Supporting Information

Toward a Comprehensive Global Emission Inventory of C$_4$–C$_{10}$ Perfluoroalkanesulfonic Acids (PFSAs) and Related Precursors: Focus on the Life Cycle of C$_6$- and C$_{10}$-Based Products

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S1 Nomenclature

S1.1. Terminology regarding chemicals

This study focuses on the global emissions inventory of perfluoroalkanesulfonic acids (PFSAs) and their precursors from the life cycle of perfluorohexanesulfonyl fluoride (PHxSF)- and perfluorodecanesulfonyl fluoride (PDSF)-based compounds. PHxSF and PDSF are two of the perfluoroalkanesulfonyl fluorides (PASFs) (see Table S1), and PASF-based compounds are a large group of chemicals containing at least one "$C_nF_{2n+1}SO_2$—" moiety[1] and can be divided into two groups: non-polymers and polymers. Major non-polymeric compounds are listed in Table S1. The polymeric compounds are so-called "side-chain fluorinated polymers" consisting of variable compositions of non-fluorinated carbon backbones with PASF-derivatives (such as perfluorohexanesulfonamidoethyl acrylate) on side chains. Non-polymeric and polymeric PASF-based compounds are precursors of PFSAs such as perfluorohexanesulfonic acid (PFHxS) and perfluorodecanesulfonic acid (PFDS).

Depending on the availability of information (structure, CAS number, trade name, etc.), we named all substances involved in this *Supporting Information* and the main text in three ways:

(i) The majority have a known structure and terminology, and these are named according to the number of carbons on the alkyl chain and the functional group, e.g. the compound with four fluorinated carbons and a sulfonic acid group is named perfluorobutanesulfonic acid (PFBS);

(ii) Those that have a known structure and/or CAS number but no terminology proposed yet are named after their registered CAS number (in the form of CAS No. *xxx-xx-x*);

(iii) For the few compounds that have a trade name but an unknown structure, terminology and CAS number, they are named after their trade name (e.g. in the form of FC *xxx*).

Table S1. The acronym, name or structure, and CAS number of some of the major non-polymers investigated.

Acronym 1	Acronym 2	Name / Structure	CAS number
Perfluoroalkanesulfonyl fluorides (PASFs)			
C_4 PASF	PBSF	$C_4F_9SO_2F$	375-72-4
C_5 PASF	PPeSF	$C_5F_{11}SO_2F$	375-81-5
C_6 PASF	PHxSF	$C_6F_{13}SO_2F$	423-50-7
C_7 PASF	PHpSF	$C_7F_{15}SO_2F$	335-71-7
C_8 PASF	POSF	$C_8F_{17}SO_2F$	307-35-7
C_9 PASF	PNSF	$C_9F_{19}SO_2F$	68259-06-3
C_{10} PASF	PDSF	$C_{10}F_{21}SO_2F$	307-51-7
Perfluoroalkanesulfonic acids (PFSAs) & their major derivatives			
PFBS	C_4 PFSA	$C_4F_9SO_3H$	375-73-5
K-PFBS	-	$K^+ C_4F_9SO_3^-$	29420-49-3
PFHxS	C_6 PFSA	$C_6F_{13}SO_3H$	355-46-4
K-PFHxS	-	$K^+ C_6F_{13}SO_3^-$	3871-99-6
PFOS	C_8 PFSA	$C_8F_{17}SO_3H$	1763-23-1
NH_4-PFOS	-	$NH_4^+ C_8F_{17}SO_3^-$	29081-56-9
K-PFOS	-	$K^+ C_8F_{17}SO_3^-$	2795-39-3
NEt₄-PFOS	-	$N(C_2H_5)_4^+ C_8F_{17}SO_3^-$	56773-42-3
PFDS	C_{10} PFSA	$C_{10}F_{21}SO_3H$	335-77-3
NH_4-PFDS	-	$NH_4^+ C_{10}F_{21}SO_3^-$	67906-42-7

Table S1 (continued). The acronym, name or structure, and CAS number of some of the major non-polymers investigated.

Acronym 1	Acronym 2	Name / Structure	CAS number
Perfluoroalkanesulfonamides (xFASAs)			
FOSA	-	$C_8F_{17}SO_2NH_2$	754-91-6
FOSE	-	$C_8F_{17}SO_2NHCH_2CH_2OH$	10116-92-4
FBSA	-	$C_4F_9SO_2NH_2$	30334-69-1
FPeSA	-	$C_5F_{11}SO_2NH_2$	82765-76-2
FHxSA	-	$C_6F_{13}SO_2NH_2$	41997-13-1
FHpSA	-	$C_7F_{15}SO_2NH_2$	82765-77-3
MeFBSA	-	$C_4F_9SO_2NH(CH_3)$	68298-12-4
MeFPeSA	-	$C_5F_{11}SO_2NH(CH_3)$	68298-13-5
MeFHxSA	-	$C_6F_{13}SO_2NH(CH_3)$	68259-15-4
MeFHpSA	-	$C_7F_{15}SO_2NH(CH_3)$	68259-14-3
MeFOSA	-	$C_8F_{17}SO_2NH(CH_3)$	31506-32-8
MeFDSA	-	$C_{10}F_{21}SO_2NH(CH_3)$	N.A.
EtFBSA	-	$C_4F_9SO_2NH(C_2H_5)$	40630-67-9
EtFPeSA	-	$C_5F_{11}SO_2NH(C_2H_5)$	162682-16-8
EtFHxSA	-	$C_6F_{13}SO_2NH(C_2H_5)$	87988-56-5
EtFHpSA	-	$C_7F_{15}SO_2NH(C_2H_5)$	68957-62-0
EtFOSA	Sulfluramid	$C_8F_{17}SO_2NH(C_2H_5)$	4151-50-2
EtFDSA	-	$C_{10}F_{21}SO_2NH(C_2H_5)$	N.A.
Perfluoroalkanesulfonamido ethanols (xFASEs)			
FBSE	-	$C_4F_9SO_2NHCH_2CH_2OH$	34454-99-4
FPeSE	-	$C_5F_{11}SO_2NHCH_2CH_2OH$	N.A.
FHxSE	-	$C_6F_{13}SO_2NHCH_2CH_2OH$	106443-63-4
FHpSE	-	$C_7F_{15}SO_2NHCH_2CH_2OH$	167398-54-1
MeFBSE	-	$C_4F_9SO_2N(CH_3)CH_2CH_2OH$	34454-97-2
MeFPeSE	-	$C_5F_{11}SO_2N(CH_3)CH_2CH_2OH$	68555-74-8
MeFHxSE	-	$C_6F_{13}SO_2N(CH_3)CH_2CH_2OH$	68555-75-9
MeFHpSE	-	$C_7F_{15}SO_2N(CH_3)CH_2CH_2OH$	68555-76-0
MeFOSE	-	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$	24448-09-7
MeFDSE	-	$C_{10}F_{21}SO_2NH(CH_3)$	N.A.
EtFBSE	-	$C_4F_9SO_2N(C_2H_5)CH_2CH_2OH$	34449-89-3
EtFPeSE	-	$C_5F_{11}SO_2N(C_2H_5)CH_2CH_2OH$	68555-72-6
EtFHxSE	-	$C_6F_{13}SO_2N(C_2H_5)CH_2CH_2OH$	34455-03-3
EtFHpSE	-	$C_7F_{15}SO_2N(C_2H_5)CH_2CH_2OH$	68555-73-7
EtFOSE	-	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	1691-99-2
EtFDSE	-	$C_{10}F_{21}SO_2N(C_2H_5)CH_2CH_2OH$	N.A.
N-Methyl perfluoroalkanesulfonamido ethyl acrylates (MeFBSEAs)			
MeFBSEA	-	$C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	67584-55-8
MeFPeSEA	-	$C_5F_{11}SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	67584-56-9
MeFHxSEA	-	$C_6F_{13}SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	67584-57-0
MeFHpSEA	-	$C_7F_{15}SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	68084-62-8
MeFOSEA	-	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$	25268-77-3

S1.2. Terminology regarding product life cycle

This emission inventory is estimated by investigating the fate of certain compounds during their life cycle (production, use and disposal phases; see Figure S1) within products that contain them. In this study, the compounds PFHxS, PFDS, and their precursors are considered as active ingredients, unreacted or partially reacted raw materials or intermediates (residuals), and byproducts (impurities). The term 'product' as used throughout this study refers to the considered compounds that are contained in those products, unless a specific type of product is referred to in the text by name. Major active ingredients ae used to name product types throughout the text, and we assign an average duration for each step in the product life cycle (steps shown in Figure S1). The duration of the use phase is also called the product lifetime.
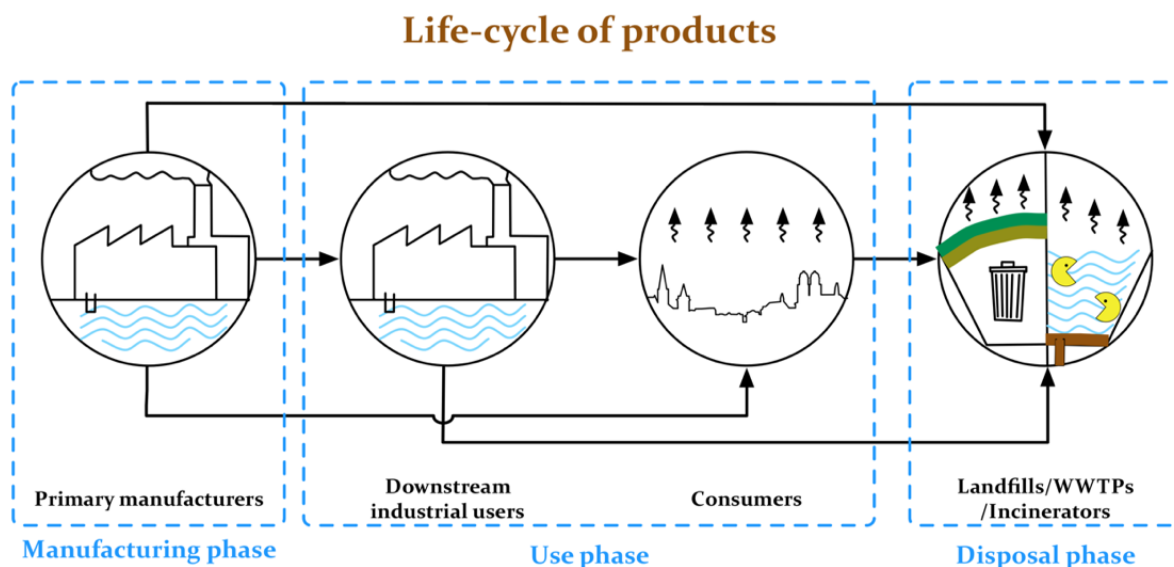
Figure S1. Scheme of the product life cycle.

