The use of PFAS in chrome plating (electroplating) is
266 substitutable. Whether or not PFAS can be replaced in the etching pre-treatment process is unclear.

267 3.5 Chemical-driven oil production

268 **Uses:** The production of crude oil and gas generally occurs in three steps: (i) primary oil recovery
269 (providing 12–15% of the oil),⁵⁹ (ii) secondary oil recovery (or “water flooding”, providing an
270 additional 15–20% of the oil); (iii) enhanced oil recovery (EOR), aiming to collect some of the
271 remaining 60–70% of the oil.⁵⁹ EOR techniques are classified in thermal processes, gas injection, and
272 chemical flooding.⁵⁹

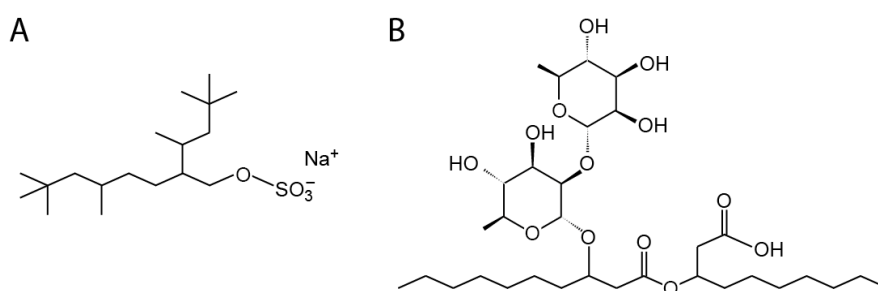
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274 Fluorinated surfactants are used during water flooding (secondary oil recovery) and in EOR.⁶⁰ When
275 used in water and chemical flooding, fluorinated surfactants increase the permeability of the
276 formation by reducing the interfacial tension between the reservoir surface and the aqueous
277 phases.⁶¹ Fluorinated surfactants also increase the wettability of the rock.⁶² In chemical flooding,

278 fluorinated surfactants are used to render the surfaces of the oil reservoirs hydrophobic and
279 oleophobic. This supports the displacement of the oil from the sand and rock formations.⁶³
280 Fluorinated surfactants are also used in fracturing rock formations penetrated by the wellbore,
281 where they act as part of a foaming agent that initiates and extends the fractures in the formation.⁶⁴
282 It has also been described that fluorinated surfactants are used to generate foam that is stable in
283 contact with the crude oil, while imbibing and transporting the oil through the subterranean
284 formation.⁶¹

285
286 Overall, PFAS are used for several different functions in chemical-driven oil production. Generally,
287 they are used because they have a very low surface tension (between 17 and 24 mN/m) and are
288 chemically and thermally stable.⁶¹

289
290 **Availability of alternatives:** Multiple efforts have been made to synthesize alternative surfactants
291 with the exact physiochemical properties as PFAS.⁶² Branched hydrocarbon surfactants are an
292 alternative which could replace fluorinated surfactants in EOR. Kiani et al. (2019)⁶² studied a non-
293 fluorinated anionic surfactant, iC18S(FO-180), CAS No. 181355-81-7, see structure in **Error!**
294 **Reference source not found.** A. C18S(FO-180) has a surface tension of around 25 nM/m and can
295 enhance the oil recovery to up to 72%.⁶²



296
297 *Figure 1:* A: surfactant iC18S(FO-180), according to Alexander et al. (2014),⁶⁵ Kiani et al. (2019),⁶² B: a
298 rhamnolipid (CAS 4348-76-9) as an example of glycolipids used as biosurfactants.

