Supporting Information

A FIRST GLOBAL PRODUCTION, EMISSION AND ENVIRONMENTAL INVENTORY FOR PERFLUOROOCTANE SULFONATE

Alexander G. Paul, Kevin C. Jones and Andrew J. Sweetman[1]

Centre for Chemicals Management, Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ. UK

[1]Corresponding Author: a.sweetman@lancaster.ac.uk

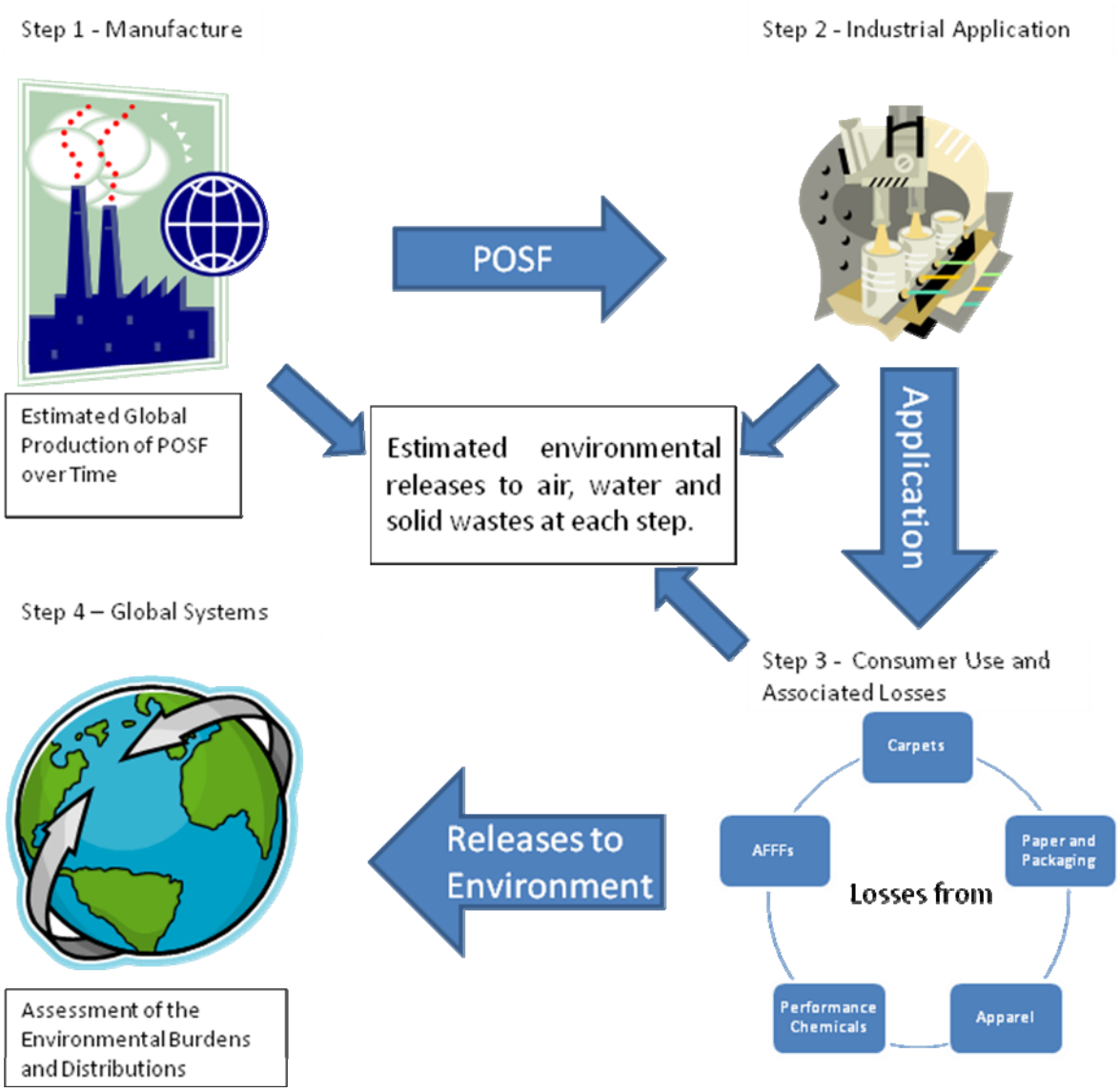

Figure SI1: A schematic diagram of the aims of this paper

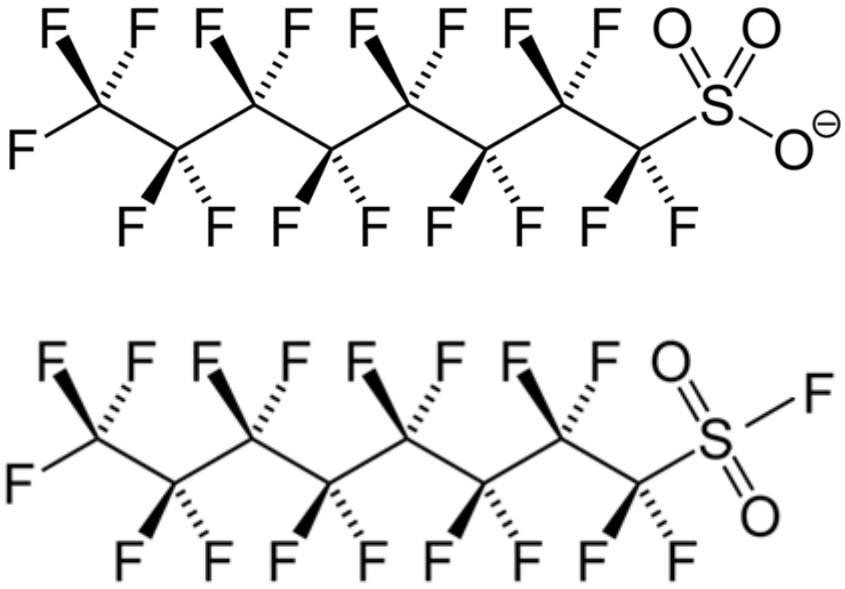

Figure SI2: top; Molecular Structure of PFOS ($C_8F_{17}SO_3^-$), and bottom; POSF ($C_8F_{17}SO_2F$)

