

Supporting Information

Sources, Fate & Transport of Perfluorocarboxylates

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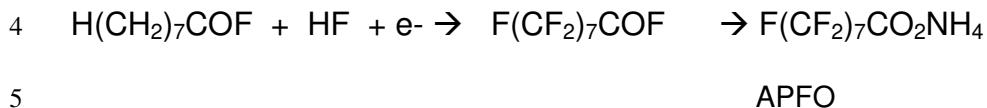
² E. I duPont de Nemours & Co., Inc., P.O. Box 80023, Wilmington, Delaware, U.S.A. 19880-0023

The supporting information provides additional details describing the basis and computations for the direct and indirect source emissions as well as environmental inventories and sinks.

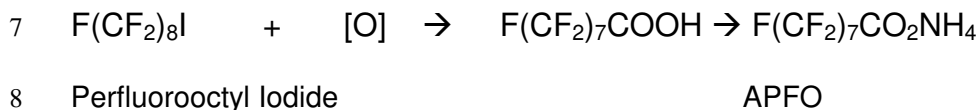
1 **FIGURE S1. Industrial Processes for Synthesis of PFCAs**

2

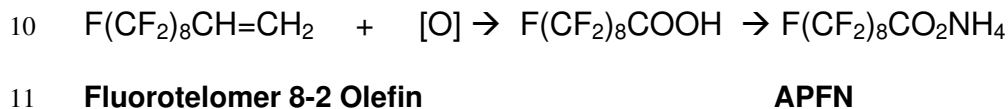
3 **Equation 1 Electrochemical Fluorination (ECF)**



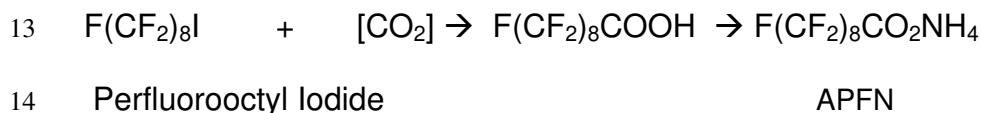
6 **Equation 2 Fluorotelomer Iodide Oxidation**



9 **Equation 3 Fluorotelomer Olefin Oxidation**



12 **Equation 4 Fluorotelomer Iodide Carboxylation**

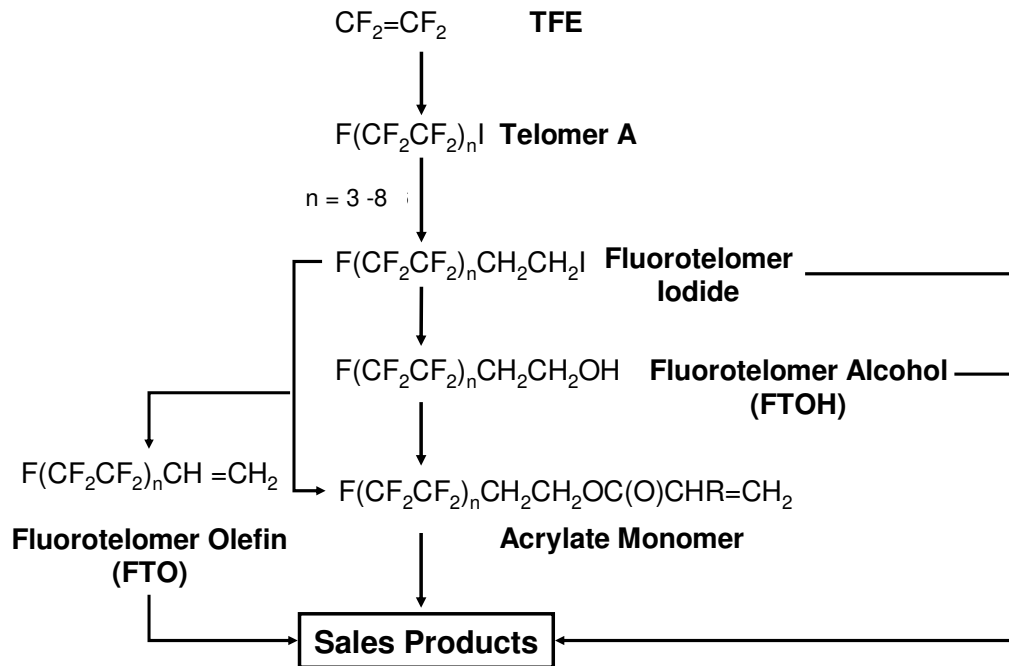


15

16 Products in Eq. 1 and 3 are actually carbon chain length mixtures.

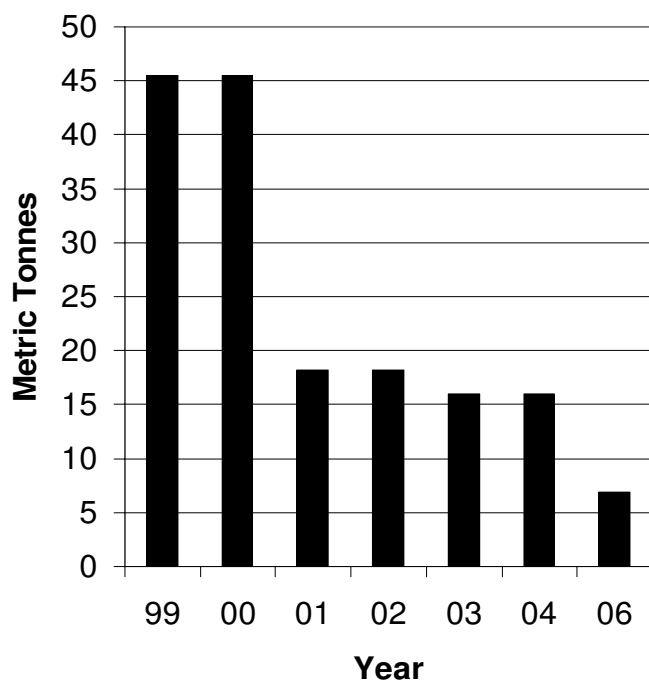
17 The ECF process produces 20-30 weight percent branched perfluorocarbon chain isomers.

