5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

No information is available in the TRI database on facilities that manufacture or process perfluoroalkyls because this chemical is not required to be reported under Section 313 of the Emergency Planning and Community Right-to-Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986) (EPA 2005b).

Perfluoroalkyls have been manufactured for their direct use in commercial products as well as for their use in industrial process streams. The most important perfluoroalkyl compounds in terms of production and use have been PFOS and PFOA; however, these substances and related perfluoroalkyl compounds are currently being phased out as a joint effort by EPA and industry.

The 3M Company, which was the principal worldwide manufacturer of PFOS and related chemicals, completed the phase-out of its PFOS production in 2002 (3M 2008a; EPA 2008f). During the same year, EPA finalized the significant new use rule for 88 perfluoroalkyl sulfonate compounds, which requires manufacturers to notify EPA 90 days prior to commencing manufacture or import of these substances for a significant new use to allow time for evaluation (EPA 2002, 2007c, 2008f). The purpose of this rule was to limit future manufacturing and importation of these substances. According to EPA, the rule allows for the continuation of a few limited, highly technical uses for which no alternatives are available, and which are characterized by very low volume, low exposure, and low releases. The significant new use rule was amended in 2007 to include 183 additional perfluoroalkyl sulfonate compounds (EPA 2007c, 2008f). Included on the current list are PFOS, PFHxS, PFOSA, and Et-PFOSA-AcOH. EPA believed that the perfluoroalkyl sulfonate compounds listed under the significant new use rule were no longer manufactured in the United States; however, during the comment period of the 2007 amendment, EPA learned of the ongoing use of tetraethylammonium perfluorooctanesulfonate as a fume/mist suppressant in metal finishing and plating baths (EPA 2007c). EPA has since excluded this from the list of significant uses. The only nation that still has manufacturers producing PFOS is China (Lim et al. 2011).

In 2006, the eight major companies of the perfluoropolymer/fluorotelomer industry agreed to participate in EPA’s PFOA Stewardship Program (EPA 2008f). This included voluntary commitments from these companies to reduce facility emissions and product content of PFOA and related chemicals on a global basis by 95% no later than 2010, and to work toward elimination of these substances by 2015. Progress
reports were provided in 2007. Data from these reports that list the content and percent reduction of PFOA, PFOA precursors, and higher PFOA homologues in products are listed in Table 5-1.

According to DuPont, PFOA is produced at trace levels as a byproduct during the manufacture of fluorotelomer products; however, DuPont specifies that PFOA is not used to manufacture its fluorotelomer products (DuPont 2008). DuPont has announced that a new manufacturing process has been developed for its fluorotelomer products that are based on short-chain chemistry. The company claims that this new process will remove >97% of trace levels of PFOA, its homologues, and direct precursors from DuPont fluorotelomer products. The chemicals that will be involved in DuPont’s new manufacturing process are not identified. Based on statements made by the 3M Chemical Company, the short chain perfluoroalkyl, PFBuS, may play a role in new technologies that will be used to reformulate products affected by the phase out of PFOA and related perfluoroalkyls (3M 2008a).

U.S. production volume data for PFOA, PFBA, and PFOS reported by manufacturers under the EPA Inventory Update Rule (IUR) are provided in Table 5-2. Production volume ranges for the ammonium salt of PFOA, ammonium perfluorooctanoate (APFO), are also listed. During the reporting year 2002, manufacturers reported that the production volumes were within the range of 15,000–500,000 pounds (6–227 metric tons) for PFOS and PFOA and within the range of 500,000–1,000,000 pounds (227–454 metric tons) for APFO (EPA 2008g). PFBA was reported as having a production volume within the range of 15,000–500,000 pounds (6–227 metric tons) during 1986; however, PFBA production volumes were not reported for subsequent years (EPA 2008g). None of the other perfluoroalkyl compounds were listed in EPA’s IUR database. Current U.S. production volume data for perfluoroalkyl compounds are not available; however, the production volume of PFBA and the production volumes of PFOS and related perfluoroalkyl sulfonate compounds are expected to be zero since 3M ceased production of these substances in 1998 and 2002, respectively (3M 2008a; Agency for Toxic Substances and Disease Registry 2008; EPA 2007c). Similarly, the current production volumes of PFOA and APFO are expected to be much less as a result of efforts by companies to reduce PFOA emissions and develop alternatives for this chemical so that it can be completely removed from process streams (EPA 2008f).