S1.3. Terminology regarding geographical distribution and units

In some cases, we divided the global emissions into two country groups according to the similarity of production history within individual countries. Country Group 1 (CG1) comprises initial producing countries such as Japan, Western Europe and the United States (US), while emissions for China are reported separately. All units including abbreviations are documented according to the International System of Units (SI), e.g., "t" represents a metric ton or tonne.

S2. Methodologies of detailed emission estimates of each individual source

In this study, we followed the methodology developed to estimate the global emission inventory of perfluoroalkylcarboxylic acids (PFCAs) by Wang et al.[2], but with refinements that are specifically made for PFSAs and introduced in our previous study investigating the global emission inventory of POSF-based compounds.[3] In this section, we list detailed information, estimations and assumptions used for the quantification of emissions from each source, so that our emission inventory can be further developed and refined in the future when more information becomes available. In Table S23 at the end of this document, we provide for all parameters their origin (estimated or assumed), estimated uncertainty level, and location of relevant details in this document.

Figure S2, below, outlines the production pathways for the compounds and their related products considered in the inventory. The assumptions and calculations are separated between i) manufacturing in

CG1 and China and ii) manufacturing of PHxSF-based products and PDSF-based products. In CG1, PHxSF and PDSF are considered to have been intentionally extracted from manufactured POSF to produce specific products, whereas in China PHxSF, PDSF, and their related products are considered to have been produced solely as unintentional impurities and remained in the production of POSF and POSF-based products; for details, see Section S2.1 below.
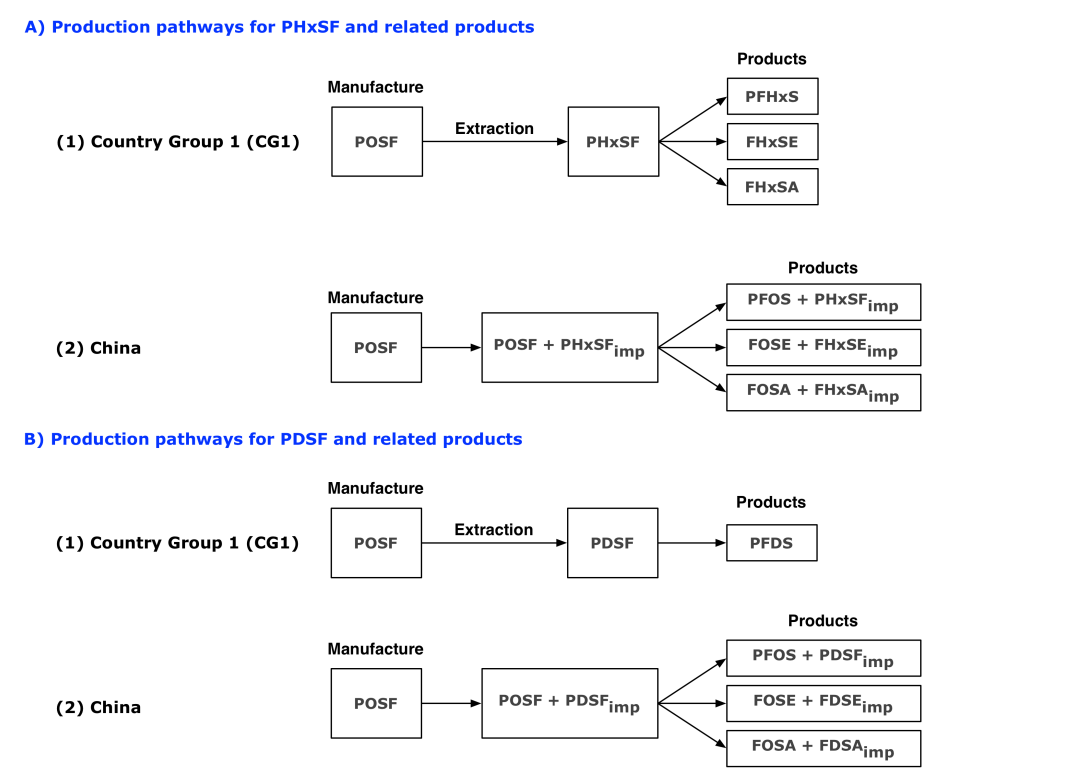
Figure S2. Overview of production pathways for PHxSF, PDSF, and their related products considered in the inventory calculations (imp = impurities). Calculations are separated by production in Country Group 1 (CG1) and in China. Part A) illustrates the production pathway for PHxSF and related products as analyzed in this study for 1) Country Group 1 and 2) China. Part B) illustrates the production pathway for PDSF and related products as analyzed in this study for 1) Country Group 1 and 2) China.

Figure S3 and Figure S4 show the general claculation steps and inputs used to calaculate emissions across the production and use and disposal phases for PHxSF- and PDSF-based products.

Calculation steps used in defining the emissions of PFSAs and their precursors from PHxSF and PDSF-based products

A) emissions of PFSAs from PHxSF-based products

Legend:
- Production volume
- Emission factors (EF)
- Other input factors
- Intermediate results
- Final results

POSF production volume (Tables S2 and S3) **−** Sulfluramid production volume in Brazil (Table S4) **×** Scaling factors (Section S2.1.1) → PHxSF production volumes (Tables S5 and S6)

$EF_{production,PFSAs}$ (Table S7) **×** → Emissions of PFSAs @ production sites

PHxSF production volumes (Tables S5 and S6) **❖** → PHxSF derivatives in products **×** Ratios of PHxSF used for PFHxS production (Section S2.1.3.3) → PFHxS production volumes **×** $EF_{use\&disp}$ (Section S2.1.3.5) → Emissions of PFSAs @ use and disposal

Emissions of PFSAs @ production sites **+** Emissions of PFSAs @ use and disposal **×** Homologue compositions of PHxSF-based products (Section S2.1.4) → Emissions of C_4-C_{10} PFSAs

B) emissions of PFSA precursors from PHxSF-based products

PHxSF production volumes (Tables S5 and S6) **×** $EF_{production,PFSA\ precursors}$ (Table S7) → Emissions of PFSA precursors @ production sites

PHxSF production volumes (Tables S5 and S6) **−** (1) PFHxS; (2) Emissions @ production sites → PFHxS precursors **×** Ratios of polymers and non-polymers (Section 2.1.3.1) → Polymers / Non-polymers

Polymers **×** Annual releases over lifetime (Section S2.1.3.7) → polymers released → Degradation via set half-lives (Section S2.1.3.7) → Emissions of PFSA precursors @ degradation of polymeric products

Polymers **×** Residual levels (Section S2.1.3.6) → residuals in polymers **×** $EF_{use\&disp,poly}$ (Section S2.1.3.6) →

Non-polymers **×** Range of degradable fractions (Section S2.1.3.5) → degradable non-polymers **×** $EF_{use\&disp,non-poly}$ (Section S2.1.3.5) → Emissions of PFSAs precursors @ use and disposal

Emissions of PFSA precursors @ production sites **+** Emissions of PFSA precursors @ degradation of polymeric products **+** Emissions of PFSAs precursors @ use and disposal **×** Homologue compositions of xFHxSA/E-based products (Section S2.1.4) → Emissions of C_4-C_{10} PFSA precursors

❖ PHxSF derivatives in products = PHxSF production volume - Emissions @ production sites

Figure S3. Flowchart of quantification steps across the life cycle in the present study for a) emissions of PFSAs from PHxSF-based products and b) emissions of PFSA precursors from PHxSF-based products.

Calculation steps used in defining the emissions of PFSAs and their precursors from PHxSF and PDSF-based products

Production volume | Emission factors (EF) | Other input factors | Intermediate results | Final results

A) emissions of PFSAs from PDSF-based products

POSF production volume (Tables S2 and S3) **−** Sulfluramid production volume in Brazil (Table S4) **×** Scaling factors (Section S2.1.1) → PDSF production volumes (Tables S5 and S6)

$EF_{production,PFSAs}$ (Table S7)

❖ PDSF derivatives in products **×** Ratios of PDSF used for PFDS production (Section S2.1.3.3) → PFDS production volumes **×** $EF_{use\&disp}$ (Section S2.1.3.5)

Emissions of PFSAs @ production sites **+** Emissions of PFSAs @ use and disposal **×** Homologue compositions of PDSF-based products (Section S2.1.4) → Emissions of C_4-C_{10} PFSAs

B) emissions of PFSA precursors from PDSF-based products

PDSF production volumes (Tables S5 and S6) **×** $EF_{production,PFSA\ precursors}$ (Table S7)

PDSF production volumes (Tables S5 and S6) **−** (1) PFDS; (2) Emissions @ production sites → PFDS precursors **×** Ratios of polymers and non-polymers (Section 2.1.3.1) → Polymers / Non-polymers

Polymers **×** Annual releases over lifetime (Section S2.1.3.7) → polymers released → Degradation via set half-lives (Section S2.1.3.7)

Polymers **×** Residual levels (Section S2.1.3.6) → residuals in polymers **×** $EF_{use\&disp,poly}$ (Section S2.1.3.6)

Non-polymers **×** Range of degradable fractions (Section S2.1.3.5) → degradable non-polymers **×** $EF_{use\&disp,non-poly}$ (Section S2.1.3.5)

Emissions of PFSA precursors @ production sites **+** Emissions of PFSA precursors @ degradation of polymeric products **+** Emissions of PFSAs precursors @ use and disposal **×** Homologue compositions of xFDSA/E-based products (Section S2.1.4) → Emissions of C_4-C_{10} PFSA precursors

❖ PDSF derivatives in products = PDSF production volume - Emissions @ production sites

Figure S4. Flowchart of quantification steps across the life cycle in the present study for a) emissions of PFSAs from PDSF-based products and b) emissions of PFSA precursors from PDSF-based products.