1 **Figure S2. Fluorotelomer-Based Product Manufacture Schematic**



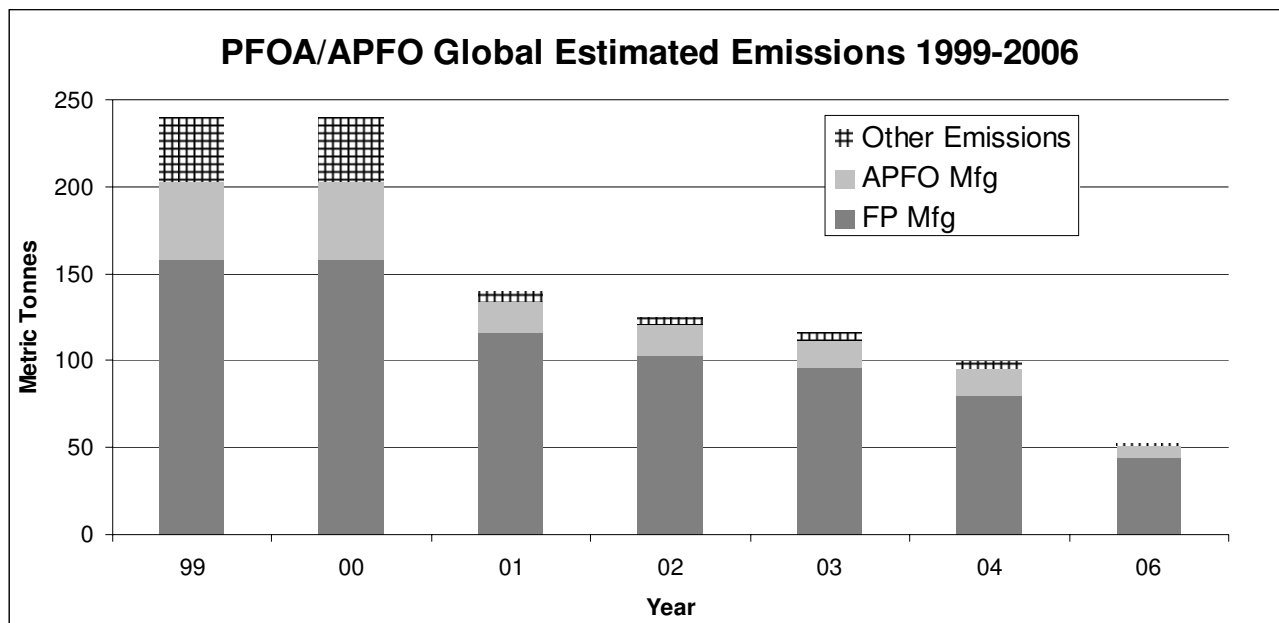
2

1 **Figure S3. Global Industry-Wide Emissions from APFO Manufacture 1999-2006**



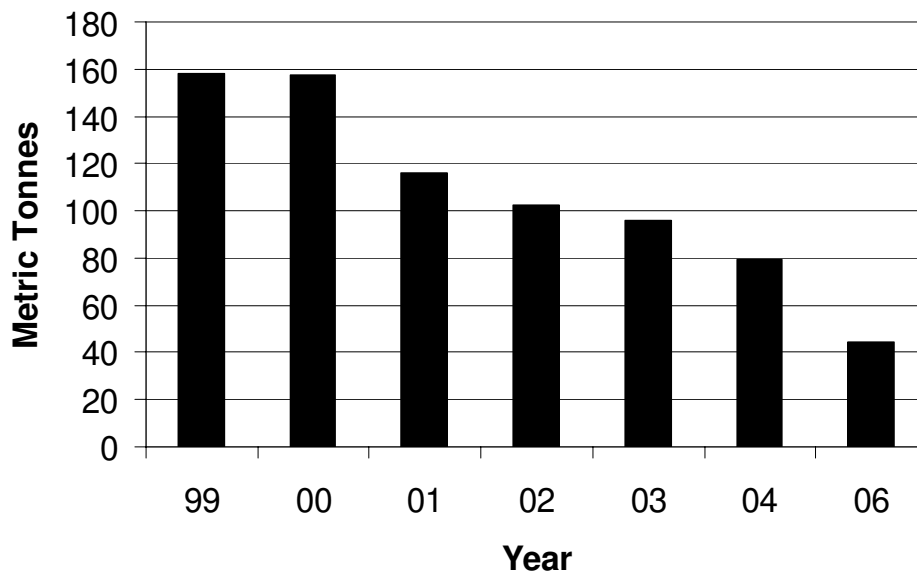
2
3 This graph shows the recent historical trend of APFO emissions from its manufacture as an industrial
4 chemical. Data for 1999-2004 are based on reported information (references 1,2,3,4). Data for 2006
5 are projected.
6 See also Table S3.