299

300 Another potential additive in EOR is hydrophobin-II (HFBII).⁵⁹ HFBII is a small cysteine-rich
301 amphiphilic protein from the hydrophobin family (HFBs). HFBs are naturally produced by fungi and
302 comprise about 100 amino acids. HFBs can self-assemble at hydrophilic-hydrophobic interfaces into
303 an amphipathic film. This protein film renders hydrophobic surfaces of gas bubbles, liquids, or solid
304 materials wettable, while hydrophilic surfaces can be turned hydrophobic.⁶⁶ The ability of HFBs to
305 self-assemble at oil-water interfaces and stabilize oil droplets makes them candidates for a PFAS-free
306 EOR process. The company BASF has filed a patent for extracting hydrocarbons from oil sand with
307 water and a hydrophobin.⁶⁷ Another patent from BASF claims the use of hydrophobins as auxiliary-
308 emulsifying agents for a drilling fluid.⁶⁸ However, HFBII can only lower the air/water surface tension
309 to 35 mN/m, which is still too high for EOR.⁵⁹ Blesic et al. (2018)⁵⁹ concluded that HFBII is not
310 promising for EOR but also noted that an appropriate co-surfactant (e.g. medium-chain alcohols) may
311 improve the performance of HFBII.

312

313 Beside hydrophobins there are other biosurfactants that have been used in microbial-enhanced oil
314 recovery (MEOR). These include glycolipids (see Fig. 1B), lipoproteins or lipopeptides, phospholipids,
315 fatty acids or natural lipids, and particulate and polymeric biosurfactants. Examples for each group
316 are given in the SI-1, Section 2.6. According to Varjani (2017),⁶⁹ oil release from porous media may
317 involve processes such as (a) dissolution of inorganic carbonates by bacterial metabolites, (b)
318 production of bacterial gases that decrease the viscosity of oil, (c) generation of surface-active
319 substances or wetting agents by some bacteria, and (d) high affinity of bacteria for solids, displacing
320 oil by growing between oil and rock.

321 There is not much information about how well MEOR works in comparison to EOR with chemicals.
322 However, MEOR has already been applied in the field. For example, in India the Oil and Natural Gas
323 Corporation Limited have developed a technology for MEOC.⁷⁰ The technology has been
324 implemented in 130 oil wells and an encouraging success rate has been reported.⁷⁰

325

326 In the US 27% of the oil reservoirs and 40% of the oil-producing carbonate reservoirs may be suitable
327 for MEOR.⁷¹ However, effective MEOR application may require substantial research on a case-by-case
328 basis, because the environment will be unique with respect to soil and rock formation characteristics
329 as well as physical and chemical conditions.⁷¹

330

331 **Alternative assessment:** Chemical identification was possible for surfactant iC18S. However, the
332 substance does not have C&L notifications or a REACH registration, which precluded an assessment
333 of human-health hazards. Regarding environmental hazards of iC18S, EPI Suite™ estimates a low BCF
334 (below 100) and a degradation half-life in water of 81 days. Whereas this half-life exceeds the EU's
335 criteria for persistent substances (40 days in freshwater; 60 days in marine water), it is still much
336 lower than the environmental degradation half-lives of PFAS.

337

338 Different amounts of data were found for different biosurfactants as identified by Varjani (2017).⁶⁹
339 According to Banat (1995)⁷² and Lazar et al. (2007),⁷³ biosurfactants are biodegradable and have low
340 toxicity, but data are scarce. There are studies available where no mutagenic effects and no
341 reproductive toxicity were observed or expected for rhamnolipids,⁷⁴ sophorolipids⁷⁵ and surfactin.⁷⁶
342 Carcinogenicity data are lacking. Where biodegradation and toxicity data are available, they show
343 that biosurfactants are readily biodegradable,^{74,75} or at least not persistent,⁷⁷ with low aquatic
344 toxicity.⁷⁴⁻⁷⁶ There are limited data on bioaccumulation, but sophorolipids have a log $K_{ow} < 4.5$,⁷⁵
345 suggesting that bioaccumulation is unlikely. For hydrophobin-II, no sufficient data for an assessment
346 were found.

347

348 **Conclusion:** PFAS have been technically important in oil recovery. Alternatives are being explored
349 and in some cases already in use. Therefore, PFAS can be replaced in the oil industry, but not equally
350 well in all types of reservoirs and probably with research and development needed on a case-by-case
351 basis. At least some of the PFAS uses are substitutable.

352

353 3.6 Processing aids for aqueous emulsion polymerization of fluoropolymers

354 **Uses:** Fluoropolymers can be produced by several methods, including suspension polymerization,
355 aqueous emulsion polymerization, solution polymerization, polymerization using supercritical CO₂,
356 and polymerization in the gas phase. The manufacturing process applied also depends on the
357 commercial grade of the fluoropolymer that is manufactured (e.g. granular versus fine-powder
358 PTFE).⁷⁸ Patents for each of the main manufacturing processes are provided in the SI-1.