Perfluorocarboxylates have been manufactured industrially by electrochemical fluorination (ECF), fluorotelomer iodide oxidation, fluorotelomer olefin oxidation, and fluorotelomer iodide carboxylation. (Prevedouros et al. 2006; Schultz et al. 2003). During the ECF process, an organic acyl or
### Table 5-1. Content (ppm) and Percent Reduction of PFOA, PFOA Homologues, or PFOA Precursors in Products from the 2006 U.S. Operations of Fluoropolymer/Fluorotelomer Companies

<table>
<thead>
<tr>
<th>Company</th>
<th>Chemicals</th>
<th>Dispersions</th>
<th>Other fluoropolymers</th>
<th>Telomers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Content (ppm) and Percent Reduction of PFOA, PFOA Homologues, or PFOA Precursors</td>
<td>Percent reduction</td>
<td>Percent reduction</td>
<td>Percent reduction</td>
</tr>
<tr>
<td>Arkema, Inc.</td>
<td>PFOA and higher homologues Precursors</td>
<td>&gt;500–1,000 0%</td>
<td>&gt;70–150 30</td>
<td>Not applicable Not applicable</td>
</tr>
<tr>
<td>Asahi Glass Company</td>
<td>PFOA, PFOA salts, and higher homologues Precursors</td>
<td>500–1,570 12%</td>
<td>0.12 Not applicable</td>
<td>Not applicable Not applicable</td>
</tr>
<tr>
<td>Ciba Specialty Chemicals Corporation</td>
<td>PFOA Higher homologues Precursors</td>
<td>0.05 kg &gt;99%</td>
<td>0.05 kg &gt;99%</td>
<td>Not applicable Not applicable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05 kg &gt;99%</td>
<td>0.05 kg &gt;99%</td>
<td>0.05 kg &gt;99%</td>
</tr>
<tr>
<td>Clariant International Ltd.</td>
<td>PFOA</td>
<td>280 34%</td>
<td>2; 300 0%</td>
<td>0.28 72%</td>
</tr>
<tr>
<td>Daikin America, Inc.</td>
<td>PFOA</td>
<td>Not applicable</td>
<td>Not applicable</td>
<td>Not applicable Not applicable</td>
</tr>
<tr>
<td>E.I. DuPont de Nemours and Company</td>
<td>PFOA, PFOA salts Direct precursors</td>
<td>547 44%</td>
<td>69 80%</td>
<td>246 kg 50%</td>
</tr>
<tr>
<td>3M/Dyneon</td>
<td>PFOA</td>
<td>0 100%</td>
<td>Not reported</td>
<td>Not applicable Not applicable</td>
</tr>
<tr>
<td>Solvay Solexis</td>
<td>PFOA and PFOA salts Higher homologues Precursors</td>
<td>600–700 59%</td>
<td>Not applicable</td>
<td>170–200 0%</td>
</tr>
</tbody>
</table>

*Percent reduction in product content of these compounds from baseline year levels. The baseline year is the year nearest to the year 2000 for which company data are available.

PFOA = perfluorooctanoic acid; PFOS = perfluorooctane sulfonic acid

Source: EPA 2008f

***DRAFT FOR PUBLIC COMMENT***
### Table 5-2. U.S. Production Volume Ranges for Perfluoroalkyls (1986–2002)
Reported under the EPA Inventory Update Rule

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>10,000–500,000</td>
<td>Not reported</td>
<td>10,000–500,000</td>
<td>10,000–500,000</td>
<td>10,000–500,000</td>
</tr>
<tr>
<td>APFO</td>
<td>10,000–500,000</td>
<td>10,000–500,000</td>
<td>10,000–500,000</td>
<td>10,000–500,000</td>
<td>500,000–1,000,000</td>
</tr>
<tr>
<td>PFBA</td>
<td>10,000–500,000</td>
<td>Not reported</td>
<td>Not reported</td>
<td>Not reported</td>
<td>Not reported</td>
</tr>
<tr>
<td>PFOS</td>
<td>Not reported</td>
<td>Not reported</td>
<td>10,000–500,000</td>
<td>Not reported</td>
<td>10,000–500,000</td>
</tr>
</tbody>
</table>

APFO = ammonium perfluorooctanoate; EPA = Environmental Protection Agency; PFBA = perfluorobutyric acid; PFOA = perfluoroctanoic acid; PFOS = perfluorooctane sulfonic acid

Source: EPA 2008g

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**PERFUROALKYLs**

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

***DRAFT FOR PUBLIC COMMENT***
sulfonyl fluoride backbone structure is dissolved in a solution of aqueous hydrogen fluoride (Savu 1994b; Siegemund et al. 2005). A direct electrical current is then passed through the solution, which replaces all of the hydrogens on the molecule with fluorines. Perfluoroacyl fluorides produced by ECF are hydrolyzed to form the perfluorocarboxylic acid, which is then separated via distillation. This method was used extensively by 3M in the production of perfluoroalkylsulfonates such as PFOS (3M 1999; Hekster et al. 2003; Schultz et al. 2003).

\[ R_h\text{COF} + HF \rightarrow R_f\text{COF} + H_2 + \text{byproducts} \]
\[ R_f\text{COF} + H_2O \rightarrow R_f\text{COOH} + HF \]

Perfluoroalkanesulfonyl fluorides produced by ECF are hydrolyzed under alkaline conditions to form the corresponding salt (Savu 1994b; Siegemund et al. 2005). Acidification followed by distillation yields the anhydrous perfluoroalkanesulfonic acid.

\[ R_h\text{SO}_2\text{F} + HF \rightarrow R_f\text{SO}_2\text{F} + H_2 \]
\[ R_f\text{SO}_2\text{F} + KOH \rightarrow R_f\text{SO}_3\text{K} + HF \]
\[ R_f\text{SO}_3\text{K} + H_2\text{SO}_4 \rightarrow R_f\text{SO}_3\text{H} + K\text{HSO}_4 \]

Perfluorosulfonamido compounds, such as PFOSA, can be formed by reacting the perfluoroalkanesulfonyl fluoride with a primary or secondary amine (3M 1999; Hekster et al. 2003; Siegemund et al. 2005).