1 **FIGURE S4. Estimated Global PFO/APFO Emissions from All Sources 1999-2006.**
2



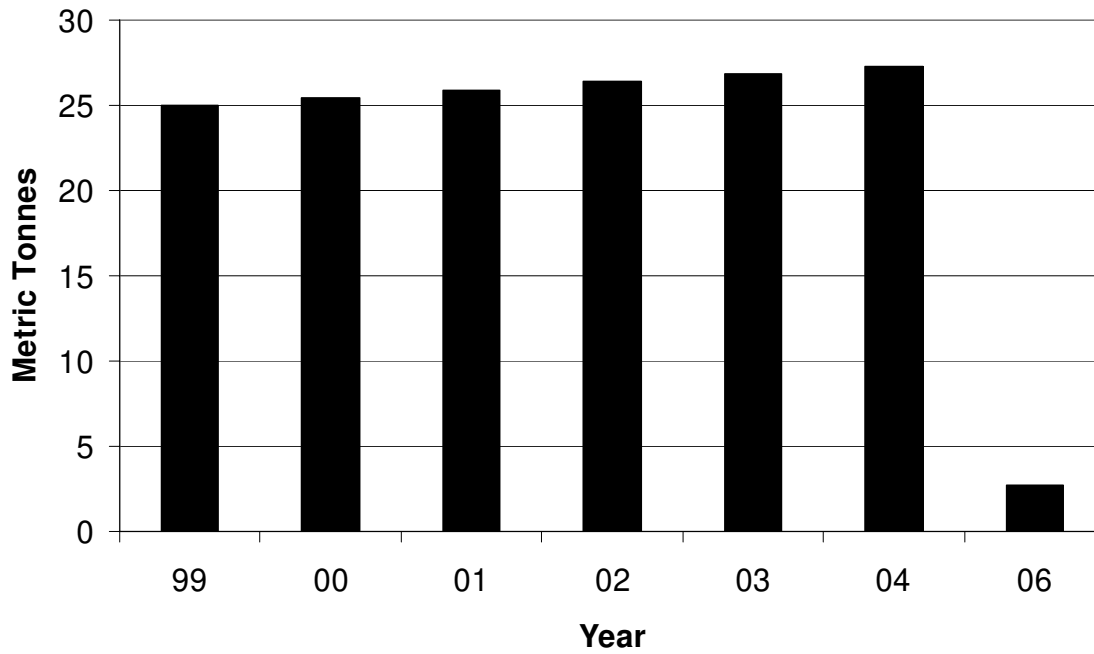
3
4
5 This graph shows the recent historical trend of PFO/APFO emissions from all sources from
6 1999-2006. The data for 2006 are projected. See also Figures S3, S5 and S6.

1 **Figure S5. Global Industry-Wide APFO Emissions from Fluoropolymer**
2 **Manufacture 1999-2006**



3
4 This graph shows the recent historical trend of APFO emissions from its use in fluoropolymer
5 manufacturing. Data for 1999-2004 are based on reported information (refs. 1,2,3,4,5). Data for 2006
6 are projected. See also data in Table S5.

1 **Figure S6. Global Industry-Wide APFO Emissions from Fluoropolymer Dispersion**
2 **Processing**



3
4 This graph shows the recent historical trend of APFO emissions from the processing of fluoropolymer
5 dispersions. Data for 1999-2004 are based on reported information (ref. 6). Data for 2006 are projected
6 based upon recent commitments to reduce these emissions. See also data in Table S6 and S7.

1 **Table S1. Chemical Abbreviations, Names & Formulas**

2

Chemical Abbreviation	Chemical Name	Chemical Formula
PFCA(s)	Perfluorocarboxylate(s)	$F(CF_2)_nCOO^-$
PFHx	Perfluorohexanoate	$F(CF_2)_5COO^-$
PFHxA	Perfluorohexanoic Acid	$F(CF_2)_5COOH$
PFHp	Perfluorohepanoate	$F(CF_2)_6COO^-$
PFHpA	Perfluoroheptanoic Acid	$F(CF_2)_6COOH$
PFO	Perfluorooctanoate	$F(CF_2)_7COO^-$
PFOA	Perfluorooctanoic Acid	$F(CF_2)_7COOH$
APFO	Ammonium Perfluorooctanoate	$F(CF_2)_7COONH_4$
PFN	Perfluorononanoate	$F(CF_2)_7COO^-$
PFNA	Perfluorononanoic Acid	$F(CF_2)_8COOH$
APFN	Ammonium Perfluorononanoate	$F(CF_2)_8COONH_4$
PFD	Perfluorodecanoate	$F(CF_2)_8COO^-$
PFDA	Perfluorodecanoic Acid	$F(CF_2)_9COOH$
PFU	Perfluoroundecanoate	$F(CF_2)_9COO^-$
PFUA	Perfluoroundecanoic Acid	$F(CF_2)_10COOH$
PFDD	Perfluorododecanoate	$F(CF_2)_10COO^-$
PFDDA	Perfluorododecdanoic Acid	$F(CF_2)_11COOH$
PFTD	Perfluorotridecanoate	$F(CF_2)_11COO^-$
PFTDA	Perfluorotridecanoic Acid	$F(CF_2)_12COOH$
PFAS	Perfluoroalkylsulfonyl products	$F(CF_2)_nSO_2-R$
POSF	Perfluorooctylsulfonyl fluoride	$F(CF_2)_8SO_2F$
PFOS	Perfluorooctane sulfonate	$F(CF_2)_8SO_3^-$
N-Et FOSE	N-ethyl fluoroocetyl sulfonamidoethanol	$F(CF_2)_8SO_2N(Et)CH_2CH_2OH$
N-Me FOSE	N-methyl fluoroocetyl sulfonamidoethanol	$F(CF_2)_8SO_2N(Me)CH_2CH_2OH$
FTOH	Fluorotelomer Alcohol	$F(CF_2CF_2)_nCH_2CH_2OH$
FTO	Fluorotelomer Olefin	$F(CF_2CF_2)_nCH=CH_2$

3

1 **TABLE S2. Commercial PFCA Products Characterization**

2
3
4

Weight % By Carbon Chain Length

Product Identification	Figure S1 Process	% Branched Isomers	8 PFO	9 PFN	10 PFD	11 PFU	12 PFDD	13 PFTD
Fluorad [®] FC-143	1	15	99	0.22	≤LOQ	nm	<LOQ	nm
Surflon [®] S-111	3	0	0.78	74	0.37	20	0.1	5
APFO - DuPont	2	0	99	nd	≤LOQ	<LOQ	<LOQ	nm

5

6 These are representative commercial PFCA products used as processing aids in the manufacture of
7 fluoropolymers.

8 $F(CF_2)_nCOO^-NH_4^+$ Commercial Product Analyses conducted by LC/MS/MS;

9 nd = not detected; nm = not measured.