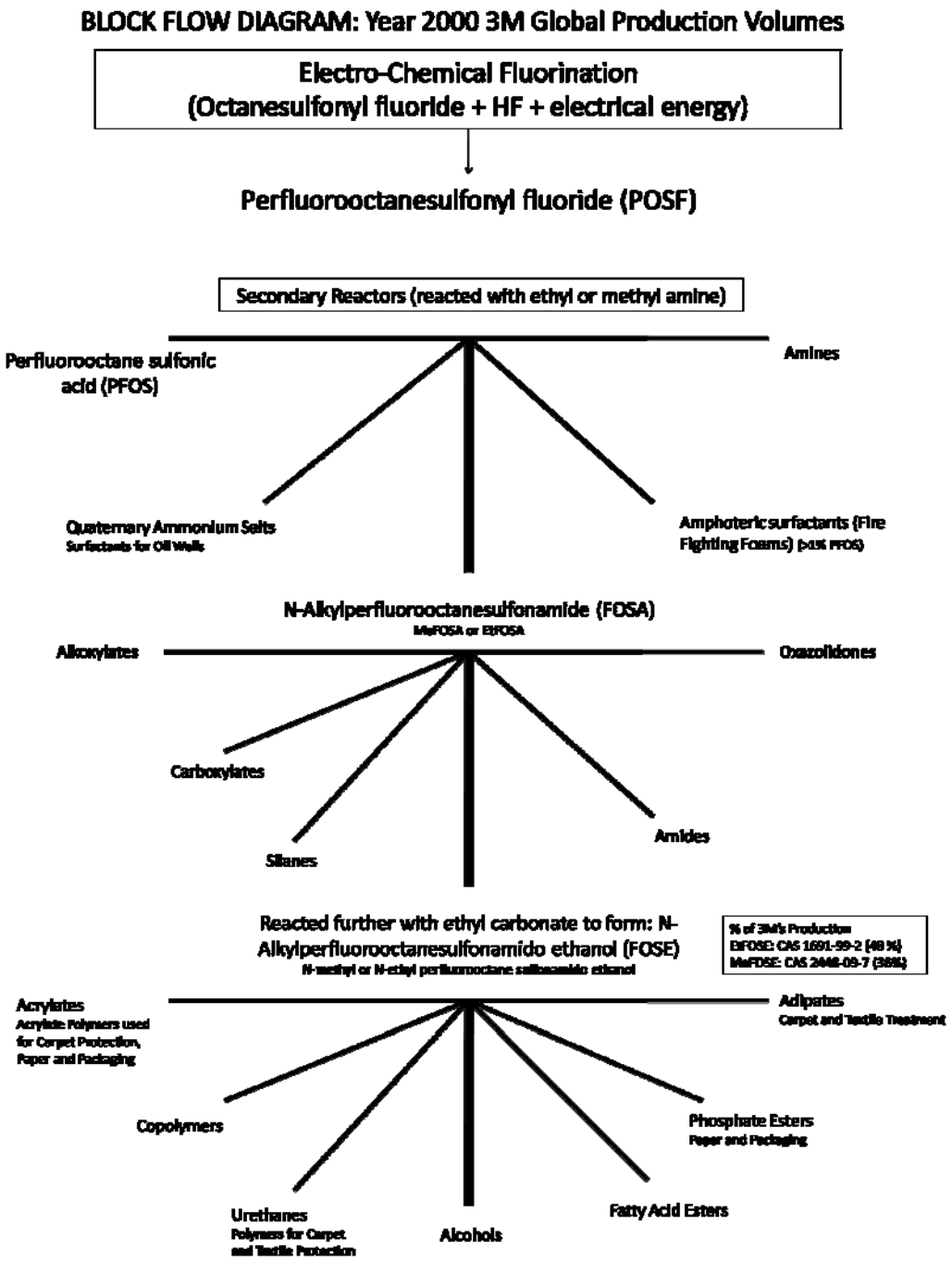

Figure SI3: PFOS and POSF production tree reproduced from 3M (1). Products typically contain 1-2% PFOS as residuals.

Description of Losses from products during application, use and disposal.

Carpet Protection. 3M's Scotchban products (e.g. FC-1367) were used to impart dirt and stain repellency to carpets. During the life of the carpet, it has been estimated that 50% of PFOS equivalents are lost through steam cleaning, 45% by vacuuming and 5% remains in-product at end of life disposal (2).

Paper and Packaging. Of 3M's three products with the largest production volumes, two were used in the paper and packaging sector. Emission of 1% during the paper manufacture was primarily to wastewater, while 3% of FCs is estimated to be disposed of as solid waste. Treated materials were not recovered during recycling. Therefore disposal was expected to be equivalent to the 1997 US rates, of 17% incinerated and 83% sent to landfill as solid waste. POSF could possibly migrate from the packaging in landfill, but this has yet to be proven, or be lost to wastewater during recycling (2). We assumed a conservative estimate that a total of 15% was lost to wastewater during application, use and pulping for recycling (see Table 2).

Textile treatment and apparel products. 3M's figures indicate that textile treatment and apparel products lose 10% POSF treatment to wastewater during treatment and 5% from solid fabric waste. Solid waste is assumed to be disposed of at the national US averages; 83% to landfill and 17% recycled. Leather and fabric products are expected to lose 10% POSF during manufacture to solid waste and wastewater. 