S2.1. Emissions from the life cycle of PHxSF/PDSF-based products

PHxSF-based and PDSF-based products (referred to here as PHxSF/PDSF-based products) are a large family of chemicals that are derivatives of the parent compounds perfluorohexanesulfonyl fluoride (PHxSF) and perfluorodecanesulfonyl fluoride (PDSF), which have been manufactured through electrochemical fluorination, either intentionally or unintentionally, since 1958. As very limited quantitative information exists on the production volumes and emissions of PHxSF/PDSF-based products, many key parameters in the emission inventory are estimated based on much more widely reported information for perfluorooctanesulfonyl fluoride (POSF)-based products. Estimated annual production volumes of PHxSF and PDSF have been estimated by scaling down known annual POSF production volumes (see Section S2.1.1), and estimated emissions from manufacturing and use and disposal are largely based on the understanding of POSF processes with updated, PHxSF- and PDSF-specific information taken into account where available.
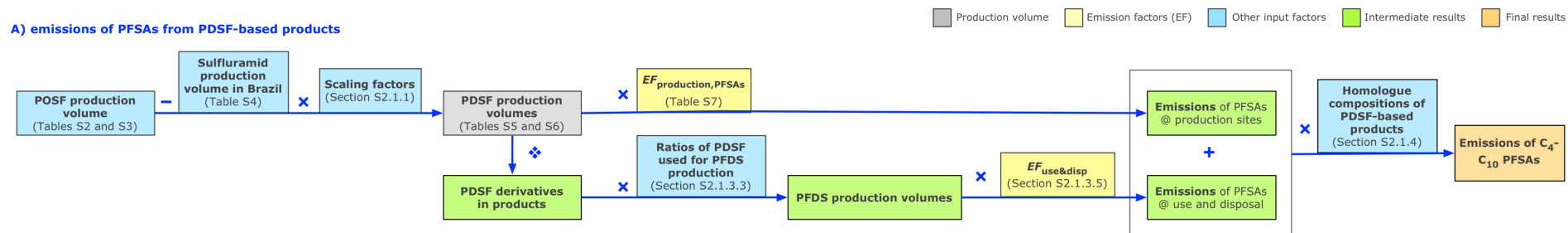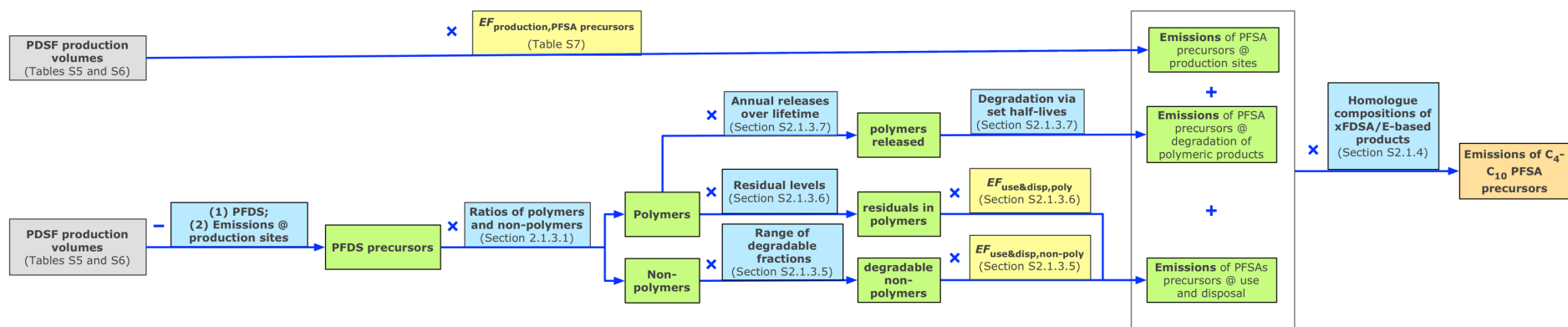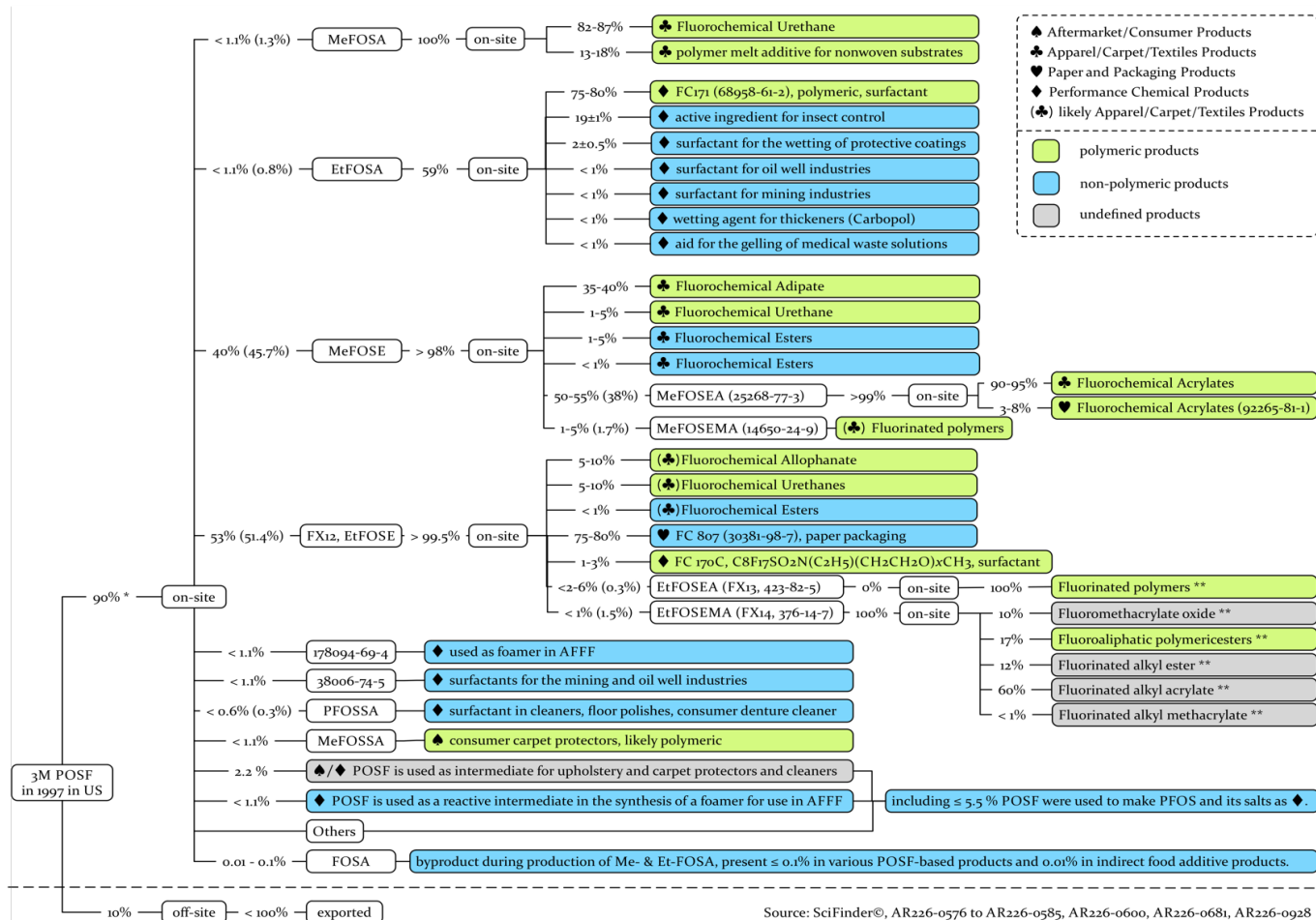
The production of POSF-based products, used here as a basis for PHxSF/PDSF-based products, can be divided into three periods: In the first period (1958–2002), the majority of products were produced in Country Group 1 (CG1) (Japan, Western Europe and the US) with some minor production in China. 3M was the first and largest manufacturer with three sites in the US (since 1958) and one site in Belgium (since 1971).[4,5] Miteni (formerly Rimar) in Italy, Dianippon Inc. in Japan, and Changjiang Chemical Plant in China (since the late 1970s) have also produced POSF-based products.[5,6] A few other companies (e.g. Air Products, BASF, Bayer, Borax Research, Ciba-Geigy, GIPKh (Russia), Tohoku Hiryo, Tokuyama Soda, and Yarsley Research) were also active in ECF;[6–9] however, no information is available yet to confirm or to quantify the production of POSF-based products by these companies. In the second period (2003–2015), producers in CG1 ceased their production one after another, while manufacturers in China[10] started large-scale production with a major downstream use to produce insecticide in Brazil.[11] In the third period (2016–2030), two scenarios are applied to China. As a lower scenario, it is assumed that these producers reduce their production quickly in response to global regulatory efforts, and China is assumed to linearly phase-out production by 2020. While as a higher scenario, China is assumed to require more time to linearly phase out production by 2025 (see Table S2).

POSF-based products including their PHxSF/PDSF-based homologue equivalent products can include diverse polymers and non-polymers in highly diverse industrial and consumer applications (see Figure S5), where only non-polymers may readily degrade to the sulfonic acid. An additional complexity is that PFHxS/PFDS can be present as impurities in PHxSF/PDSF-based products that can be released during the product life cycle. Moreover, PHxSF/PDSF-based products are a mixture containing a majority of C_6/C_{10}-based components (including residuals) and a small amount of their lower and higher homologues that can degrade to different PFSA homologues. In order to deal with these complexities and establish a global emission inventory of PFSA homologues and their precursors, we made use of the information collected from our previous study on POSF,[3] considered a large number of published documents related specifically to PFHxS/PFDS (references discussed and provided throughout this document), and applied a stepwise approach to assessing PFSA emissions from the life cycle of PHxSF/PDSF-based products.