10 <LOQ = less than the limit of quantification, detectable but not quantifiable (<0.01);

11 ≤LOQ = Detectable, close to 0.01;.

12

1 **Table S3. Estimated Industry-Wide Global Historic PFO Emissions from APFO**
 2 **Manufacture (ref. 2)**
 3

Time Period	# of Years	Estimated Average Annual APFO Production (t/yr)	Est Average Annual PFO Emissions (t/yr)	Estimated Total PFO Emissions [§] (t)
1995-2002	8	200 - 300	20 – 40 (see Fig. S3)	160 - 320
1980-1994	15	100 - 150	10 - 15	150 - 225
1965-1979	15	30 - 50	3 - 5	45 - 75
1951-1964	14	5 - 25	0.5 – 2.5	7 – 35
Total Global Historic Emissions (tonnes)				400 – 700*

4 * Rounded to the nearest 100 t = metric tonnes

5 § Value is total emissions for the given time period

- 6
- 7 • 1951 was the starting year for the computations because it was the first year APFO was
 - 8 manufactured and used in the commercial manufacture of fluoropolymers by DuPont. The
 - 9 amount of APFO was determined based on the annual production of fluoropolymers from 1951
 - 10 to present.
 - 11 • Production in earlier time periods was estimated to be 50% of the amount manufactured in
 - 12 1995-2004 for the period 1980-1994; 30% of the amount manufactured in 1980-1994 for the
 - 13 period 1965-1979; and 10% of the amount manufactured in 1965-1979 for the period 1951-
 - 14 1964.

15

16 **Example Calculations**

- 17 • $(40t \times 8yrs) + (15t \times 15yrs) + (5t \times 15yrs) + (2.5t \times 14yrs) = 320 + 225 + 75 + 35 = 655$ rounded to
- 18 nearest 100 is **700 tonnes**.
- 19 • $(20t \times 8yrs) + (10t \times 15yrs) + (3t \times 15yrs) + (0.5t \times 14yrs) = 160 + 150 + 45 + 7 = 362$ rounded to
- 20 nearest 100 is **400 tonnes**.
- 21 • The upper bound of annual emissions (40) for 1995-2002 was estimated by the following
- 22 computation : $[6 \text{ years (1992-2000)} \times 45 \text{ t/yr.}] + [2 \text{ years (2001-2002)} \times 18 \text{ t/yr}] = 306$ tonnes
- 23 over eight years. $(306 \div 8 \text{ years}) = 38$; rounded to the nearest 10 the upper bound is 40. See
- 24 also Figure S3.

1 **Table S4. Estimated Global Historic PFN Emissions from APFN Manufacture**
 2

Time Period	# of Years	Estimated Average Annual APFN Production (t/yr)	Est Average Annual APFN Emissions (t/yr)	Est. Total APFN Emissions [§] (t)
1995 – 2004	10	15 - 75	2 – 7.5	20 -75
1985 – 1994	10	20 - 100	2 - 10	20 - 100
1975 – 1984	10	25 - 50	2.5 - 5	25 – 50
Total Global Historic Emissions (tonnes)				70 - 200*

3

4 * Rounded to nearest one significant figure. t = metric tonnes

5 § Value is total emissions for the given time period

6

- 7 • The time periods and annual production are estimates assuming growth since APFN was first
 8 patented for use in making fluoropolymers (ref. 7, also see p. 15).
- 9 • Manufacturing emissions have been estimated to be 10% of amount of APFN manufactured,
 10 comparable in percentage to the amount cited in the main manuscript for APFO.
- 11 • APFN is manufactured as a mixture of perfluorocarboxylates (See Table S2).
- 12 • See also the description of the PVDF process that follows for more details on how the annual
 13 APFN production amounts were estimated.

14 **Example Calculations**

- 15 • $(8t \times 10\text{yrs}) + (10t \times 10\text{yrs}) + (5t \times 10\text{yrs}) = 75+100+50 = 225$ rounded to nearest 100 is 200
 16 tonnes.
- 17 • $(3t \times 10\text{yrs}) + (2t \times 10\text{yrs}) + (2.5t \times 10\text{yrs}) = 30+20+25 = 75$ rounded to nearest 10 is 80 tonnes.

1 **Table S5. Estimated Industry-Wide Global Historic APFO Emissions from**
 2 **Fluoropolymer Manufacture**
 3

Time Period	# of Years	Est Average Annual APFO Emissions (t/yr)	Estimated Total APFO Emissions [§] (t)
1995 – 2004	10	100 - 200	1,000 – 2,000
1980 - 1994	15	50 - 100	750 – 1,500
1965 – 1979	15	20 - 30	300 - 450
1951 - 1964	14	3 - 15	42 - 210
Total Global Historic Emissions			2,000 – 4,000*

4
 5 * Rounded to the nearest one thousand. t = metric tonnes

6 § Value is total emissions for the given time period

- 7 • 60% of APFO used in the manufacture of fluoropolymers is emitted to land and water.
- 8 • 1951 was the starting year for the computations because it was the first year of commercial
- 9 fluoropolymer manufacture by DuPont. Recent references provided sufficient information to
- 10 estimate emissions from 1995-2004 (3,4,5).
- 11 • APFO use in earlier time periods was estimated to be 50% of the amount used in 1995-2004 for
- 12 the period 1980-1994; 30% of the amount used in 1980-1994 for the period 1965-1979; and
- 13 10% of the amount used in 1965-1979 for the period 1951-1964.

14 **Example Calculations**

- 15 • $(200t \times 10\text{yrs}) + (100t \times 15 \text{ years}) + (30t \times 15 \text{ years}) + (15t \times 14 \text{ years}) = 4,160$ or **4,000** tonnes
- 16 rounded to the nearest 1000.
- 17 • $(100t \times 10\text{yrs}) + (50t \times 15 \text{ years}) + (20t \times 15 \text{ years}) + (3t \times 14 \text{ years}) = 2,092$ or **2,000** tonnes
- 18 rounded to the nearest 1000.