359 The most commonly employed polymerization methods include suspension polymerization and
360 aqueous emulsion polymerization. Suspension polymerization generally does not involve
361 (fluorinated) surfactants; it results in larger polymer particles than aqueous emulsion
362 polymerization⁷⁹ and is used, e.g., for granular PTFE.⁷⁸ Aqueous emulsion polymerization has
363 traditionally involved the presence of a fluorinated surfactant, which is used to stabilize the polymer
364 particles formed.⁷⁹ Aqueous emulsion polymerization is used to produce fine-powder and dispersion
365 products.^{78,80}

366 **Availability of alternatives:** Fluoropolymer manufacturers are exploring novel processes to eliminate
367 the use of PFAS in aqueous emulsion polymerization. For the production of polyvinylidene fluoride
368 (PVDF), processes with fluorine-free emulsifiers have been implemented by multiple
369 manufacturers.^{81,82} One manufacturer has made this transition since 2008,⁸¹ and its patents disclose
370 varied processes that use fluorine-free alternative emulsifiers including blocks of polyethylene glycol,
371 polypropylene glycol and/or polytetramethylene glycol,⁸³⁻⁸⁷ alkyl phosphonate,⁸⁸ vinyl/acrylic acids,⁸⁹
372 polyvinyl/acrylic acids,⁹⁰ alkanesulfonates,⁹¹ siloxanes,⁹² and 3-allyloxy-2-hydroxy-1-propane sulfonic
373 acid salts.⁹³ More information on the specific substances is provided in Section S2.7 in the SI-1. The
374 same section in the SI-1 also includes patents from several other manufacturers on fluorine-free
375 emulsifiers in the polymerization of PVDF, but it is unclear whether or not they are actually in use.

376

377 Fluorine-free emulsifier-based processes for manufacturing other fluoropolymers, including fine-
378 powder and dispersion PTFE, have been patented,⁹⁴⁻⁹⁸ but, to the best of our knowledge, are not yet
379 implemented.

380 **Alternative assessment:** Some of the patents by Arkema from 2006 to 2020⁸³⁻⁸⁷ use multiple
381 combinations of 14 glycol-based polymers as emulsifiers. The hazards of these emulsifier would
382 depend on which of the substances are used. As these are all polymers, EPI SuiteTM could not be run
383 and hazard data were collected from CLP and REACH registrations only. Of the seven substances with
384 available data in CLP and REACH, four would constitute a reduction of hazards. However, there is also
385 one substance that is on the REACH Authorization list because of endocrine-disrupting properties,
386 one that is toxic to aquatic life with long-lasting effects and one that may damage fertility or the
387 unborn child (for more information see SI-1 and SI-2).

388 All five patents from Arkema⁸³⁻⁸⁷ state that the invention “is generally practiced” with PEG, PPG,
389 and/or PTMG as the sole emulsifiers. PPG and PEG have REACH registrations that provide evidence
390 that the substances are not mutagenic, toxic to reproduction, toxic to the aquatic environment,
391 persistent, or bioaccumulative. PPG also has evidence that it is not carcinogenic, whereas PEG has no
392 evidence for this endpoint. PPG and PEG would be clear improvements in both human-health and
393 environmental hazards. For PTMG there are no sufficient data for an assessment. Overall, the use of
394 a polyolefin glycol emulsifier most likely constitutes a reduction in human-health and environmental
395 hazard. However, the patent mentions a variety of terminal groups that may be used in the
396 polyolefin glycols. Because biodegradation of PEG and PPG needs alcoholic end groups,⁹⁹ some of
397 these end groups may impair the degradability of the substances.

398 The alternative assessment of the 26 other emulsifiers patented by Arkema⁸⁸⁻⁹³ shows again that
399 most of them would most likely constitute a reduction in human-health and environmental hazard.
400 However, there are also substances among them that are very toxic to aquatic life with long-lasting
401 effects and one substance that is suspected of damaging fertility or the unborn child (for more

402 information see SI-1 and SI-2). Again, it very much depends on which of the emulsifiers are actually
403 used as patents tend to cover the broadest scope of possibilities.