Figure S5. Substance flow of POSF-based products manufactured by 3M in 1997 in the US. Chemicals included are labeled using their acronym or chemical abstracts service (CAS) number.

In this approach, as established and carried out previously with POSF[3], we divided the product life cycle of PHxSF/PDSF-based products into two phases based on data availability: (i) production and (ii) use and disposal. Note that our estimates are normalized to "PHxSF/PDSF-equivalents" ($C_6F_{13}SO_2F$/$C_{10}F_{21}SO_2F$) based on the PHxSF ($C_6F_{13}SO_2-$)/PDSF ($C_{10}F_{21}SO_2-$) moiety in relevant compounds to consistently integrate data from different sources. In addition, we used perfluorohexanesulfonamides/sulfonamido ethanols (xFHxSA/Es) and perfluorodecanesulfonamides/sulfonamido ethanols (xFDSA/Es) as a surrogate of direct precursors that can degrade and partially yield respective PFSAs in the environment and biota.

We first focus on emissions data reported at primary production sites where POSF-based chemicals have been produced based on several industrial documents regarding (i) production volumes of several POSF-based chemicals and (ii) mass flows at three production sites (see Section S2.1.2). In the mass flow studies, flows into environmental media (air, water and soil) were reported. These calculated emissions factors for POSF-based products at production sites are used to represent emissions factors of PHxSF/PDSF-based products from production sites given a lack of more chemical-specific information for these homologues.

Second, we focus on emissions that occurred during product use and disposal by the downstream industrial users and end consumers (see Section S2.1.3). These include (i) direct emissions of PFSAs that are active ingredients and impurities in products and (ii) direct emissions of non-polymeric PFSA precursors that are unreacted residuals in both polymeric and non-polymeric products. It should be noted that our estimates describe the generic fate of grouped PHxSF/PDSF-based products (i.e. polymers and non-polymers), since it is neither practical nor realistic to attempt to assess the release and fate of each individual species during the use and disposal phase.

We then focus on indirect emissions of PFSAs from the degradation of non-polymeric PHxSF-based products released into the environment as based on laboratory degradation studies of POSF-based products (see Section S2.1.3.8). We also considered the release of PFHxS/PFDS precursors from the degradation of polymeric PHxSF/PDSF-based products using an estimated range of potential degradation rate constants. The degradation of precursors is calculated using the CliMoChem multimedia environmental fate model, which is introduced and described further in Section S3.

In the final step, all estimates are broken down on a homologue basis based on available information on the relevant homologue compositions of POSF-based products, which is assumed to also be representative of PHxSF/PDSF-based products (see Section S2.1.4).

The emissions of PFHxS, PFDS and their precursors as impurities from the emissions of POSF-based products as calculated in our previous inventory study[3] were also included and added to the C_6 and C_{10} emission inventories developed here. The relevant C_6 and C_{10} impurity emissions of both inventories from this study were also added to one another. This provides a combined, holistic inventory that considers all emitted PFHxS- and PFDS-based products across the three product group inventories.

S2.1.1. Production volumes of PHxSF and PDSF

Given the very limited information available on production volumes for PHxSF/PDSF-based products, annual production volumes of POSF were used as a basis to estimate these values as elaborated in the 'Methods' section in the main text. The production volumes of POSF were estimated mainly based on industrial survey results (see Table S2 and Table S3). 3M reported annual production levels in the United States in 1997 of POSF (4,083,000 lbs), PHxSF (501,634 lbs), and PDSF (24,171 lbs),[12] and these were used to identify scaling factors of PHxSF and PDSF production. These factors of 12% for PHxSF and 0.6% for PDSF were applied to the annual estimated POSF production levels from our previous study in CG1[3] to estimate annual production levels of PHxSF and PDSF in CG1.

To the best of our knowledge, little to no public information exists regarding any historical, intentional production of PHxSF and PDSF within China. However, manufacturers in China are known to have produced POSF and POSF-based products, and C_6 impurities have been measured and reported in these C_8 products. The average reported fraction of PFHxS within three PFOS samples from Chinese manufacturers is 9.3%[13], and this impurity level was applied to estimated annual Chinese POSF production volumes from our previous study[3] to estimate annual Chinese production volumes of PHxSF (as unintentional impurities in POSF). For PDSF in China, the impurity level of C_{10} in C_8 products was not found to be reported, and it was therefore assumed to be represented by the same scaling factor of 0.6% based on 3M production. This factor was applied to Chinese POSF production levels from our earlier study[3] to define PDSF production in China (as unintentional impurities in POSF).

While some intentional production of PHxSF and PDSF-based products are expected to have more recently taken place in China (likely following the 2008 European Union directives on PFOS [14] and the listing of POSF, its salts, and PFOS in the Stockholm Convention in 2009 [15]), no public information was found to be available to quantify these levels. This intentional production could therefore not be considered in the inventory calculations here. These volumes are, however, expected to be much lower than the cumulative unintentional production as impurities in POSF-based products that have been considered in the inventory.

Table S2. Estimated annual 3M, CG1, and Chinese POSF production volumes in 1958–2002 in tonnes.[3]

Year	3M [t]	CG1 [t]	Year	3M[t]	CG1 [t]	Year	3M [t]	CG1 [t]	China [t]
1958	21	26	1973	339	423	1988	1905	2381	0
1959	42	53	1974	360	450	1989	1905	2381	0.5
1960	64	79	1975	381	476	1990	2177	2722	0.75
1961	85	106	1976	533	667	1991	2177	2722	1
1962	106	132	1977	686	857	1992	2177	2722	1.25
1963	127	159	1978	838	1048	1993	2177	2722	1.5
1964	148	185	1979	991	1238	1994	2177	2722	1.75
1965	169	212	1980	1143	1429	1995	2903	3629	2
1966	191	238	1981	1295	1619	1996	2903	3629	2.25
1967	212	265	1982	1448	1810	1997	2903	3629	2.5
1968	233	291	1983	1600	2000	1998	2903	3629	2.75
1969	254	318	1984	1753	2191	1999	2903	3629	3
1970	275	344	1985	1905	2381	2000	3494	4368	3
1971	296	370	1986	1905	2381	2001	175	218	3
1972	318	397	1987	1905	2381	2002	121	151	30

Table S3. Estimated annual POSF production volumes in 2003–2015 in CG1 and China in tonnes.[3]

Year	CG I [t] lower	CG I [t] higher	China [t]
2003	50	160	50
2004	50	160	100
2005	73	162	170
2006	50	100	250
2007	25	50	250
2008	0	0	250
2009	0	0	130
2010	0	0	100
2011	0	0	130
2012	0	0	130
2013	0	0	150
2014	0	0	170
2015	0	0	170

Development of POSF production estimates (as taken from our earlier study[3]):

1958–2002: The estimates of production volumes were based on 3M's POSF production history reported to the Stockholm Convention.[16] Following Armitage et al.,[17] it was assumed that production increased linearly from zero to one fifth of 1985-1989 production levels between 1957 and 1975 and that production increased linearly between 1975 and 1985. POSF production in China is reported to have started on a very small scale in the 1970s with very limited production and use,[18] and it started to increase in the early 1990s and reached a reported production of circa 3 t/yr in 1997 or 1998.[19] Therefore, we assumed a linear increase in production from 0.5 t/yr in 1989 to 3 t/yr in 1999 and that it remained at 3 t/yr before rising to 30 t/yr in 2002, when larger scale production started.

2003–2015: After 3M ceased its global production in 2002, there were still a few producers in CG1 producing POSF-based products: About 50–160 tonnes were produced in 2003 in Belgium, Germany, Italy and Japan;[20] and 73–162 tonnes were produced in 2005.[21] We assumed that the production in CG1 decreased linearly thereafter and only negligible amounts were produced after 2008 due to regulatory efforts, such as being regulated under the EU Directive 2006/122/EC and the Stockholm Convention Annex B. During this same period, large-scale production began in China in 2003. Reported annual production before 2004 was less than 50 t/yr, expanded to about 250 t/yr in 2006 and 2008, declined to 130 t/yr in 2009 and 100 t/yr in 2010.[6,10,18,22,23] Production values in 2015 were estimated at 170 t/yr.[24]

2016-2030: For China, we assumed that the 2015 level of production (i) linearly decreased and reached a negligible level by 2020 (lower scenario) and (ii) linearly decreased and reached a negligible level by 2025 (higher scenario). This is based on China's ratification of the Amendments to Annexes A, B and C of the Stockholm Convention specifying that from March 26, 2014 efforts should be made to develop substitutes for current exempted uses of PFOS and POSF as soon as possible and before the exemptions expire, and to gradually eliminate their production and use.[25] The national project co-financed by the Global Environment Facility are being implementation to support the reduction and phase-out of ongoing uses of PFOS in China between 2017 and 2021.[26] No production is assumed to exist during this period for CG1.

Consideration of China's POSF used in Brazil (as taken from our earlier study[3]):

Sulfluramid is an insecticide widely used to prevent leaf-cutting ants from destroying crops in Brazil and across South America. It uses EtFOSA as an active ingredient, which is synthesized from POSF largely produced in China. This POSF use is therefore considered in the inventory calculations and subtracted from the POSF available for production of PHxSF and PDSF. Annual amounts of EtFOSA that have been imported to, sold in, and exported by Brazil to nineteen nearby countries were considered in the inventory based on a recent study.[27] We assumed linear growth of EtFOSA production from 0 t/yr in 1992 until the first recorded value of 30 t/yr identified by the study in 2004. The Brazilian production level was assumed to remain at 2013 levels in 2014 and 2015, and for the years after 2015, we assumed that EtFOSA production and application ceases (as a lower scenario) or remains constant at the 2015 level (39.7 t/yr) until 2030 (as a higher scenario). Given that Sulfluramid application in Brazil is currently dependent on POSF production in China, the higher scenario assumes that Brazil would be able to produce their own POSF and EtFOSA in the years following China's projected phase-out of POSF production.