73% of POSF is expected to washout of the garment during its lifetime. Many treated fabrics are single use (medical garments and HEPA filters), so 99.9% is sent to solid waste (2). Overall, it was assumed that apparel products lost 82% of POSF to wastewater.

Performance chemicals. Products containing POSF include paints, waxes and polishes for which some loss (8%) was assumed to occur during mix tank start up and shut down (2). The remainder was assumed to be lost during consumer application (e.g. spray cans etc). Performance chemicals are used in aviation hydraulic fluids as corrosion inhibitors where use and disposal is expected to be well controlled.

Fire fighting foams. Perfluorocarboxylate acid (PFCA) AFFFs were developed and used in the 1960s, but later replaced by POSF (3) based products, which were used extensively from the 1970s onwards (4-6). The US market in 1985 was approximately 6.8 million litres (4). Assuming 0.5-1.5 percent POSF concentration, this equates to 34 - 102 tonnes of POSF released each year using 3Ms figures in the US. This fits within 3Ms product range, where 21 products, excluding AFFFs accounted for 87% of POSF production. Large stocks of AFFFs are currently held which are available for use until 2011.

Table SI1: A summary of POSF losses depending on use category.

Application	Percentage Losses			
	Air	Water	Solid	Other (controlled)
Carpets	0	47	53	0
P&P	0	15	85	0
Apparel	0	82	18	0
Performance Chems	7.7	0	0	92.3
AFFFs	0	100	0	0

