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2.4 PFAS Reductions and Alternative PFAS Formulations

Concern regarding the persistence, bioaccumulation, and possible ecological and human health effects of long-chain PFAAs has led manufacturers to use replacement PFAS chemistries, which include reformulating or substituting longer chain substances with generally shorter chain perfluoroalkyl or polyfluorinated substances that should not transform to long-chain PFAAs, or replacing manufacturing processes with nonfluorinated chemicals or alternate methods (USEPA 2006; OECD 2017). Manufacturing reductions and phaseouts are described in this section.

2.4.1 3M Voluntary Phaseout of Certain Long-Chain PFAS

In early 2000, 3M was the principal worldwide manufacturer of PFOA and POSF-derived PFAS (for example, PFOS) (Buck et al. 2011). This represented about 80–90% of global POSF-based production (Prevedouros et al. 2006), with 3M the sole U.S. manufacturer of PFOS (USEPA 2003). In 2000, 3M announced a voluntary, unilateral phaseout (this only applied to 3M) of POSF-derived PFAS, which at the time represented more than 95% of the company's perfluorooctanyl production (3M Company 2000). The 3M phaseout included the six-, eight-, and ten-carbon PFSAs (PFHxS, PFOS, and PFDS) and related precursors, as well as PFOA (Buck et al., 2011). 3M reportedly completed most of the phaseout by the end of 2002, with the remaining phaseout completed by 2008 (USEPA 2017; 3M Company 2017).

At the time of the phaseout, 3M's POSF-derived PFAS were used in several applications:

- ~41% for paper and packaging protectors
- ~36% for textiles, leather, and carpet treatment and fabric protectors
- ~19% as industrial surfactants, additives, and coatings (including electroplating and etching surfactants, household additives, insecticides, and other applications)
- ~3% in firefighting foam (3M Company 2000).

The paper and packaging protectors included POSF-based side-chain fluorinated polymers and phosphate diesters (Wang et al. 2013).

PFOA produced by 3M was primarily used as a fluoropolymer processing aid, with only about 3% of PFOA production used for other applications: mostly in antistatic coatings in medical films, with limited quantities used for electronics applications (for example, to create a humidity barrier on printed circuit boards and to coat precision bearings with silicone oil) (3M Company 2003).

This phaseout applied only to 3M, and only to select PFAS. 3M subsequently used (and reportedly continues to use) ECF to produce PBSF-based PFAS (for example, the four carbon PFSA: PFBS) (OECD 2013; Wang et al. 2015). Any new manufacture and/or import of the PFAS phased out by 3M requires USEPA review based on the Significant New Use Rules (SNURs) described in Section 2.4.2. Based on the 2012 Chemical Data Reporting effort, no company reported manufacture or import of PFOS into the United States (reporting was required for quantities greater than 25,000 pounds) (USEPA 2018).

When 3M stopped producing PFOA in the early 2000s, it is reported that the manufacture of PFOA was continued by other domestic and international producers using fluorotelomerization (USEPA 2003; Wang et al. 2014). Domestic PFOA production was later phased out by the eight major domestic producers, as described in Section 2.4.3. Global production is summarized in Section 2.4.4 and Section 2.4.5.

In December 2022, 3M issued a press release stating the company would discontinue the manufacturing of PFAS and the use of PFAS in its products by the end of 2025. This will include discontinuing the manufacturing of all fluoropolymers, fluorinated fluids, and PFAS-based additive products and the use of PFAS across their product portfolio.

2.4.2 USEPA Significant New Use Rules (SNURs)

In conjunction with these voluntary reductions and phase-outs, USEPA used its authority under the Toxic Substances Control Act (TSCA) to finalize SNURs between 2002 and 2020 to require notification to USEPA before any manufacture (including import) of select PFAS, which include, but are not limited to, some of the PFAS included in 3M's voluntary phaseout of PFOS and related chemicals (Section 2.4.1). The July 2020 SNUR restricts products containing certain PFAS that have been phased out from being imported into the United States (USEPA 2021). According to USEPA (2021), this SNUR levels the playing field for companies that had already voluntarily phased-out the use of long-chain PFAS under EPA's PFOA Stewardship Program. As of February 2023, 1,422 PFAS are on the TSCA Chemical Substance Inventory, a list of all existing chemical substances that are either currently or have historically been manufactured (including imported) or processed in the United States. Of these, 711 are considered "active" in commerce, meaning they were manufactured (including imported) or processed over the 10-year period ending June 21, 2016, or more recently. Updates to the TSCA inventory are published generally on a quarterly basis, including the number of chemicals on the "active" inventory (USEPA 2023). USEPA has reviewed more than 300 of the commercially active PFAS under the New Chemicals Program and regulated about 200 PFAS with consent orders and/or new chemical SNURs (USEPA 2021). A new proposed SNUR has been added regarding 300 PFAS that "have not been manufactured (including imported) or processed for many years and are consequently designated as inactive on the TSCA Chemical Substance Inventory" (USEPA 2023).