1 **Table S6. Aqueous Fluoropolymer Dispersion APFO Emissions Mass Balance**
 2 **(ref.6)**
 3

APFO Destinations	Wt% of Input APFO in Aqueous Fluoropolymer Dispersions
Decomposed in Dispersion Processing	62%
Air Emission	16%
Wastewater Emission	5%
Solid Waste Emission	5%
Undetermined	12%
Total	100%

4

5 • The historic amount of PFCAs in fluoropolymer dispersions can be estimated starting from the
 6 average annual production of APFO in Table S3. Assuming that 90% of APFO production was
 7 used for fluoropolymer manufacture then multiplying by 16% to assign the appropriate amount
 8 of PFCAs to fluoropolymer dispersion products followed by multiplying by 40% for
 9 environmental emissions from dispersion processing the annual and total environmental
 10 releases can be estimated. These values are given in Table S7.

11

1 **Table S7. Estimated Industry-Wide Global Historic APFO Emissions from**
 2 **Aqueous Fluoropolymer Dispersion Processing**
 3
 4

Time Period	# of Years	Est Average Annual APFO Emissions (t/yr)	Estimated Total APFO Emissions [§] (t)
1995 – 2002	8	12 - 17	100 – 140
1980 - 1994	15	6 – 9	90 – 140
1965 – 1979	15	2 – 3	30 – 45
1951 - 1964	14	0.3 – 1	3 – 14
Total Global Historic Emissions			200 – 300*

5
 6 * Rounded to nearest hundred t = metric tonnes

7 § Value is total emissions for the given time period

- 8 • Begin with values from Table S3, Column 3; 90% of APFO production is used in manufacture
 9 of Fluoropolymers (multiply by 0.9); 16% of Fluoropolymers manufactured with APFO are
 10 Dispersion Products (multiply by 0.16); As high as 40% of APFO present in Dispersion
 11 Products is emitted to the environment (multiply by 0.4)

12 **Example Calculations**

- 13 • The lower bound estimate for 1995-2002 : $200 \times 0.9 \times 0.16 \times 0.4 = 12$. 12×8 years = 96,
 14 rounded to the nearest 10 equals 100.
 15 • The upper bound estimate for 1995-2002 : $300 \times 0.9 \times 0.16 \times 0.4 = 17$. 17×8 years = 136,
 16 rounded to the nearest 10 equals 140.

1 **Polyvinylidene Fluoride (PVDF) Polymerization**
2

- 3 • The following patent citations were used as a basis for setting the range for the percent APFN
4 surfactant on weight of vinylidene fluoride (VF) monomer which is used in Tables S9 and S10. In
5 addition, private communication from J. Franklin (see pages 17-18) was also considered.
6

7 **PVDF Emulsion Polymerization Patent Citations**

- 8 - all cite PFCA salts of varying chain lengths as suitable for use
9

	<u>Weight Percent PFCA Surfactant</u>
12 US 3,475,396 (ref. 8)	
13 Column 2, Line 66	0.5 – 3.0
14 Claim 4	2 – 6
15 Claim 7	0.5 – 3.0
16 US 3,640,985 (ref. 9)	
17 Col 3. Lines 10-35	0.05 – 5.0 ; usually 0.05-2.0
18 US 3,708,463 (ref. 10)	
19 Col 3-4 Lines 60-75, 1-17	0.1 – 1.5 ; 0.5 – 1.0 preferred
20 US 4,569,978 (ref. 11)	
21 Col. 2. Lines 33-37	0.05 – 0.5 ; 0.1- 0.2 preferred 22

- 23 • These patents cite the use of perfluorocarboxylates (PFCAs) as a surfactant in the emulsion
24 polymerization of vinylidene fluoride to make polyvinylidene fluoride (PVDF).
25 • Current PVDF manufacturers have confirmed that APFN is the surfactant that is and has been used
26 commercially since the mid 1970s.
27 • Based on 15,000 tonnes of PVDF manufactured in 2002 by emulsion polymerization and a range
28 of use of 0.1 to 0.5 weight percent, the amount of AFFN used in 2002 ranges between 15 to 75
29 tonnes.
30 • Note: PFCA surfactants are not used in the suspension polymerization process for manufacturing
31 PVDF.
32 • For the Purpose of this Assessment, the following ranges of surfactant use and PVDF production
33 were used:
34

1 **Table S8. Estimated Historic Use of APFN in PVDF Production**
2
3

Time Period	Estimated PVDF Production (tonnes)	Estimated Weight Percent APFN Surfactant Used	Estimated APFN Production (tonnes per year)
1995 - 2004	15,000	0.1 – 0.5	15 – 75
1985 - 1994	10,000	0.2 – 1.0	20 – 100
1975 - 1984	5,000	0.5 – 1.0	25 – 50

- 4
- 5 • The use range for 1995-2005 reflects the information provided on the next pages to establish a
6 lower bound and the patent information cited on the prior page which indicates that APFN use may
7 be greater to establish the estimated upper bound of 0.5 wt%.
 - 8 • Higher APFN use in earlier years is used for the periods before 1995 as the patents indicate this.
9 Estimated surfactant use is reduced over time to reflect industry improvements in process
10 efficiency.

28 September 2005

James Franklin
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Brussels, Belgium

CONSUMPTION OF APFN IN THE MANUFACTURE OF PVDF

Specific consumption of fluorinated surfactant

The production of polyvinylidene fluoride (PVDF) by emulsion (dispersion) polymerization in the presence of a long-chain fluorinated surfactant was first commercialized by the Pennwalt Corporation in the 1970s, on the basis of a process developed by Diamond Shamrock (US Patent 3,475,396).