Table S4. Estimated total amounts (in tonnes) of EtFOSA technical product in Brazil from import and production between 1993 and 2015 based on a recent study[27] and using our assumption of a linear growth from 0 t/yr in 1992 to the 30 t/yr in 2004 identified by the study.[27] These amounts were subtracted from annual POSF production values used in the inventory calculations of PHxSF and PDSF.

Year	EtFOSA [t]	Year	EtFOSA [t]	Year	EtFOSA [t]
1993	2.5	2001	22.5	2009	23.3
1994	5	2002	25	2010	30.9
1995	7.5	2003	27.5	2011	36.0
1996	10	2004	30	2012	31.8
1997	12.5	2005	30	2013	40.6
1998	15	2006	31	2014	40.1
1999	17.5	2007	31	2015	39.7
2000	20	2008	30		

Resulting production estimates of PHxSF and PDSF:

The resulting annual estimates of production for PHxSF and PDSF in CG1 and China using the annual POSF production levels (introduced in Table S2 and Table S3 above) are shown below in Table S5 and Table S6 after subtracting exported POSF from Chinese production for insecticide production in Brazil and applying the scaling factors (Section S2.1.1).

Table S5. Estimated annual production volumes of PHxSF and PDSF in CG1 and China in 1958–2002 in tonnes.

Year	CG1 PHxSF	CG1 PDSF	Year	CG1 PHxSF	CG1 PDSF	Year	CG1 PHxSF	CG1 PDSF	China PHxSF	China PDSF
1958	3.1	0.2	1973	50.8	2.5	1988	285.7	14.3	0	0
1959	6.4	0.3	1974	54.0	2.7	1989	285.7	14.3	0	0
1960	9.5	0.5	1975	57.1	2.9	1990	326.6	16.3	0.1	0
1961	12.7	0.6	1976	80.0	4.0	1991	326.6	16.3	0.1	0
1962	15.8	0.8	1977	102.8	5.1	1992	326.6	16.3	0.1	0
1963	19.1	1.0	1978	125.8	6.3	1993	326.6	16.3	0	0
1964	22.2	1.1	1979	148.6	7.4	1994	326.6	16.3	0	0
1965	25.4	1.3	1980	171.5	8.6	1995	435.5	21.8	0	0
1966	28.6	1.4	1981	194.3	9.7	1996	435.5	21.8	0	0
1967	31.8	1.6	1982	217.2	10.9	1997	435.5	21.8	0	0
1968	34.9	1.7	1983	240.0	12.0	1998	435.5	21.8	0	0
1969	38.2	1.9	1984	262.9	13.1	1999	435.5	21.8	0	0
1970	41.3	2.1	1985	285.7	14.3	2000	524.2	26.2	0	0
1971	44.4	2.2	1986	285.7	14.3	2001	26.2	1.3	0	0
1972	47.6	2.4	1987	285.7	14.3	2002	18.1	0.9	0.5	0

Table S6. Estimated annual production volumes of PHxSF and PDSF in 2003–2015 in CG1 and China in tonnes.

	CG I PHxSF [t]		CG I PDSF [t]		China PHxSF [t]	China PDSF [t]
Year	lower	lower	higher	lower		
2003	6	19.2	0.3	1.0	2.1	0.1
2004	6	19.2	0.3	1.0	6.5	0.4
2005	8.8	19.4	0.4	1.0	13.0	0.8
2006	6.0	12.0	0.3	0.6	20.4	1.3
2007	3.0	6.0	0.2	0.3	20.4	1.3
2008	0	0	0	0	20.4	1.3
2009	0	0	0	0	9.9	0.6
2010	0	0	0	0	6.4	0.4
2011	0	0	0	0	8.7	0.6
2012	0	0	0	0	9.1	0.6
2013	0	0	0	0	10.2	0.7
2014	0	0	0	0	12.1	0.8
2015	0	0	0	0	12.1	0.8

S2.1.2. Releases of non-polymeric compounds from production sites

Given that very little information is available on emissions of PHxSF/PDSF-based products from production sites, calculated emissions from POSF-based product production sites were applied to define manufacturing emission factors for PHxSF/PDSF-based products. There are more than 600 intermediate steps associated with the production of PASF-based compounds, and each step may release PASF-based compounds into the environment. We assumed emission factors at all production sites to be identical and remain the same over entire periods. Based on information about the chemical compositions of waste streams, physicochemical properties of these chemicals, and industry emission reduction measures, we

applied emission factors for PHxSF/PDSF, PFHxS/PFDS, and *x*FHxSE/As and xFDSE/As during two time periods (1958–1997 and 1998–2030) (see Table S7). These were derived using the release data from 3M production sites for the C_8 homologues summarized in Table S8 and further explained below. We used *x*FHxSE/As and *x*FDSE/As as a surrogate for direct PFSA precursors. Other potential precursors were likely released from production sites as well, but they were not monitored during the reported POSF-based manufacturing measurements, and thus cannot be included here.

Table S7. Estimated emission factors of PHxSF/PDSF, PFHxS/PFDS, *x*FHxSA/Es, xFDSA/Es being released from production sites between 1958 and 2030, in % of the total annual production mass.

		Release to			Total
		air	water	land treatment	
1958-1997	PHxSF/PDSF	0.81%	0.0%	0.6%	1.4%
	PFHxS/PFDS	0.0%	0.54%	1.0%	1.5%
	*x*FHxSA/Es; xFDSA/Es	0.004%	0.06%	1.1%	1.1%
1998-2030	PHxSF/PDSF	0.20%	0.0%	0.0%	0.2%
	PFHxS/PFDS	0.0%	0.27%	0.0%	0.3%
	*x*FHxSA/Es; xFDSA/Es	0.001%	0.03%	0.0%	0.0%

Table S8 shows self-reported releases from 3M's production sites in the US and includes corresponding references. These releases were used with the following considerations to estimate the emission factors:

1958–1997: In the US, 3M produced POSF-based products mainly at their facility in Decatur, AL with some minor production in Cottage Grove, MN (pilot plant production only) and Cordova, IL (ceased before 1997).[28,29] Based on the targeted monitoring conducted in 1997–1999 and the production data for 1997–1999, 3M reported that about 4% of the non-polymeric POSF-based compounds produced in the Decatur facility entered the environment, either through direct release to air and natural waters after waste treatment processes or through land treatment (normally for agriculture) via POSF-based products contained in activated sludge (see Table S8). The reported emission levels to water in Table S8 were derived from the measurements conducted after a carbon adsorption treatment was installed in 1998, which reduced possible release to natural waters by 50%. Thus, we doubled our estimates accordingly to represent the emissions to water in the time before 1998. Additionally, there were also some minor releases of PFOS to water from the Cottage Grove facility. It should be noted that in 3M's report, the actual amount of solid wastes generated from the Decatur facility in 1997 was estimated to be about 490 tonnes (about 70% incinerated and 30% landfilled in a hazardous waste landfill), which is much higher than the 37 tonnes we used for our estimates.[30] However, 3M's estimates were likely derived from the total fluorine content,[29] and therefore includes not only all polymeric and non-polymeric POSF-based wastes, but also other fluorinated by-products. Consequently, we could not use this estimate in our calculations.

1998–2015: In 1998, a carbon adsorption treatment system was installed as part of the wastewater treatment process at the Decatur facility. It reduced releases from the wastewater treatment system by 40% to air and by 50% to natural waters in 1998 compared to the levels in 1997.[30] In 1999, the release to air was further reduced to about 25% of the level in 1997,[29] which we used to represent the emission level to air for the whole period. In addition, sludge from the Decatur facility started to be transported to an offsite landfill instead of being used for land treatment.[30] Hence, we adjusted the factors accordingly (see Table S7).

Table S8. Reported exposure information profile from 3M's production sites in the US, in tonnes. All data were normalized to "POSF-equivalents" and combined with the POSF production volume of 1850 t in the US in 1997.[12] N.Q. = not quantified; N.A. = not available; *x*FOSA = *x*-perfluorooctanesulfonamide; *x*FOSE = *x*-perfluorooctylsulfonamido ethanol; *x*FOSE(M)A = *x*-perfluorooctanesulfonamidoethyl (methyl)acrylate.

Site	Chemical	Releases [t] to			Solid waste *** [t]	Reference
		Air	Water *	Land treatment **		
Cottage Grove	PFOS	N.Q.	0.5	0.0	3.4	[31]
Decatur	POSF	15.0	0.0	11.8	N.Q.	[29]
	FOSA	N.Q.	0.2	0.0	N.Q.	[32]
	PFOSSA	N.Q.	0.2	3.0	N.Q.	[33]
	EtFOSA	0.0	0.1	0.0	N.Q.	[34]
	MeFOSA	0.1	N.Q.	N.Q.	4.9	[35]
	EtFOSE	0.0	0.0	6.3	18.2	[36]
	MeFOSE	0.0	0.1	10.4	14.3	[37]
	EtFOSEA	N.Q.	0.0	N.Q.	N.Q.	[38]
	EtFOSEMA	N.Q.	N.Q.	N.Q.	N.Q.	[39]
	MeFOSEA	N.Q.	N.Q.	N.Q.	N.Q.	[40]
	PFOS	0.0	4.5	18.2	N.Q.	[31]
	Sum incl. PFOS	15.1	5.0	49.8	37.4	this study
	Total incl. PFOS	8.9****	4.7	N.A.	489*****	[41]

 * The data presented is part of wastewater testing conducted in 1998, since the individual chemicals of interest were not analyzed in 1997. The 1998 data has not been adjusted for production levels in 1997, since most production remained at a similar level. It is noted that an interim carbon adsorption treatment system was installed as part of wastewater treatment in 1998, which reduced the discharge of PFOS to the Tennessee River by about half, i.e. the discharge in 1997 was likely double the amount shown here. Additionally, it is not possible to distinguish the amount of chemicals generated from specific reaction steps during production of various compounds or whether their presence may be the result of hydrolysis of more complex molecules.

** The land treatment of Decatur sludge was discontinued in early 1998. Thereafter, sludge was transported to an off-site landfill after passing through a thickener and a sludge press.