2.4.3 USEPA PFOA Stewardship Program

In January 2006, USEPA initiated the 2010/2015 PFOA Stewardship Program (USEPA 2006). Most PFOA produced in 2003 (around the time of the phaseout described in Section 2.4.1) was used as a processing aid in the manufacture of fluoropolymers, such as PTFE (USEPA 2003), and this was likely still the case at the time the stewardship program began.

The eight major manufacturing or processing companies that participated in the program are reportedly those that manufactured or processed the majority of these chemicals, including Arkema, Asahi, BASF Corporation (successor to Ciba), Clariant, Daikin, 3M/Dyneon, DuPont, and Solvay Solexis (USEPA 2018). There may be other manufacturing or processing companies that did not participate in the program (USEPA 2015). USEPA indicated that the eight participating companies successfully met the program goals, meeting a 95% reduction by 2010 in global facility emissions and product content, and eliminating production (100% reduction) of PFOA, certain longer chain PFCAs (higher homologues such as PFNA and PFDA), and related PFOA precursors (for example, 8:2 FTOH) by 2015 (USEPA 2017). Even though the program goals were met by the eight companies, the ongoing use of PFOA stock and imported materials has not been fully restricted (USEPA 2018). Products manufactured and imported prior to 2015, and materials with ongoing uses, may still contain these PFAS (USEPA 2018), and PFOA may be present as a trace contaminant in some other PFAS and fluoropolymer products (3M Company 2003). As discussed in Section 2.4.5, production is ongoing in other nations. Additional information on current US regulatory activities can be found in Section 8.2.

2.4.4 Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a United Nations treaty signed in 2001 aimed at reducing or eliminating the production, use, and release of key POPs. POPs are defined as synthetic, organic compounds that, to varying degrees, resist photolytic, biological, and chemical transformation (KEMI 2004, 2015; USEPA 2017). Chemicals listed as POPs satisfy screening criteria for persistence, bioaccumulation, long-range environmental transport, and adverse effects (Stockholm Convention 2001). The Stockholm Convention targets PFAS in these ways:

- In 2009, *Annex B of the Stockholm Convention* (which restricts production and use) was amended to include PFOS (and its salts and POSF), because it is persistent in the environment and is not known to transform at any environmental condition. Currently, the United States has not ratified the amendment (KEMI 2017). Annex B is not an outright ban; it allows certain approved uses and exemptions of POPs. Prior to 2019, approved, ongoing uses for PFOS under Annex B included select applications in photoimaging, semiconductor coatings and etching agents, metal plating, insect baits, chemically driven oil production, aviation hydraulic fluids, some medical devices, and color printer electronic parts (UNEP 2008, 2009).
- Additionally, the following amendments and recommendations have been made:
    - In May 2019, Annex B was amended to discontinue several of the previously allowed ongoing uses (UNEP 2019).
    - Annex A was amended in May 2019 to prohibit and/or eliminate the production and use of PFOA (its salts and PFOA-related compounds), with certain exemptions (UNEP 2019).

- the POPs Review Committee recommended in October 2019 to list PFHxS (and its salts and related compounds) in Annex A without specific exemptions (UNEP 2019)

2.4.5 Global Manufacture and Use of PFAS

PFAS are still manufactured globally, despite some PFAS (most notably PFOA and PFOS) no longer being produced in the United States, Europe, and Japan; for further information, see OECD's Country Information page on the OECD Portal on Per and Poly Fluorinated Chemicals (OECD 2017), "Risk Reduction Approaches for PFASs" (OECD 2015), and "Toward a New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances" (OECD 2018). In addition to the domestic reductions discussed in Section 2.4.1 and Section 2.4.3, some of the phase-outs and restrictions are summarized below.

In 2017, the South Australia state government took initial steps to develop legislation banning environmentally harmful foams, such as Class B firefighting foams containing PFAS (SA EPA 2017).