US Patent 4,569,978 filed by Pennwalt on 17 April 1985 describes the use of fluorinated surfactants including Surfion S111 (the main component of which is APFN). Surfactant levels of 0.05 to 0.5 weight percent, based on the weight of monomer used, are claimed in Claim 1. As is usual in the patent literature, the first claim is very broad and one of its objectives is to prevent potential competitors from even approaching the preferred operating conditions, which are more closely defined in further claims. Thus, in the case of US Patent 4,569,978, the "preferred" range of surfactant levels is given as 0.1-0.2 % (Claim 15).

According to informed industry sources, this range is consistent with current industrial practice. In the case of coating-grade PVDF, for which latex particle size is of paramount importance, surfactant concentrations higher than 0.2% would yield a too low particle diameter, while using less than 0.1% would result in an unstable latex.

Global production of PVDF by the emulsion process

The 2002 production capacities for PVDF in the major industrial regions, taken from Ring *et al* (2002), are given in the table below:

Producer	Location	Process	Capacity, ktonne/year
Atofina (now Arkema)	Calvert City, KY, USA	Emulsion	8.4
Ausimont (now Solvay Sole)	Thorofare, NJ, USA	Emulsion	7.7
Solvay (now Dyneon)	Decatur, AL, USA	Suspension	2.3
Atofina (now Arkema)	Pierre Bénite, France	Emulsion	2.2
Solvay	Tavaux, France	Suspension	5.0
Central Glass	Ube, Japan	Emulsion?	0.3
Daikin	Settsu, Japan	Suspension?	0.1
Kureha	Iwaki, Japan	Suspension	1.2
TOTAL			27.2

The installed capacity for manufacture of PVDF by the emulsion process is thus about 18.6 ktonne/year, or 68 % of overall PVDF capacity. The suspension process does not use any fluorinated surfactants.

Actual production and consumption of PVDF is lower than installed capacity. Ring *et al* (2002) estimate overall 2001 production in the US, Western Europe and Japan at 14.2 ktonne (only 52 % of estimated 2002 installed capacity for the combined emulsion and suspension processes). On the other hand, there is limited production in China, Russia and possibly other countries. For the purpose of estimating APFN consumption in the manufacture of PVDF, we will conservatively assume production by the emulsion process to be 75 % of 18.6 ktonne/year, i.e., about 14 ktonne/year in 2002.

1
2 **Consumption of APFN in the production of PVDF by the emulsion process**
3
4 We will conservatively assume that all the PVDF produced by the emulsion process uses pure APFN as a
5 surfactant. Multiplying the production of emulsion-grade PVDF (14 ktonne/year) by the specific consumption of
6 APFN (0.1-0.2 %), we estimate the annual consumption of APFN for this purpose to be 14-28 tonne/year. This
7 is the estimated range for year 2002. Consumption would have been smaller in earlier years when PVDF
8 production was lower.

9
10 **Reference**

11
12 Ring, K-L, Kälin T, Kishi A, 2002. Fluoropolymers. SRI International, CEH Marketing Research Report
13

1 **Table S9. Estimated Industry-Wide Global Historic APFN Emissions from PVDF**
 2 **Fluoropolymer Manufacture**
 3

Time period	# years	Estimated Annual APFN Use in PVDF Production (t / yr.)	Estimated APFN Emissions (t / yr.)	Estimated Total APFN Emissions [§] (t)
1995-2004	10	15 -75	9 - 45	90 - 450
1985-1994	10	20 – 100	12 - 60	120 - 600
1975-1984	10	25 - 50	15 - 30	150 - 300
			Total Global Historic Emissions	400 – 1,400*

4
 5 * Rounded to nearest hundred.; t = metric tonnes; § Value is total emissions for the given time period

- 6 • 60% of APFN is estimated to be emitted during PVDF manufacturing, the same emissions
 7 value as for APFO use in fluoropolymer manufacture.

8 **Example Calculations**

- 9 • The upper bound estimation for 1995 – 2004: (75 t./yr. x 60%) = 45 t ; 45 t x 10 yrs = 450
 10 tonnes.
 11 • The lower bound estimation for 1995 – 2004 : (15 t/yr. x 60%) = 9 t ; 9 t x 10yrs. = 90 tonnes.

1 **Table S10. Estimated Industry-Wide Global Historic APFN Emissions from PVDF**
 2 **Fluoropolymer Industrial Processing**
 3

Time Period	# of Years	Annual APFN emissions (t)	Estimated Total APFN Emissions [§] (t)
1995 – 2004	10	0.6 -1.2	6 - 12
1985 – 1994	10	0.4 – 0.8	4 – 8
1975 – 1984	10	0.2 – 0.4	2 - 4
Total Global Historic Emissions (tonnes)			10 - 20*

4
 5 * Rounded to nearest one significant figure; t = metric tonnes;

6 § Value is total emissions for the given time period

- 7 • It is estimated that between 100-200 ppm of APFN remains in all PVDF made by emulsion
 8 polymerization and that when it is processed by industrial users 60% of the APFN is destroyed
 9 and 40% is emitted, most likely to air. These 60% and 40% values are best estimates derived
 10 from the published valued for the disposition of APFO during fluoropolymer dispersion
 11 processing.(ref. 6)

12 **Example Calculation**

- 13 • The upper bound estimate for 1995-2004: (15,000 tonnes PVDF produced x 200ppm x 40%) =
 14 1.2 tonnes.
 15 • The lower bound estimate for 1995-2004: (15,000 tonnes PVDF produced x 100ppm x 40%) =
 16 0.6 tonnes.