*** A review of plant records for 1998 shows that 63% of the fluorochemical containing wastes were sent to incinerators, and 33% and 4% of the wastes were disposed of in hazardous and non-hazardous waste landfills, respectively.

**** This value was estimated for 1998 after emission reduction measures took place. [29]

***** This amount was likely estimated based on the fluorine content and non-specific fluorochemical categories. [29]

The emission factors for *x*FOSAs and *x*FOSEs (used here to represent *x*FHxSAs, *x*FHxSEs, *x*FDSAs, and *x*FDSEs) are derived from reported emissions to air, water and soil (through land treatment). These precursors substances emitted to water are assumed to remain in the water compartment (and sediments) based on the level three fugacity modeling estimates using the US EPA EPISuite software package.[42] For those that were emitted to soil, we assumed lower and upper bounds of 20% and 80%, respectively, for the fractions that remain in soil, with the remaining fractions ultimately volatilizing into air from soil. These lower and upper bounds were applied to the emission inventory scenarios and derived from previous studies that (i) 76% of EtFOSE in an activated sludge aeration basin would be lost to the atmosphere;[43] and (ii) at 25 °C and after 120 days, about 30% and 50% of the original dose of EtFOSE is lost due to volatilization or formation of products other than those monitored in microbially active and inactive sediments, respectively.[44] Due to the significantly higher estimated yield to PFOS from *x*FOSA/Es in soil than in air (see Table S18), the higher inventory scenario was assigned as the 80% fraction remaining in soil (with the remaining 20% volatilizing to air). The emission factors in China for this period were assumed to remain at pre-1998 levels. Given that some of the emissions in Table S8, particularly for *x*FOSA/Es, were not quantified by 3M (listed as 'N.Q.'), it is possible that some emissions may have occurred but could not be considered in the calculation of the emission factors. This could have led to a slight underestimation of these emission factors (Table S7).

S2.1.3. Releases of PHxSF/PDSF-based compounds from the use and disposal of relevant products

In contrast to releases from production sites, releases of PHxSF/PDSF-based compounds during use and disposal are much more complex. According to 3M's sales information,[30] the majority of POSF-based products were sold to downstream industrial users who either applied them or incorporated them into their products that were then sold to end users. Similarly, PHxSF/PDSF-based compounds might therefore be released into the environment during different stages of the product life cycle including during use, further processing and disposal by downstream industrial users, during the supply chain steps between downstream industrial users and end users, and during use and disposal by end users.

Due to a lack of information, it is very difficult to estimate releases of PHxSF/PDSF-based products (including unreacted residuals) from use and disposal using a bottom-up approach, not only because of the distinct lifetimes of an enormous variety of products and their globally widespread use, but also due to the complex pathways that may lead to environmental releases (see Figure S6).
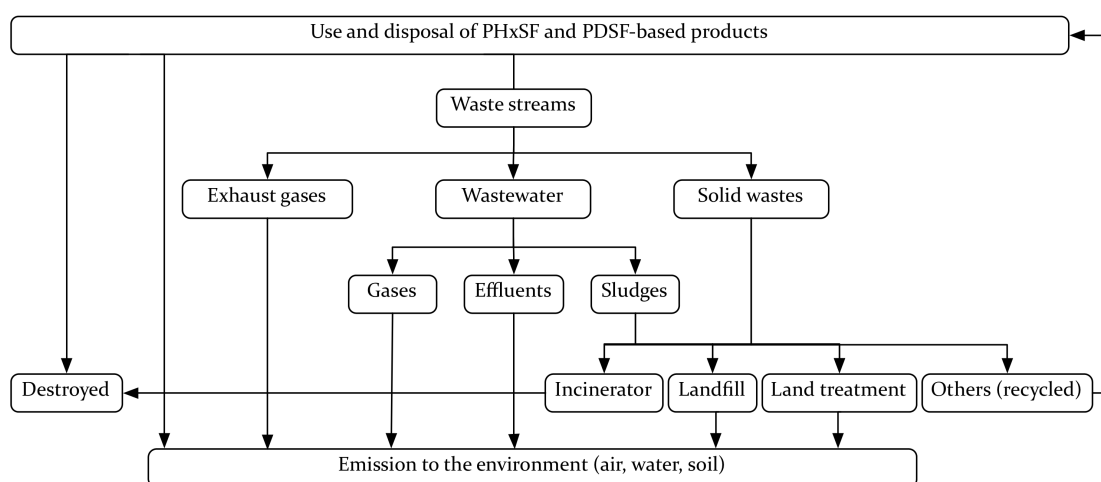

Figure S6. Scheme of the fate of PHxSF- and PDSF-based products during use and disposal.

Depending on the use and disposal of PHxSF/PDSF-based products, they can either be destroyed, directly emitted into the environment (air, natural water and/or soil), or discharged to the waste streams (exhaust gases, wastewater and/or solid wastes).[30] We assumed that in CG1, wastewater and solid wastes are generally sent to various treatment facilities, where the compounds may be destroyed, contained, recovered, or released into the environment. For instance, in wastewater treatment plants, a majority of POSF-based compounds are concentrated in activated sludge, whereas only a small amount remains in the aqueous phase and is released either to air during treatment processes[45,46] or to a natural water body through the effluents.[47–50] Activated sludge may be further processed for land treatment or other uses, landfilled, or incinerated. Note that landfilled POSF-based compounds can still be slowly released into the environment through outgassing[46] or through transport in leachates.[51] To date, no mass-balance-based study on the fate of PHxSF/PDSF-based compounds during product use and disposal or after disposal has been undertaken. Therefore, in the next sub-sections we estimate releases of PHxSF/PDSF-based compounds during use and disposal of PHxSF/PDSF-based products in a generic manner with the following assumptions:

1) The proportions of polymeric and non-polymeric compounds manufactured by all manufacturers are identical and constant over a given time period.
2) Polymeric compounds may first degrade into non-polymeric compounds, which may then further degrade and form PFSAs. Polymeric products may also contain both PFSA impurities and

unreacted residuals (e.g. *x*FHxSA/Es) that are PFSA precursors and are steadily released over the lifetime of polymeric products.

3) Like polymeric products, non-polymeric products also contain both PFSA impurities and unreacted residuals that are PFSA precursors and are steadily released during the lifetime of non-polymeric products. In addition, some non-polymeric compounds with a complex molecular structure may break down into simpler precursor molecules (e.g. *x*FHxSA/Es and xFDSA/Es) and then partially form PFSAs in the environment and biota after being released.

S2.1.3.1. Non-polymeric:polymeric ratios of PHxSF-based compounds produced

The amount of non-polymeric and polymeric PFHxS-based products historically produced in CG1 is unclear, and insufficient data exists in order to reasonably estimate the ratios. Instead, two scenarios are applied across all years for PFHxS-based products in CG1 to account for the range of potential values: 1) 20% non-polymeric and 80% polymeric; and 2) 80% non-polymeric and 20% polymeric. Based on the use information for PDSF submitted by 3M stating that PDSF was used as an intermediate for the purpose of PFDS production[52], produced PDSF in CG1 is assumed to be entirely used for production of PFDS in the inventory, and therefore no polymers are considered to be produced, and a ratio is not applicable.

For historical Chinese PHxSF and PDSF-based production included in the inventory as an impurity in POSF-based products, ratios were assigned based on the historical production of POSF-based products in China. Until 2008, a ratio of 50% polymeric and 50% non-polymeric products was assumed as China began extensively using polymeric products in textile, carpet and leather surface treatments in a similar amount to the uses of non-polymeric products.[22] It is reported that uses of PFOS and related substances in surface treatments ceased in China after 2008 due to new global regulatory requirements,[22,23] and the remaining production of non-polymeric products in China were mainly used in metal plating, AFFF synthesis and Sulfluramid (insecticide) formulation.[22] Although EtFOSE, a raw material for the production of polymeric products, was likely still being produced in 2012 in China,[53] we assumed that POSF-based products for surface treatments are produced at only a negligible level in China after 2008, since the same producers started a transition to produce PBSF- and PHxSF-based products for surface treatments in the same period.[53] This intentional production of PHxSF-based products after 2008 is not quantifiable given the lack of data in the public domain and can therefore not be estimated (see Section S2.1.1). Consequently, we changed the non-polymeric:polymeric ratios of products manufactured in China after 2008 to 100% vs 0%.

S2.1.3.2. Average lifetime of PHxSF/PDSF-based products (non-polymeric and polymeric)

To our knowledge, no information on the average lifetime of PHxSF or PDSF-based products is available, as they have been applied in countless products with very distinct lifetimes and unknown fractions in each application field. For our calculations, polymeric PHxSF-based products in the emissions inventory are assumed to be represented by polyurethanes used in carpet and textile treatments with an average lifetime of 10 years based on published life-cycle waste stream estimates done for 3M[41] and on a recently advertised 3M carpet product warranty[54]. No polymeric products are considered in the inventory of PDSF-based product emissions.

In contrast, non-polymeric products (such as industrial and household surfactants and AFFFs) are designed for a one-time use or multiple uses over a short period. Some non-polymeric products may have much longer lifetimes than others. For instance, some compounds blended into paints may be released only slowly during the long lifetime of paints, and AFFFs may be stored for 5–15 years before they are used or

disposed of.[55,56] To simplify the calculations, we assumed an average lifetime of 2 years for all non-polymeric PHxSF and PDSF-based products.

S2.1.3.3. Proportions of PFHxS/PFDS as ingredients or residuals in PHxSF/PDSF-based products

In our calculations, we do not take into account the release of PFHxS/PFDS residuals from PHxSF/PDSF-based products since the average residual level is likely very low (0.005–0.1% on a mass basis estimated by Armitage et al.[17] for C_8 homologues) and likely much lower than our uncertainty range.

In CG1, the amount of produced PHxSF used to manufacture PFHxS is unclear, and insufficient data exists in order to reasonably estimate a single value. Instead, 1% (lower scenario) and 5% (higher scenario) were assumed to cover a range of potential values. Based on use information on PDSF submitted by 3M stating that PDSF is used as an intermediate for the purpose of PFDS production[52], 100% of the PDSF in CG1 in the inventory was allocated to PFDS production.