Canada embarked on an Environmental Performance Agreement with four major manufacturers to phase out PFOA and related compounds from 2010 to 2015 (CEPA 2006). In 2008, Canada prohibited the use of most PFOS, with select exemptions such as use of existing stocks of PFOS-based firefighting foams, and then added PFOS to the Virtual Elimination List in 2009 and to the Prohibition of Certain Toxic Substances Regulations in 2016 (CEPA 2018). By 2016, Canada prohibited the import, manufacture, use and sale of PFOS, PFOA, and other long-chain PFCAs (and salts and precursors), with limited exemptions (CEPA 2018), and subsequently in 2018, Canada proposed further modification to those restrictions (Government of Canada 2018).

In 2009, the European Union (EU), through the European Chemicals Agency (ECHA), regulated PFOS as a POP, and use of PFOS is limited to certain restrictions (Vierke et al. 2012). In 2017, the EU banned the sale, use, and import of PFOA, its salts and PFOA-related substances through Annex XVII of the European Chemicals Regulation (REACH), with phase-outs occurring through 2032 and certain allowed uses. ECHA is currently considering restrictions for other long-chain PFCAs, their salts and precursors, as well as other compounds, such as PFHxA (ECHA 2018). On February 7, 2023, ECHA proposed restrictions on PFAS as a class; this proposal was prepared by Denmark, Germany, the Netherlands, Norway, and Sweden (ECHA 2023).

In Japan, there are restrictions on the manufacture, import, export, and use of PFOS and its salts (OECD 2015).

The global reduction anticipated with the U.S. phaseout of PFOA has potentially been offset by increased production of PFOA and related PFAS in China, India, and Russia (OECD 2015). PFAS manufacture began in China in the 1980s (World Bank 2017, 2017), and PFOS production in China increased coincident with the long-chain PFAA phaseout in the United States (CONCAWE 2016; OECD 2015). In 2016, PFOS and its derivatives were still being produced in Germany, Italy, and China (TTE 2016), but by early 2017, China was the only known producer of PFOS. China has ratified the Stockholm Convention on POPs and was awarded a grant from the Global Environment Facility (GEF) in 2017 to support the reduction of PFOS in China (World Bank 2017). China has developed some guidance for restriction and limitations of some PFAS (OECD 2015). In Brazil, EtFOSA, which is a precursor to FOSA and PFOS and used in the pesticide sulfluramid, which is still being produced on an industrial scale, is allowed as an approved use by the Stockholm Convention (Löfstedt Gilljam et al. 2016). Section 1.1.2.2 includes information about PFAS use in pesticides.

There does not appear to be a comprehensive reference publicly available to document the individual PFAS and the quantity of PFAS produced over the years. This is possibly because these data are proprietary or because quantities produced did not meet USEPA reporting requirements under TSCA, but could also be due to modifications to chemistries and products over the years (Lindstrom, Strynar, and Libelo 2011), complexity of the issue, and the general lack of publicly available data (OECD 2018). That said, some estimates of production and emissions of select PFAS have been made based on the limited available data.

Prevedouros et al. (2006) estimated global emission of PFCAs at about 3,500–8,000 tons between the 1950s and 2002, with approximately 80% of emissions related to fluoropolymer manufacture (and use), based on overall annual production estimates of:

- APFO (ammonium salt of PFOA)-about 335–525 tons per year between 1951 and 2002
- APFN (ammonium salt of PFNA)-about 60–225 tons per year between 1975 and 2004
- POSF (building block for PFOS)-about 9,550 tons per year from 1960 to 2002.

Other production and emissions estimates for PFCAs are available from OECD (2015) and Wang et al. (2014), and for PFOS

and PFOS precursors from Armitage et al. (2009) and Paul, Jones, and Sweetman (2009). OECD (2015) called for a new, comprehensive survey to evaluate both historical and ongoing emissions.

2.4.6 PFAS-Based Replacement Chemistry

With the emerging awareness of potential health and environmental impacts of some PFAS and related limitations on production of some PFAS, such as the SNURs (Section 2.4.2) and 2010/2015 PFOA Stewardship Program (Section 2.4.3), manufacturers began efforts to replace the use of long-chain PFAS chemistries with nonfluorinated chemicals, alternate technologies, and/or other, shorter chain PFAS (Wang et al. 2013). For example, decorative chrome plating typically now uses less toxic chromium III instead of chromium VI so that PFAS are not needed (Wang et al. 2013).