404 **Conclusion:** PFAS emulsifiers have been technically important in aqueous emulsion polymerization.
405 Alternatives have been developed for PVDF, but not yet for other fluoropolymers. The alternatives
406 found for PVDF show that manufacturers need to carefully evaluate and manage their alternatives as
407 some of the patented substances are toxic to aquatic life or toxic for reproduction. According to
408 Arkema, during nearly 15 years of research, many alternatives have been studied; some only enabled
409 a good polymerization process but were not able to meet the risk objectives and some were able to
410 meet both, which proves that it is possible to produce PVDF with alternative emulsifiers exhibiting a
411 good eco toxicological profile. Beyond the question of PFAS emulsifiers, the essentiality of using
412 fluoropolymers would also have to be assessed.

413

414 3.7 Semiconductor industry

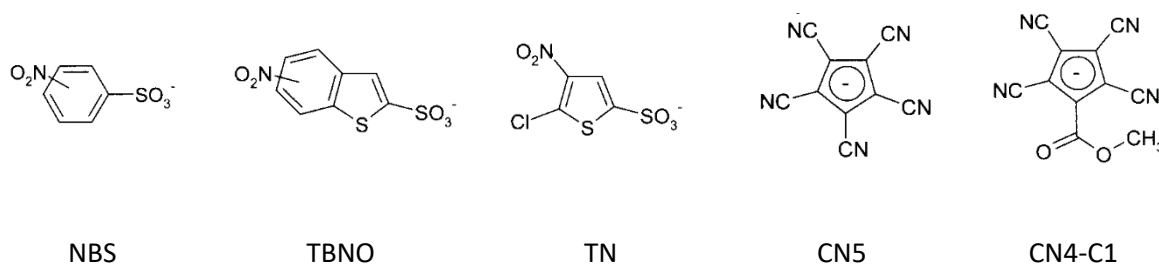
415 **Overview:** Semiconductor manufacturing is a multi-step sequence of photolithography and chemical
416 processing steps, comprising over 500 steps in total.⁴⁷ Photolithography is the process by which the
417 circuits are created on the semiconductor wafers.¹⁰⁰ Here, a thin film of a photoresist (light-sensitive
418 polymer) is first applied to a substrate, such as silicon-based wafers. Then, light is used to transfer a
419 geometric pattern from a photomask to the photoresist on the wafer. The photoresist is altered
420 when exposed to light, and this allows structures to be built up on the wafer.¹⁰⁰ Photoresists require
421 the presence of (fluorinated) photoacid generators (PAGs) that enable the etching of images smaller
422 than the wavelength of visible light.⁴⁷ Other uses of PFAS in the semiconductor industry include, e.g.,
423 developer and rinse solutions. More information is provided in the SI-1.

424 3.7.1 Photoacid generators (PAGs)

425 **Uses:** PAGs are components of a photoresist formulation that are able to generate strong acids
426 under light irradiation. PAGs based on PFOS were used for a long time and then replaced by PAGs
427 based on perfluorobutane sulfonic acid (PFBS) or PAGs based on functionalized

428 fluoroethanesulfonates.¹⁰¹ However, these alternative substances are also PFAS, so there is still a
429 need for fluorine-free alternatives.

430 **Availability of alternatives:** One of several requirements in the design of a substance that can form a
431 strong acid is the ability to delocalize the negative charge of the resulting anion. This can be
432 achieved, for example, through the π -system of a benzene ring. The isomers of
433 nitrobenzenesulfonate (NBS) are an example of such PAGs.¹⁰¹ Preliminary work has also shown that
434 acceptor-substituted thiosulfonate anions exhibit good performances as strong acid generators.
435 Specific examples include benzo[b]thiophene-2-sulfonic acid, 4(or 7)-nitro-, ion(1-) (TBNO) or 2-
436 thiophenesulfonic acid, 5-chloro-4-nitro-, ion(1-) (TN). Another possibility for strong acid generation
437 are PAGs based on acceptor-substituted aromatic anions, such as pentacyanocyclopentadienide
438 (CN5) or methoxycarbonyl-tetracyanocyclopentadienide (CN4-C1)¹⁰² (Figure 2).