Year	Smithwick et al	Prevedouros et al	3M Global Production Total	This Paper Est Global POSF Prodn.	This Paper Est Global POSF Prodn.
1968					
1969					
1970		450	312	400	400
1971		450	390	500	500
1972		450	468	600	600
1973		450	546	700	700
1974		450	624	800	800
1975		450	725	930	930
1976		450	924	1185	1185
1977	1100	450	1123	1440	1440
1978	1200	450	1322	1695	1695
1979	1300	450	1521	1950	1950
1980	1400	3000	1720	2205	2205
1981	1500	3000	1919	2460	2460
1982	1600	3000	2118	2715	2715
1983	1700	3000	2317	2970	2970
1984	1800	3000	2516	3225	3225
1985	1900	3000	2714	3480	3480
1986	1900	3000	2913	3735	3735
1987	1900	3000	3112	3990	3990
1988	1900	3000	3311	4245	4245
1989	1900	3000	3510	4500	4500
1990	2200	3000	3627	4650	4650
1991	2200	3000	3627	4650	4650
1992	2200	3000	3627	4650	4650
1993	2200	3000	3627	4650	4650
1994	2200	3000	3627	4650	4650
1995	2900	4500	3627	4650	4650
1996	2900	4500	3627	4650	4650
1997	2900	4500	3627	4650	4650
1998	4500	4500	3627	4650	4650
1999	4500	4500	3627	4650	4650
2000	4500	4500	3627	4650	4650
2001	500	1400	390	500	1500
2002	300	200	234	300	1300
2003				0	1000
2004				0	1000
2005				0	1000
Tonnes	43500	82600	74626.5	95675	100675
Notes	Ref (7)	Ref (3)	~78% 3M Production	Without remaining producers	Global production continuing with remaining producers

Table SI2: Raw Estimated Production Data Corresponding to Figure 1

Water Losses Assuming Carpet Usage is Correct	E.F. (yr-1)
Apparel - All POSF lost within 2 years	0.5
Carpets- 45 % lost to water within 10 years	0.045
AFFF losses to water (10% use per year)	0.1
P&P (15% loss during application / recycling)	0.015

Carpets	48
Paper and	24
Apparel	13
Performan	6
AFFF	10
Total %	100

Year	1970	1971	1972	1973	1974	1975	1976
Production	400	500	600	700	800	930	1185
Carpets	192	240	288	336	384	446	569
Paper and Packaging	96	120	143	167	191	222	283
Apparel	50	63	75	88	100	117	149
Performance Chemicals	24	30	36	42	48	56	71
AFFF	38	48	57	67	77	89	113
Total Production	400	500	600	700	800	930	1185

10 YEAR EMISSION FACTOR

Year	**1970**	**1971**	**1972**	**1973**	**1974**	**1975**	**1976**
Production	**192**	**240**	**288**	**336**	**384**	**446.4**	**568.8**
1970							
1971	8.6						
1972	8.6	10.8					
1973	8.6	10.8	13.0				
1974	8.6	10.8	13.0	15.1			
1975	8.6	10.8	13.0	15.1	17.3		
1976	8.6	10.8	13.0	15.1	17.3	20.1	
1977	8.6	10.8	13.0	15.1	17.3	20.1	25.6
1978	8.6	10.8	13.0	15.1	17.3	20.1	25.6
1979	8.6	10.8	13.0	15.1	17.3	20.1	25.6
1980	8.6	10.8	13.0	15.1	17.3	20.1	25.6
1981		10.8	13.0	15.1	17.3	20.1	25.6

Table SI3: Part of the time stepped matrix used to calculate releases to water per year from carpets. The process was repeated for each; Carpets, Paper and Packaging, Apparel, Performance Chemicals and AFFFs.

Environmental Budget Rational

The estimated PFOS releases provided by this study have been used to predict environmental burdens using a simple mass balance approach which has then been compared to environmental monitoring data. However, it is important to point out that these calculations only provide an indicative reply on a series of assumptions. The primary assumption is that, based on a knowledge of its physical-chemical properties, PFOS will predominantly reside in the aquatic compartment. A rational for these assumptions is available in the supplementary information.

Although some POSF-derived isomers are volatile (e.g. NEtFose, MEtFose), PFOS is regarded as non-volatile (8). PFOS has been measured in the particulate-phase of the atmosphere in both urban and rural areas (9). However, particle-phase atmospheric transport was deemed to be negligible contributing just <0.1% to the Great Lakes (10), while levels of particulate-phase PFOS decreases rapidly when sampling at sea away from land (11). Similarly, soils and sedimentation are not considered to be major repositories, as the mass-loading of PFOS in water has been shown to increase after contact with both contaminated soils (12) and sediments in WWTPs (13). PFOS continues to be measured in rivers (14) and lakes (10) indicating current sources, however, these compartments are expected to supply oceans over time. Finally, oceans were considered to be the primary compartment for the mass balance as they represent a far larger volume compared to freshwaters. This resulted in simplified mass balance calculations.