Some of the replacement chemicals are said to achieve the same performance effectiveness of some of their predecessors. A carpet manufacturer has found that performance of fluorine-free alternatives is "equivalent or superior to the fluorinated treatments" pg. 66, (CalEPA 2018). Conversely, a 2015 study concluded that there are no nonfluorinated alternatives that provide equivalent technical performance in textiles (Danish EPA 2015). Refer to Section 3 for a discussion of PFAS-free AFFF that meets U.S. Department of Defense performance specifications.

Several studies suggest some of the alternate PFAS chemistries may or may not be less hazardous than the long-chain predecessors, although publicly available information on most replacement chemicals is limited (Wang et al. 2015 RIVM 2016; OECD 2015). Documentation regarding the USEPA's review of hundreds of "shorter chain-length PFAS telomeric" substitutes is available under the TSCA New Chemicals Program (OECD 2013; USEPA 2017), and other documentation regarding replacement PFAS chemistries is available from the Performance Fluoropolymer Partnership (2021) and American Chemistry Council (2021). Draft toxicological evaluations have been provided for public comment by the USEPA for GenX chemicals and PFBS (USEPA 2018, 2018) with the PFBS Toxicity Assessment finalized in 2021 (USEPA 2021), and the GenX Toxicity Assessment finalized in 2021 as well (USEPA 2021) . For further discussion of toxicity documentation for select PFAAs and replacement chemistries, see Section 7.

Although a full discussion of such PFAS chemistries is not possible here, it is important to be aware of the trend toward shorter chain chemistries, as some of these PFAS increasingly may be detected in the environment. Some replacement PFAS have been detected in the environment and generated public concern and regulatory actions; however, information on significant environmental contamination by replacement PFAS is limited, and most are not detected by standard analytical methods (Wang et al. 2013). Some PFAS used as replacement chemicals, such as HFPO-DA and ADONA (used as replacements for APFO/PFOA in PTFE manufacture), and F-53B (11-Chloroeicosafluoro-3-1455 oxaundecane-1-sulfonic acid [11Cl-PF3OUdS or F-53B Minor], 9-Chlorohexadecafluoro-3-1456 oxanonane-1-sulfonic acid [9Cl-PF3ONS or F-53B Major]) (used as a replacement for PFOS in plating), have recently been added to USEPA Method 537.1 (USEPA 2018). Certain treatment processes used to remove these chemicals from waste streams may not be as effective as with longer chain PFAS (Sun et al. 2016).

Alternate PFAS chemistries are being used to replace long-chain PFAAs that have been phased out of production and/or use. In many cases, although similar legacy PFAAs were manufactured and used by many companies, these same companies have transitioned to the use of many different types of other PFAS as alternative chemicals. Many of these replacement PFAS are structurally similar to their long-chain predecessors, and are typically also manufactured using electrochemical fluorination (ECF) or fluorotelomerization (Wang et al. 2015; CONCAWE 2016). Some of these fluorinated substitutes may transform to form short-chain PFAAs. Some short-chain PFAAs, PFECAs (both per and poly), and related chemicals were manufactured as early as the 1980s, or earlier (Wang et al. 2015). Some PFAS used to replace long-chain PFAS are presented below (Hori et al. 2006; OECD 2007; Herzke, Olsson, and Posner 2012; Buck 2015; Wang et al. 2013; Wang et al. 2014; Wang et al. 2015; KEMI 2015; Sun et al. 2016; Holmquist et al. 2016):

- short chain homologues of the long-chain PFAAs, including PBSF-based derivatives (for example, 4-carbon chain PFBS in lieu of POSF-based six-, eight-, and ten-carbon chain compounds) in many applications, including surface treatment
- perfluorohexane sulfonyl fluoride (PHxSF, which can transform to PFHxS and is considered to be phased out in the United States) as an alternative to PFOS, primarily in China
- fluorotelomer-based products such as FTOH, for example, those with a six-carbon perfluorohexyl chain, including 6:2 fluorotelomer-based compounds in AFFF formulations and other six-carbon fluorotelomer-based products, side-chain fluorinated polymers, and PFPE products for surface treatment of food contact materials
- per- and poly-fluoroalkyl ether acids used as polymerization aids in manufacture of fluoropolymers, such as GenX chemicals (perfluoroalkyl ether acids) and ADONA (polyfluoroalkyl ether acids) used as a replacement for

APFO in the manufacture of PTFE, as well as other types of perfluoroalkyl ether acids, also referred to as cyclic or polymeric functionalized PFPEs as a replacement for APFN in the manufacture of polyvinylidene fluoride (PVDF)
- 6:2 fluorotelomer-based compounds, a PFBS-based compound, and PFAS known as F-53 and F-53B in lieu of PFOS in metal plating applications.

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