439 *Figure 2: Fluorine-free PAGs proposed by Glodde et al. (2010)¹⁰¹ and Liu et al. (2010).¹⁰²*

440 Glodde et al. (2010)¹⁰¹ and Liu et al. (2010)¹⁰² evaluated some basic performance metrics of the five
441 non-fluorinated PAG anions in photoresist formulations with triphenylsulfonium (TPS) and compared
442 the results to photoresist formulations of perfluorobutanesulfonate as anion with TPS (TPS PFBS).
443 The fluorine-free formulations showed promising results in optical clarity and thermal stability
444 compared to TPS PFBS. However, the fluorine-free PAGs did not perform as well as the TPS PFBS
445 with respect to sensitivity, line-width roughness, and resolution. Fluorine-free PAGs developed by
446 IBM are described in various patents (see SI-1) and have also been officially announced.¹⁰³

447 **Assessment of alternatives:** An assessment of alternatives could be carried out for the PAGs where
448 the chemical structures were known. No REACH registrations were found for the corresponding CAS

449 numbers, but C&L notifications were found for two isomers of NBS. C&L data for NBS indicated that
450 this substance has no CMR properties. Environmental hazard data were estimated for NBS, TBNO, TN
451 and CN5, all of which indicate lower environmental hazard than for PFAS. Persistence values were
452 calculated between 21-42 days. All calculated BCF values were below 1.

453 **Conclusion:** According to the estimated persistence and bioaccumulation potential of these
454 compounds, the alternatives reviewed seem to be less hazardous than PFOS or PFBS and also seem
455 to be capable of generating strong acids. However, as mentioned above, these fluorine-free PAGs
456 have some technical limitations which are prohibitive to high-volume manufacturing. Thus, there is
457 still a need for additional research and development of fluorine-free PAG alternatives. In addition to
458 research focused on the replacement of PFAS with safe and effective non-fluorinated alternatives,
459 research is also needed to develop new technologies for PFAS removal and destruction, as long as
460 PFAS cannot be replaced in these applications. As the viability of photolithography chemicals
461 requires the simultaneous satisfaction of multiple overlapping performance requirements, and the
462 manufacture of semiconductors relies on many interlocking steps, the use of fluorine-free PAGs will
463 require additional technology innovation and process adaptations to ensure viable and effective
464 solutions that can be manufactured reliably

465 3.7.2 Immersion liquid, developer solution and rinse solution

466 **Use:** Besides use in photoresists, PFAS are also used in other parts of immersion lithography. A
467 patent from the Taiwan Semiconductor Manufacturing Company¹⁰⁴ describes the use of fluorinated
468 surfactants as additives to developer and chemical rinse solutions. PFAS are used in these solutions
469 to lower the contact angle of the solutions and, thus, reduce watermark defects after dry spinning.
470 The employment of PFAS may also help to avoid pattern collapse during spin-drying.¹⁰⁴

471 **Availability of alternatives:** A patent from BASF¹⁰⁵ refers to the aforementioned patent
472 US20080299487¹⁰⁴ and discloses that a new liquid (and a method of using it) for immersion
473 photolithography of photoresist layers has been developed that allows for a high aspect ratio for
474 line-space dimensions of 20 nm and below without causing pattern collapse, line edge roughness,

475 and watermark defects, without the use of fluorinated surfactants. The patent remains vague
476 regarding the alternative substance/s employed and describes only the possible anionic and cationic
477 functional groups, see SI-1. However, it is mentioned that the newly developed fluorine-free liquid
478 may be used as an immersion liquid for immersing photoresists during irradiation, as developer
479 solution for photoresist layers, and as chemical rinse solution for rinsing the patterned material
480 layers.¹⁰⁵ It is also mentioned that the method does not only work for immersion photoresist layers,
481 but also for extreme UV (EUV) and electron beam (eBeam) photoresist layers. EUV lithography
482 recently became ready for mass production and is the most suitable candidate for the next pattern-
483 feature size (5 nm node).^{106,107}

484 **Assessment of alternatives:** No information is available on the hazards of the alternatives proposed.