As we consider historical PHxSF and PDSF production in China as unintentional impurities remaining in POSF, the amount of produced PHxSF/PDSF used to manufacture PFHxS/PFDS in China in the inventory follows the use of POSF for PFOS production. Between 2003-2008, it was reported that textile treatment, metal plating, semiconductor production, and AFFFs were the main industries in China utilizing POSF-based compounds and having POSF consumption amounts of 100 t/yr, 25t/yr, 0.5 t/yr and 80 t/yr, respectively.[23] Thus, we estimated that 12.5% of PHxSF/PDSF produced in China were converted to PFHxS/PFDS and its salts as impurities in respective PFOS-based products based primarily on the demand from metal plating.

Between 2009-2015, the use of polymeric POSF-based products likely ceased in China with ongoing uses there focusing on metal plating, AFFF synthesis, and Sulfluramid formulations.[22] Consequently, we adjusted our estimate to being 30% of PHxSF/PDSF manufactured in China was converted to PFHxS/PFDS and its salts as impurities in respective PFOS-based products by assuming that the use of PFOS in metal plating remained at the same level as in 2009 (30–40 tonnes).[6]

S2.1.3.4. Proportions of PFCAs as impurities in PHxSF and PDSF-based products

During the electrochemical fluorination of octanesulfonyl fluoride, some perfluorocarbon chains are unintentionally reacted to perfluoroalkane carbonyl fluorides through the electrochemical oxidation and are subsequently hydrolyzed to perfluoroalkyl carboxylic acids (PFCAs) by moist air or in the subsequent reactions.[57] Gramstad and Haszeldine isolated a 1% yield of perfluorooctanoyl fluoride from electrochemical fluorination of octanesulfonyl fluoride.[58] PFCA impurities are therefore present in all POSF-based products and can therefore be expected in homologue PHxSF- and PDSF-based products as well. Since PFCAs cannot degrade into PFSAs under any natural conditions, the fractions of PFCAs as impurities in products were subtracted from the total release of non-polymeric compounds in our calculations. Given that very limited information is available on the impurity levels in PHxSF/PDSF-based products, PFCA impurity levels in POSF-based products were applied to be representative.

It is noted that the impurity levels of PFCAs in POSF-based products vary considerably (see Table S9). Three studies determined C_5–C_{12} homologues as major PFCA impurities in commercial PFOS products,[59] ranging from 0.71 to 4.84 wt%. In another report, 3M published that their studies of eight samples have identified the presence of PFOA impurities ranging from 0.02 to 0.16 wt% in their commercial POSF-based products.[60] In addition, perfluoroalkyl carbonyl fluorides formed during the manufacture of POSF may

react with reactants added during subsequent reactions of POSF and form derivatives such as perfluorooctanamides (FOAMs, $C_7F_{15}CONH(R)$, R = CH_3 or C_2H_5).[61] Jackson et al. detected varied levels of MeFOAM or EtFOAM (between 0.003 and 0.673 wt%) in eight out of ten commercial products tested. [61] The authors also found that FOAM levels are considerably lower in more recent ECF material produced in China (0.003 wt%) and in 3M's post-2001 formulations (not detected), suggesting that cleaner synthetic techniques and additional purification steps are now being used.[61] Due to lack of an analytical standard, the lower and higher homologues of FOAMs in products could be detected but not quantified.[61]

Hence, the exact levels of PFCAs and PFCA derivatives formed during the manufacture of POSF-based and thus also PHxSF/PDSF-based products and present as impurities in these products are still unclear. In our calculations, we assumed that 1.5 wt% of PFCA-related impurities formed for the whole period (1958–2030). This is derived from the geometric mean of PFCA impurity levels listed in Table S9. The fate of these impurities is either release into the environment (for products produced prior to 2001) or removal from the products through purification procedures (for products produced after 2001). However, the fate of PFCA impurities is not within the scope of this study and is only subtracted from the estimates of PHxSF/PDSF-based compounds and not considered further.

Table S9. Reported homologue compositions of PFCA impurities in commercial POSF-based products, in wt% of POSF-based products. N.R. = not reported; N.D. = not detected; N.M. = not measured.

Product	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	Ref.
3M PFOS	N.R.	N.R.	N.R.	N.R.	0.79	0.002	0.0005	0.0002	0.0004	N.R.	N.R.	62
PFOS (FC-95)	0.1	0.28	N.R.	N.R.	0.33	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.	63
3M PFOS*	1.21	0.82	1.28	0.59	0.59	0.11	N.D.	0.24	N.M.	N.M.	N.M.	64

* Production lot #217

S2.1.3.5. Releases of PFHxS, PFDS, and their direct precursors during use and disposal of non-polymeric products

The estimated releases of PHxSF/PDSF-based compounds during use and disposal of non-polymeric products was divided into two groups: PFHxS/PFDS and PFHxS/PFDS precursors. To simplify, we assumed lower (10%) and higher (100%) bound scenario fractions that are ultimately released into the environment during use and disposal over a product lifetime of 2 years. These lower and higher bound values themselves may not be realistic, but they are expected to cover the range of actual emissions.

For PFHxS and PFDS, we assumed that all emissions enter into natural water bodies. Among PFHxS precursors, many compounds with complex molecules could break down into simpler molecules through biodegradation and then form PFSAs through biotic and abiotic degradation. For example, this has been shown through experimental studies of wastewater treatment processes for 6:2 fluorotelomer sulfonamide alkylamine (FTAA)[65], which is an analogue to recently identified PFHxS-related substances from a review of product patents (e.g. compound with CAS number 50598-28-2).[66] This can likely happen both in the real environment (soil and sediment) or in the technosphere (wastewater treatment plants and landfills). It is currently not possible to quantify the proportion of each compound (with simple structures such as xFHxSA/Es or with complex structures such as SAmPAPs) emitted to each medium (air, water and soil).

As a simplification, we made the following generic assumptions:

1) For products manufactured in CG1, we assumed that 1% (lower scenario) or 10% (higher scenario) of PFHxS precursors released are compounds with simple molecules (assumed as xFHxSA/Es) and the rest of the 90–99% released are compounds with complex molecules. For products produced in

China, we estimated the proportions to being 5% (lower scenario) or 10% (higher scenario) simple molecules with the remaining being complex molecules.

2) The degradation of non-polymeric compounds with complex molecules to those with simpler molecules was considered in the inventory. By looking at the molecular structures of the POSF-based compounds in products by 3M (see Figure S5), most of these compounds are xFOSE-based esters. Therefore, theoretically the yields of xFOSEs from the hydrolysis of the ester bond can reach 100%. However, the fate of these non-polymers (e.g., released, incinerated, landfilled), their distribution in environmental media (e.g., soil, water, sediment) and their corresponding degradation half-lives in these media remain currently unclear. The only directly relevant study estimated that the half-life of a EtFOSE-based phosphate diester (SAmPAP) (C_8) in microbially active marine sediment is likely longer than 380 days at 25°C and 3400 days at 4 °C.[44] In another study on the biodegradation of a polyfluoroalkyl phosphate diester (diPAP), a fluorotelomer-based counterpart of SAmPAP, in activated sludge,[67] about 5% of the degradation product, flurotelomer alcohol (FTOH), was observed to have volatilized in the air over the course of 92 days. In the same study, the authors suggested that the actual yields in the environment can be even higher than in the laboratory.[67] Using this information for POSF-based compounds, we assumed that all PHxSF and PDSF-based compounds with complex molecules break down into xFHxSA/Es or xFDSA/Es with 2% and 10% volatilized in the air as the lower and higher scenarios, respectively, in the same year as they are released. The fate of the remaining 90–98% of the complex molecules into xFHxSA/Es or xFDSA/Es that have been emitted to compartments other than air (water, soil, groundwater, sediments, etc.) is not certain, especially regarding the distribution among compartments and the timescale of their degradation therein. To consider these emissions, we set up two scenarios to represent a potential range. For the lower scenario containing the remaining 98% of complex molecules, 15% were assumed to degrade in the year they were produced into soil, 10% into water, and 2% into air, respectively. For the higher scenario containing the remaining 90% of complex molecules, 50% were assumed to degrade in the year they were produced into soil, 40% into water, and 10% into air, respectively. For the originally released simple molecules, they are assumed to be equally distributed among the air, water, and soil compartments.

3) Following the distribution of POSF-based products in Figure S5, 98% of all xFHxSA/Es and xFDSA/Es emissions were assumed to be xFHxSEs or xFDSEs and the remaining 2% were assumed to be xFHxSAs or xFDSAs. Emissions of PFHxS and PFDS, both direct and residuals, were assumed to enter surface water.

S2.1.3.6. Release of residuals from use and disposal of polymeric products

For polymeric products, we quantified the release of residuals. Several studies have been conducted to measure the levels of selected non-polymeric residuals in various polymeric and non-polymeric POSF-based products, and they suggest that the levels vary considerably (see Table S10). Given limited information, we assumed that POSF-based non-polymeric residual levels in polymeric products are also representative of PHxSF- and PDSF-based polymeric products and range from 0.1 to 5% (by mass) as the lower and higher scenarios, respectively. During use and disposal of polymeric products, (semi)volatile residuals are steadily emitted into air, and non-volatile residuals are released into the wastewater or solid wastes being treated, landfilled, or incinerated. Due to a lack of information, we can assess neither the proportions of (semi)volatile and non-volatile residuals remaining in the products nor the absolute proportions of residuals that are emitted into the environment. However, a study[68] detected semi-volatile

MeFOSE and EtFOSE being the predominant residuals in 3M apparel/carpet/textile POSF-based products and having a much higher concentration (by a factor of about 100) than the other detected residuals. Hence, we applied the assumption that 98% of non-polymeric residuals in polymeric products are semi-volatile *x*FHxSEs or *x*FDSEs and 2% are semi-volatile xFHxSAs or *x*FHxSAs that are 100% steadily volatilized into air over the generic product lifetime of 10 years, although this might be an overestimation of actual emissions.