The fluorotelomer iodide oxidation process was developed by DuPont and has served as the basis for their fluoropolymer production chemistry (Hekster et al. 2003; Savu 1994a; Siegemund et al. 2005). It begins with the preparation of pentafluoroiodoethane from tetrafluoroethane. Tetrafluoroethane is then added to this product at a molar ratio that gives a product of desired chain length. Finally, the product is oxidized to form the carboxylic acid. The process produces linear perfluorocarboxylic acids of even carbon numbers as illustrated below.

\[ 5\text{C}_2\text{F}_4 + \text{IF}_5 + 2\text{I}_2 \xrightarrow{\text{catalyst}} 5\text{C}_2\text{F}_5\text{I} \]
\[ \text{C}_2\text{F}_5\text{I} + n\text{C}_2\text{F}_4 \rightarrow \text{C}_2\text{F}_5(\text{C}_2\text{F}_4)_n\text{I} \]
\[ \text{C}_2\text{F}_5(\text{C}_2\text{F}_4)_n\text{I} \xrightarrow{\text{SO}_3} \text{C}_2\text{F}_5(\text{C}_2\text{F}_4)_{n-1}\text{CF}_2\text{COOH} \]
Ammonium perfluorononanoate is currently manufactured in Japan through fluorotelomer olefin oxidation (Prevedouros et al. 2006). Fluorotelomer iodide carboxylation has also been used to produce ammonium perfluorononanoate (Prevedouros et al. 2006). The ECF process resulted in a mixture of linear and branched isomers, whereas the telomerization processes yielded predominantly linear products. It has been reported that the 3M ECF process resulted in approximately 70% linear and 30% branched isomers for PFOS and 78% linear and 22% branched isomers for PFOA (Benskin et al. 2009).

5.2 IMPORT/EXPORT

Information regarding the import and export of perfluoroalkyl compounds are limited; however, some PFBA is may be imported for commercial use (ATSDR 2008; 3M 2008a).

5.3 USE

Applications of perfluoroalkyl compounds have made use of their unique surfactant properties (Schultz et al. 2003). The alkyl tails of perfluoroalkyls make these substances both hydrophobic (water-repelling) and oleophobic (oil-repelling) (3M 1999; Kissa 2001; Schultz et al. 2003). Because of these properties, perfluoroalkyls have been used extensively in surface coating and protectant formulations (Kissa 2001). Major applications have included protectants for paper and cardboard packaging products, carpets, leather products, and textiles that enhance water, grease, and soil repellency (Hekster et al. 2003; Schultz et al. 2003). These compounds have been widely used in industrial surfactants, emulsifiers, wetting agents, additives, and coatings as well (3M 1999; Schultz et al. 2003). Perfluoroalkyls have been used in firefighting foams since they are effective in extinguishing hydrocarbon fueled fires (Schultz et al. 2003). Perfluoroalkyls have also been used as processing aids in the manufacture of fluoropolymers such as nonstick coatings on cookware, membranes for clothing that are both waterproof and breathable, electrical wire casing, fire and chemical resistant tubing, and plumbing thread seal tape (DuPont 2008; EPA 2008f).

5.4 DISPOSAL

Information concerning disposal of individual perfluoroalkyl products may be found on Material Safety Data Sheets (MSDS) from the manufacturers of the chemicals. Two methods are generally recommended for the disposal of fluoropolymer dispersions. The first method involves precipitation, decanting, or filtering to separate solids from liquid waste. The dry solids are then disposed of in an approved industrial solid waste landfill or incinerated, while the liquid waste is discharged to a waste water
treatment facility (Plastics Europe 2012). The second method involves incineration at temperatures >800°C using a scrubber to remove hydrogen fluoride (Plastics Europe 2012). Currently, several companies under the direction of EPA are performing incineration testing on commercially available fluoropolymers and fluorotelomers to determine whether these disposal processes result in the formation and release of perfluoroalkyl compounds into the environment (EPA 2008f). According to perfluorochemical facility assessment reports, historical disposal of perfluoroalkyl containing waste has been through onsite and offsite landfills, through sludge incorporation (subsurface injection), and through incineration (3M 2007b, 2008a; Agency for Toxic Substances and Disease Registry 2005). Pilot scale studies in which carpet samples were incinerated using a rotary kiln incinerator indicated that most perfluoroalkyls were effectively destroyed in combustors (Lemieux et al. 2007). Similar conclusions were reached by Yamada et al. (2005) when studying the incineration of textiles and paper treated with fluorotelomer-based acrylic polymers.