485 **Conclusion:** It seems that the alternative described by Klipp et al. (2012)¹⁰⁵ fulfills the technical
486 functions needed and has potential also for future developments in the semiconductor industry. As
487 such, it is a step into the application of PFAS-free alternatives, which may make PFAS in these uses
488 substitutable. More information would be needed on the physicochemical properties and hazards of
489 these materials.

490 **Conclusion:** Even though PFAS may currently be essential in some uses in the semiconductor
491 industry, it has been recognized that PFAS are problematic for the environment and efforts are being
492 made to replace PFAS with fluorine-free alternatives.¹⁰⁸ The Semiconductor Industry Association
493 reported that the semiconductor industry globally has successfully completed the phase-out of
494 PFOS,⁴⁷ but PFOS has often been replaced by other shorter-chain PFAS. The two examples above
495 show that fluorine-free alternatives have been patented but that more research is needed to
496 implement them.

497

498 4 Discussion

499 The case studies illustrate the diversity and complexity of the task of a PFAS phase-out. In several
500 cases, the technical function of PFAS directly derives from their water- and oil-repellency and it is
501 relatively clear that PFAS can be replaced by PFAS-free water- or oil-repellent substances (bicycle
502 lubricants, carpets, cleaning products). In chrome plating and fluoropolymer production, the
503 technical function of PFAS is also well-defined, but the conditions and requirements are so
504 demanding that finding alternatives is challenging. Finally, in the semiconductor industry and in oil
505 recovery, PFAS have several different technical functions and/or are used in a multitude of process
506 steps, which makes it more difficult to find suitable alternatives, and many different substances
507 and/or process modifications may be needed.

508 4.1 Availability of alternatives

509 An extensive search of the available literature was conducted. However, the list of identified
510 alternatives is not exhaustive and there might be more (and maybe even better) alternatives. An
511 important point regarding patents is that patents generally reflect an early stage of research and
512 development and cover a broad range of options that might work in processes to be further
513 developed. Therefore, they mostly do not describe solutions that are ready to be implemented, and
514 further research and development over several years may be needed before a viable solution is
515 available.

516 Alternatives that are already on the market were identified for four of the seven case studies: bicycle
517 lubricants, carpets, household cleaning products, and chrome plating. We did not investigate
518 industrial cleaning products as the specifications for these products might differ substantially
519 between different use areas. The identified alternative products and processes in the four use areas
520 will not be suitable for all specific uses in these areas. However, they show that innovation has
521 happened and that there are feasible options to replace PFAS in these uses. The case of chrome-

522 plating illustrates that sometimes a change in process conditions (underpressure) can be as effective
523 as finding a chemical substitution.

524 Alternatives for processing aids in aqueous emulsion polymerization have been identified for PVDF
525 but not for other fluoropolymers. However, there are numerous patents that describe
526 fluorosurfactant-free polymerization processes for other fluoropolymers as well, suggesting that it is
527 also possible to make fine-powder PTFE without fluorinated processing aids, but that it is more
528 challenging than for PVDF. Developing PFAS-free emulsifiers requires extensive research and
529 development and a long-term investment (probably more than 5 years). Furthermore, the solution
530 found by one manufacturer will be patent-protected and not directly available for others, which also
531 explains why, e.g., in China PFOA is still used.

532 The uses of PFAS in chemical-driven oil production and the semiconductor industry and the
533 availability and suitability of alternatives are more difficult to assess. There are alternatives to PFAS
534 also in chemical-driven oil production, but it is unclear how well they work compared to PFAS and
535 what level of performance is necessary in each application. Substantial research might be needed on
536 a case-by-case basis; ultimately, only technical experts in the area of oil drilling might be able to
537 assess the alternatives. A similar situation occurs in the semiconductor industry. PFAS in the
538 semiconductor industry are used in so many different steps and for so many different functions that
539 it is difficult to judge the alternatives, in particular as processes build on each other and are very
540 complex. However, the examples investigated here (PAGs and immersion liquid, developer solution
541 and rinse solution) show that there is awareness of the PFAS problem in the field and that research
542 into alternatives is ongoing.