Figure 2 from the paper, with original data points and R^2 values

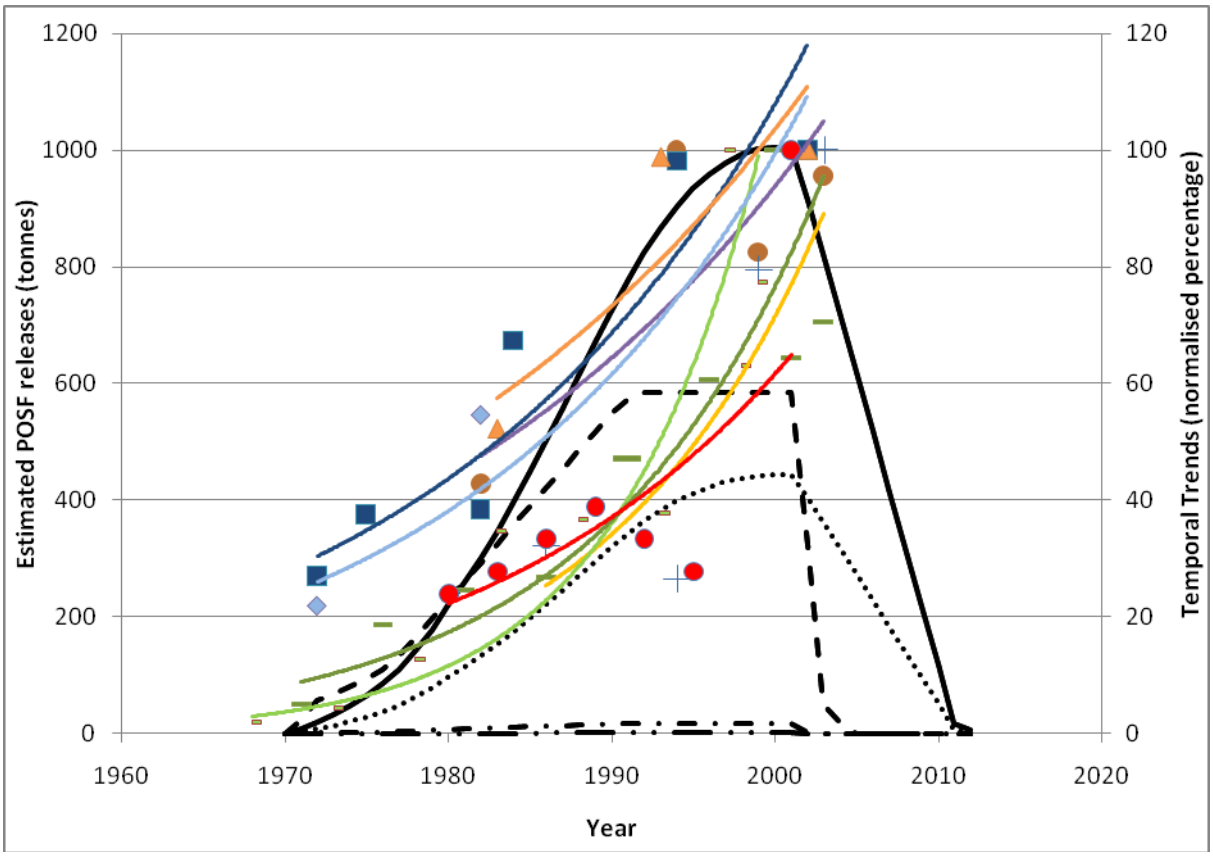

Figure 2: Estimated POSF releases from 1970 – 2012 and exponential temporal trends in biota. Note: 2012 is when AFFFs are scheduled to be restricted and treated carpets end their natural life, and that the projection to zero is based on 3Ms production only, therefore some emissions will continue from remaining producers. Temporal trends in biota have been normalised to 100% for each species / dataset.

Usage depicted as; Carpets (——), Paper and Packaging (− · −), Apparel (− − −), Performance Chemicals (— · ·), AFFFs (·····), and Biota trendlines; Ringed Seals (15) from Arctic locations; Qeqertarsuaq (purple; R^2 = 0.757) and Ittoqqortoormiit (yellow; R^2 = 0.691), Baltic Guillemot Eggs (16) (pooled; light green; R^2 =0.91 and mean; dark green; R^2 = 0.882), Polar Bears from western (7) (light blue; R^2 = 0.908) and eastern Canadian Arctic

(dark blue; $R^2 = 0.875$), Herring Gull from Norway (17) (orange; $R^2 = 0.789$) and Lake Trout from Lake Ontario (18) (red; $R^2 = 0.594$).

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