1 **Table S11. PFCA Impurities in POSF-Based Products**

2

Time Period	# of Years	Annual Global POSF Production (t)	Estimated Total PFCA Emissions [§] (t)
2002	1	200	0.04 – 0.3
2001	1	1,400	0.3 – 2
1995 – 2000	6	4,500	5 – 43
1980 – 1994	15	3,000	9 – 72
1960 – 1979	20	450	2 – 14
Total Global Historic Emissions			20 – 130*

3

4 * Rounded to nearest ten t = metric tonnes

5 § Value is total emissions for the given time period

- 6
- Data from the major global producer represents 80-90% of global production.
 - 7
 - Use the range of 200 – 1,600 ppm (ref.12) as the PFCAs impurity level in POSF-Based
 - 8 Products.
 - 9
 - According to the source of these values (ref. 13), they represent the PFCAs impurity level on a
 - 10 100% active ingredient basis, *not* on a sales product basis as stated in reference 12. Hence, we
 - 11 have used POSF production as the 100% active ingredient basis for our estimation.

12

13 **Example Calculation**

- 14
- The upper bound estimate for 1995-2000 : (4,500 tonnes x 6yrs x 1600ppm) = 43 tonnes.
 - 15
 - The lower bound estimate for 1995-2000 : (4,500 tonnes x 6yrs x 200ppm) = 5 tonnes.

1 **Table S12. Degradation of POSF-Based Raw Materials to PFCAs (ref.14)**
 2

Time Period	# of Years	Annual POSF Production (t)	Estimated Total PFCa Emissions [§] (t)*
2002	1	200	0.001 – 0.06
2001	1	1,400	0.007 – 0.4
1995 – 2000	6	4,500	0.1 – 8
1980 – 1994	15	3,000	0.2 – 14
1960 – 1979	20	450	0.05 – 3
Total Global Historic Emissions (tonnes)			1 – 30*

3

4 * Rounded to nearest integer and hundred t = metric tonnes

5 § Value is total emissions for the given time period

- 6 • Using 0.1 to 3 wt% POSF Raw materials and 0.5 to 1% POSF raw materials degradation to PFCAs
- 7 • 1% was recommended as the upper bound for degradation to PFCAs by the authors of the
- 8 degradation study. (refs.13)
- 9 • Should future degradation research results reveal greater or less degradation, the values computed
- 10 in this table will need to be recomputed.

11 **Example Calculation**

- 12 • The upper bound estimate for 1995-2000 : (4,500 x 6yrs x 3% x 1%) = 8 tonnes.
- 13 • The lower bound estimate for 1995-2000 : (4,500 x 6yrs x 0.1% x 0.5%) = 0.1 tonnes.

1 **Table S13. POSF-Based Aqueous Fire-Fighting Foam (AFFF)**
 2

Time Period	# of Years	Annual POSF Production¹⁵ (t)	POSF-based Product for AFFF	Estimated Total PFCA Emissions[§] (t)
2002	1	200	10	0.01 – 0.1
2001	1	1400	70	0.07 – 0.7
1995-2000	6	3700	1100	1 - 10
1980-1994	15	1800	1400	1 - 14
1970-1979	10	450	200	0.2 - 2
		Total Global Historic Emissions (tonnes)		3 – 30*

3

4 * Rounded to one significant figure. t = metric tonnes

5 § Value is total emissions for the given time period

6 • AFFF product is estimated to be 5% of the Total POSF Production per year of the major POSF
 7 manufacturer who is known to have been the major producer of AFFF products based on POSF
 8 chemistry. This is why the values in column 3 are not the same as in Tables S11 and S12.
 9 Additional AFFF use information is available in references 16 and 17.

10 • Example Calculation: $(3700 \times 0.05) \times 6\text{yrs} = 1100$ (rounded to nearest hundred)

11 • * Range is for AFFF Product composition containing between 0.1 and 1.0 weight % PFCAs

12

13 **Example Calculation**

14 • $(1100 \times 0.01) = 10$; $(1100 \times 0.001) = 1$ tonne.

1 **Table S14.**
 2 **Estimated Industry-Wide PFCA Impurities in Fluorotelomer-Based Products**
 3 (ref.18)
 4

Time Period	# of Years	Average Annual Fluorotelomer A Production¹⁹ (t)	Estimated Total PFCA Emissions[§](t)
1995-2004	10	4,000	0.2 – 20
1980-1994	15	1,500	0.1 – 10
1974-1979	5	500	0.01 – 1
Total Global Historic Emissions (tonnes)			0.3 – 30*

5

6 * Rounded to one significant figure t = metric tonnes

7 § Value is total emissions for the given time period

- 8 • 1-100 ppm PFCAs as Impurity in Fluorotelomer-based Products (refs. 18,19). The amount of
 9 fluorotelomer-based products in a given year is estimated to be 5 times the amount of Telomer
 10 A production, hence multiplication by 5 to compute the estimate. This factor of 5 is based on
 11 the known “average” composition of a fluorotelomer-based product and the amount of Telomer
 12 A required to produce such and average product, roughly one part Telomer A produces 5 times
 13 the amount as product.
- 14 • All estimated emissions values rounded to one significant figure.

15

16 **Example Calculations**

- 17 • The upper bound estimate for 1995-2004: (4000 tonnes x 10yrs x 100ppm x 5) = 20 tonnes
- 18 • The lower bound estimate for 1995-2004: (4000 tonnes x 10yrs x 1ppm x 5) = 0.2 tonnes

1 **Table S15. Estimated Industry-Wide Releases of PFCAs from Degradation of**
 2 **Fluorotelomer-Based Raw Materials to PFCAs**

3

Time Period	# of Years	Average Annual Fluorotelomer A Production (t)	Estimated Total PFCa Emissions [§] (t)
1995-2004	10	4,000	4 – 80
1980-1994	15	1,500	2 – 45
1974-1979	5	500	0.3 – 5
Total Global Historic Emissions (tonnes)			6 – 130*

4

5 * Rounded to one significant figure t = metric tonnes

6 § Value is total emissions for the given time period

- 7 • Using 1.0 to 2.0 wt% based on Fluorotelomer A and 1–10% degradation to PFCAs.
- 8 • In biodegradation studies, 8-2 fluorotelomer alcohol degradation to PFOA reported values are
 9 between 3 – 7% (refs.20,21,22), with the most recent data between 3-6%.(refs.21,22) In gas-phase
 10 atmospheric studies, the conversion of 8-2 fluorotelomer alcohol to PFOA was estimated to be
 11 between 1 – 10%. (ref. 23) From these studies, we selected the smallest and largest values of 1 and
 12 10% as the lower and upper bounds for biodegradation.
- 13 • Should future degradation research results reveal greater or less degradation, the values computed
 14 in this table will need to be recomputed.