543 **4.2 Alternative assessment**

544 In the assessment of alternatives, we used a simple and pragmatic approach (information present in
545 the C&L and REACH databases, estimates from EPI Suite™, where possible). A more detailed
546 assessment would not have been feasible because of the large number of substances to be assessed

547 and the lack of information about many of the substances. For an initial comparison for the purposes
548 of illustrating the process and the data needs, the approach is sufficient.

549 The lack of publicly accessible information about many of the alternatives limits the scope of
550 alternative assessments. For many substances, even the chemical identity was not known (and not
551 revealed by the manufacturers contacted) and basic physicochemical properties and results from
552 degradation and toxicity tests were lacking. In several cases, some qualitative information was
553 available (“plant-based”; list of substance groups used such as polyolefin glycols or possible anionic
554 and cationic groups), and for some substances, the chemical identity and structure were available so
555 that some basic properties could be estimated.

556 Several alternatives were sufficiently characterized so that at least a partial comparison of their
557 properties with those of the PFAS used could be performed. Often, the alternatives offer significant
558 improvements compared to PFAS, at least with respect to persistence. However, it has to be
559 reiterated that more chemical property and toxicity data for the alternatives need to be generated
560 and made available in the public domain.

561 4.3 Transition to PFAS-free alternatives

562 For the consumer products investigated, the transition to PFAS-free alternatives is feasible without
563 substantial problems. Alternatives are available and labeled and marketed as PFAS free or fluorine
564 free. Regulatory requirements may help to transition to these alternatives. An example is the US
565 State of California, where they request carpet and rug manufacturers whose products contain PFAS
566 to submit a Priority Product Notification (PPN) by August 30, 2021.¹⁰⁹ Within seven month after
567 submitting the PPN, manufacturers need to remove the PFAS from the products.

568 In the area of chrome plating, a substantial step forward has been made and even in hard-chrome
569 plating, where use of chromium (VI) was seen as a necessity, processes based on chromium (III) have
570 been developed and are used by two manufacturers,^{56,110} and also for the process with chromium
571 (VI), PFAS-free versions exist. However, approximately 22% of the authorizations under REACH are

572 still for chrome plating with hexavalent chromium,¹¹¹ which shows that more efforts are needed to
573 support the transition.

574 In the areas of fluoropolymer production, oil recovery, and the semiconductor industry, the situation
575 is more complex. Because of the demanding and highly diverse conditions or the many interlinked
576 processes with many different PFAS uses, much broader assessments are required. In all three areas,
577 the need for a replacement of PFAS has been recognized and research and development are
578 underway. However, it is not clear to what extent and by how many manufacturers the alternatives
579 are already in use and how much of the market is still based on processes using PFAS. In these areas,
580 it may be desirable to establish technical expert committees that act as an interface between
581 science/engineering and policy making. This would create greater transparency and make it easier
582 for policy makers to follow the process and facilitate next steps. Stronger requirements to reduce
583 emissions of PFAS-containing waste through, e.g., stronger regulation and enforcement would
584 increase the need to look for PFAS-free alternatives.

585 Finally, the transition requires better access to information about both PFAS uses and alternatives
586 and their properties. For a group of chemicals of such high concern to environmental and human
587 health, it is justified to require more transparency and publicly accessible data. What is needed at a
588 minimum is information about the chemical identity and some minimum data on toxicity,
589 degradability, and intended uses. This information should be available to the general public, and also
590 within supply chains. A situation in which a product manufacturer receives a PFAS-free chemical from
591 a chemical manufacturer and uses it in a consumer product without knowing the identity of the
592 chemical, but just relies on the safety-data sheet, is not desirable.

593 Overall, the phase-out of PFAS may proceed on several different “tracks” with different timescales
594 and priorities. One set of factors that determine these timescales and priorities are, obviously, the
595 amounts of PFAS used and the extent to which the uses are open and dispersive. Another set of
596 factors are the complexity of the assessment tasks and the amount of research and development

597 needed. For a task of such high importance, but also complexity, a roadmap outlining these different
598 tracks and corresponding timelines will be desirable.

599 **Supporting Information available**

600 A list of the manufactures contacted, additional information on the case studies including
601 information on an eighth case study (climbing ropes). An MS Excel document listing data from the
602 alternative assessments.

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616

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