15 **Example Calculations**

- 16 • For the period 1995-2004, the upper bound estimate: (4,000 tonnes x 10yrs x 2% x 10%) = 80
 17 tonnes
- 18 • For the period 1995-2004, the lower bound estimate: (4,000 tonnes x 10yrs x 1% x 1%) = 4
 19 tonnes

20

1 **Table S16. Analysis of PFCAs in Consumer Spray Application Products**

- 2 • LC/MS/MS Assay of Spray Application Consumer Products purchased at retail prior to withdrawal
3 by the major manufacturer of POSF-based products.

Consumer Product Sample	PFHx	PFHp	PFO	PFN	PFOS
Fabric Protector	60	5	5	7	n.d.
Protector for Leather	100	100	78	10	n.d.
Cleaner for Rugs & Carpets	100	11	9	9	500
Cleaner for Fabric and Upholstery	100	5	5	10	454

- 4 • Table Values are in *parts per million*. Rounded to nearest whole number.
5 • Single point determination to estimate analyte concentration for all analytes other than PFO.
6 • Quantitative analysis using 9 point calibration run in duplicate with spike recovery for PFO
7 determination.
8 • n/d = not detected
9 • No perfluorocarboxylic acids with greater than nine carbons were detected.

11 **Analytical Method Summary** (See also ref. 24)

12 Sample Preparation

- 13 • The foam sample was sprayed into a 20 mL scintillation vial and capped.
14 • The vial was placed in the dark at room temperature until the sample was in a liquid state (e.g., 3
15 hours)
16 • The liquid sample was weighed and diluted with methanol (e.g., 10 mg diluted with 10 mL of
17 methanol). An additional sample was weighed and spiked with analog.
18 • The sample was pipetted into a HPLC vial with an internal standard.
19 • The sample concentration was determined using LC/MS/MS

21 Analytical Method LC/MS/MS

22 Mobile phase A: 2 mM ammonium acetate with 5% methanol; Mobile phase B: Methanol

23 Column: Spherisorb ODS C₁₈ 2.1 x 200 mm 5 μ temp: 65 °C; 45 Minute Gradient

- 24 • Initial conditions: 15 % B; Linear gradient for 41 minutes to 67 %B; Initial conditions at 41.01
25 minutes; Initial conditions for 4 minutes.

26 LC/MS/MS instrumentation

27 Waters Quattro fitted with an Agilent 1100 operated in the negative ion electrospray. The following
28 transitions were monitored: 313>269, 363>319, 413>369, 499>80, 463>419, 513>469, 563>519,
29 613>569

30 A six point calibration which was run twice at the beginning and end of the analysis with an R > 0.99.
31 Samples were quantitated using the eight carbon analog. Spike recovery for the samples ranged 99-
32 104%.

1 **Table S17. Environmental Inventory and Sink Calculations**

2

INVENTORIES	Concentration (g/m ³)	Surface Area (m ²)	Depth (m)	Amount (g)	Amount (tonnes)	
Min. Ocean Inventory	1.50 x 10 ⁻⁸	1.5 x 10 ¹⁴	50	1.13 x 10 ⁸	113	
Max. Ocean Inventory	4.39 x 10 ⁻⁷	1.5 x 10 ¹⁴	150	9.88 x 10 ⁹	9878	
Min. Freshwater Inventory	5.0 x 10 ⁻⁸	4.0 x 10 ¹²	20	4.00 x 10 ⁶	4	
Max. Freshwater Inventory	1.0 x 10 ⁻⁵	4.0 x 10 ¹²	20	8.00 x 10 ⁸	800	
	Concentration (g/g)	Surface Area (cm ²)	Depth (cm)	Density (g/cm ³)	(1 – Porosity)	Amount (tonnes)
Min. Sediment Inventory	2.0 x 10 ⁻¹¹	4.0 x 10 ¹⁶	5	2.4	0.3	3
Max. Sediment Inventory	5.0 x 10 ⁻¹⁰	4.0 x 10 ¹⁶	5	2.4	0.3	343
SINKS	Inventory (tonnes)	Sed. Rate (cm/yr)	Depth (cm)	Loss (tonnes/yr)		
Min. Sediment Burial	3	0.1	5	0.06		
Max. Sediment Burial	343	0.3	5	21		
	Inventory (tonnes)	Res. Time (yr)	Loss (tonnes/yr)			
Min. Deep Sea Transport	113	500	0.22			
Max. Deep Sea Transport	9878	300	33			

- 3
- 4 • References for the values in the above table are given in the manuscript.
- 5 • Ocean and freshwater inventories are calculated by multiplying ocean water concentration (g/m³)
- 6 by surface area (m²) and depth (m).
- 7 • The sediment inventory is calculated by multiplying the sediment concentration (g/g) by the
- 8 surface area (cm²), mixing depth (cm), density (g/cm³) and 1 - porosity.
- 9 • For all inventories, grams are converted to metric tonnes by dividing by 10⁶.
- 10 • The sediment burial loss is calculated by first calculated a sediment residence time (yr) by dividing
- 11 the mixing depth (cm) by the sedimentation rate (cm/yr).
- 12 • The annual loss from sediment burial (tonnes/yr) is calculated by dividing the sediment inventory
- 13 (tonnes) by this residence time (yr).
- 14 • The annual loss by deep-sea transport (tonnes/yr) is calculated by dividing the surface ocean
- 15 inventory (tonnes) by the residence time of deep ocean water (yr).

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