Table S10. Reported residual levels (on a mass basis) in POSF-based products. N.A. = not available.

Categories	Site	Sample Nr.	Lower	Higher	Aver.	Ref.
Paper and Packing	UK	N.A.	N.A.	1.0%	N.A.	69
Total POSF-based Prod.	UK	N.A.	0.0%	7.0%	2.4%	69
Total POSF-based Prod.	Global	N.A.	0.1%	3.0%	N.A.	70
3M Carpet Treatment Prod.	Global	N.A.	0.3%	5.0%	N.A.	28
Total 3M Prod.	Global	N.A.	N.A.	N.A.	1-2%	28
3M Apparel/Carpet/Textiles Prod.	Global	8	0.7%	5.3%	N.A.	68

S2.1.3.7. Release of precursors from the degradation of polymeric products

The degradation of side-chain fluorinated polymers (referred to as polymers) into direct PFHxS and PFDS precursors (i.e., *x*FHxSA/Es or *x*FDSA/Es) was estimated and included in the emission inventory using the non-polymeric:polymeric ratios of PHxSF and PDSF-based compounds (see Section S2.1.3.1). Polymer products were all assumed to be released from the material they were applied to (i.e. from carpets via cleaning, general use) at a rate of 10% per year throughout their lifetime of 10 years (with all of the product released by the end of the product lifetime). Once released, the polymeric product was then assumed to be susceptible to degradation, releasing PFHxS or PFDS precursors into the environment. Since the degradation kinetics of such polymers are unclear, a hypothetical lower and higher scenario were applied in the inventory calculations: degradation from a half-life of 10 years (higher scenario) and degradation from a half-life of 100 years (lower scenario). Released precursors were assumed to be released into air (20%), water (40%), and soil (40%).

S2.1.3.8. Indirect emissions from degradation of non-polymeric species

We considered the formation of PFHxS and PFDS in the environment and biota from degradable PHxSF- and PDSF-based compounds, namely from non-polymeric compounds released from production sites (estimated in Section S2.1.2) and from non-polymeric compounds as ingredients or residuals released during use and disposal of both polymeric and non-polymeric products (estimated in Sections S2.1.3.5 and S2.1.3.6). Degradation of non-polymeric compounds may involve different mechanisms with distinct degradation products and yields dependent on the physicochemical properties of each compound and on the media. Given that no information is available on the degradation of specifically PHxSF- and PDSF-based compounds, information available for the respective POSF-based homologue compounds were taken to be representative: For instance, POSF has a low water solubility (<294 ng/ml)[71] and likely stays in air, where it does not react with OH radicals[72] but can be slowly hydrolyzed by moist air and form PFOS.[58] *x*FOSEs have rather high air-water partition coefficients[73] allowing a fraction of them in wastewater and solid waste to volatilize into air[45,46] and partially degrade into PFOS by OH-radical oxidation.[74] *x*FOSEs that accumulate in sludge undergo aerobic microbial biodegradation to form PFOS.[43,75,76] In vitro and in vivo tests also show that biodegradation of EtFOSE takes place in biota and forms PFOS.[77,78] Furthermore, non-

polymeric compounds with complex molecules such as SAmPAPs may break down into simpler molecules such as EtFOSE through biodegradation[44,79] and then form PFOS through biotic and abiotic degradation.[74,80]

The cumulative degradation of xFHxSA/Es and PHxSF to PFHxS (and of xFDSA/Es and PDSF to PFDS) was estimated using the CliMoChem global multimedia mass-balance model. In the model's calculations, it considers values for each of the degradation half-lives and yields for each of these precursors in individual environmental compartments. These model inputs are shown and discussed in Section S3.3.

S2.1.4. The homologue compositions of PHxSF and PDSF-based products

For PHxSF/PDSF and PFHxS/PFDS emitted to the environment in CG1, we assumed their homologue compositions based on the information available to describe the homologue composition of commercial PFOS products (see Table S11). In our calculations, we assumed that the geometric and arithmetic means represent the lower and higher scenarios, respectively, and shifted the distribution to be representative for the C_6 and C_{10} products. Based on the relative reported C_9 impurity level of 4%–12% in PDSF-based surfactant FC-120 produced by 3M[81], the estimated homologue composition of C_9 in PDSF-based products was adjusted accordingly. The applied homologue distributions for PHxSF- and PDSF-based products in the inventory are provided in Table S12 and Table S13.

Table S11. Reported homologue compositions in two commercial PFOS-based products, in % (on a mass basis) of PFOS-based products. N.R. = not reported; N.D. = not detected; N.M. = not measured.

Product	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	Ref.
NH4-PFOS, FC-93 *	0.1–2	0.1–2	0.1–2	0.1–2	19–23	N.R.	N.R.	82
PFOS, Lot #217	1.72	N.M.	7.31	N.M.	86	N.M.	N.D.	64
arithmetic mean	3.3	4.1	5.2	4.1	84.7	1 **	1 **	this study
geometric mean	1.1	0.99	1.8	0.9	84.5	0.1 **	0.1 **	this study

* This product is diluted in solvents; the intended content of PFSAs is 25%. We therefore multiply each range by 4.
** The actual levels have not been reported and therefore the arithmetic and geometric mean cannot be calculated. In our calculations, we assumed the lower and upper bounds (0.1% and 1%) as the lower and higher scenarios.

Table S12. Applied estimated homologue compositions (lower-higher range) in the inventory for PHxSF/PFHxS-based and PDSF/PFDS-based products based on reported concentrations in POSF-based products and PDSF-based products, in % (on a mass basis) of PHxSF/PFHxS and PDSF/PFDS-based products.

Product	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
PHxSF/PFHxS-based	1.8-5.2	0.9-4.1	84.5-84.7	0.1-1	0.1-1	0.1-1	0.1-1
PDSF/PFDS-based products	0.1-1	0.1-1	1.1-3.3	0.9-4.1	1.8-5.2	4.7-12.5*	87.5-95.3

* This range is based on the relative reported C_9 impurity level in C_{10} surfactant FC-120 produced by 3M.[81]

Included Chinese production levels of PHxSF and PDSF in the inventory are considered to have been produced unintentionally as impurities in produced POSF (see SI section S2.1.1). They consequently do not contain any homologue impurities of their own.

For xFHxSA/Es and xFDSA/Es released into the environment, we assumed their homologue compositions based on commercial products that contain xFOSA/Es as main ingredients (see Table S13). In our calculations, we used the minimum and maximum values as the lower and higher scenarios (see Table S14).

Table S13. Reported homologue compositions in various commercial POSF-based products, in % (on a mass basis) of *x*FOSA/E-based products. N.R. = not reported; N.D. = not detected; N.M. = not measured.

Product	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	Ref.
EtFOSE, L-10059, FM-3422	0.11	0.03	0.51	0.82	96.09	N.R.	N.R.	83,84
EtFOSE, Lot 547, FM-3924	1.52	1.34	3.52	1.40	87.16	N.R.	N.R.	83,84
EtFOSE, FC-10	2–6	1–3	3–7	2–6	80–90	N.R.	N.R.	85
MeFOSE, L-1276	1.62	1.34	5.05	1.69	83.88	0.87	N.R.	83
EtFOSA, FX-12	N.R.	N.R.	N.R.	1.1–6	93–98.9	N.R.	N.R.	86
EtFOSEA, FX-13, 423-82-5	4–6	1–3	3–5	2–4	83–85	N.R.	N.R.	87
EtFOSEMA, FX-14, 376-14-7	4–6	1–3	3–5	2–4	83–85	N.R.	N.R.	88
FC-171, CAS 68958-61-2	N.R.	N.R.	N.R.	1.1–6	89–97.9	N.R.	N.R.	89
FC-750, CAS 1652-63-7 *	1–4	0.1–1	1–5	1–4	40–44	N.R.	N.R.	90
FC-170C, CAS 29117-08-6 *	3–7	0.5–1.5	3–7	1–5	68	N.R.	N.R.	91
FC-135, CAS 1652-63-7 *	1–4	0.1–2	1–5	1–4	40–44	N.R.	N.R.	92
FC-129, CAS 2991-51-7 *	1–5	N.R.	1–5	1–3	40–60	N.R.	N.R.	93
minimum	0.11	0.03	0.51	0.82	80	0.87	0.1 **	this study
maximum	6	3	7	6	98.9	1 **	1 **	this study

* These products are diluted in solvents and were not taken into account for the lower and higher scenarios.
** The levels of C_9 and C_{10} homologues have not been reported. In our calculations, we assumed a lower and upper bound (0.1% and 1%) as the lower and higher scenarios.

Table S14. Applied, estimated homologue compositions (lower-higher range) in the inventory for *x*FHxSA/E-based products based on reported homologue concentrations in POSF-based products, in % (on a mass basis) of *x*FHxSA/E-based products.

Product	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
*x*FHxSA/E-based products	0.5-7	0.8-6	80-98.9	0.9-1	0.1-1	0.1-1	0.1-1
*x*FDSA/E-based products	0.1-1	0.1-1	0.11-6	0.03-3	0.51-7	0.82-6	80-98.9

S3. Parameterizations for the CliMoChem model

S3.1. Overview of the model

The CliMoChem model was used for the global fate modeling of the emission inventories in this study, and the main details of the model are explained in the section *Modeling and comparison with field measurements* in the main text.

S3.2. Mode of entry and geographical distribution of emissions

The distribution of emissions from CG1 countries were set to follow those applied for POSF-based compounds as used in our previous study[3]. Using the ten latitudinal zones set within the model, 50% of emissions from manufacturing in CG1 were assumed to enter Zone 3 (36–54°N) and the other 50% to Zone 4 (18–36°N). This is based on the location of the two main POSF manufacturing facilities in Antwerp, Belgium and Decatur, Alabama. Use and disposal emissions from products made in CG1 were distributed 90% to Zone 3 and 10% to Zone 4 where most of the products were assumed to have been marketed (e.g., Western Europe, North America, Japan).

The distribution of emissions from PHxSF/PDSF-based product manufacturing in China was based on estimated emissions by Chinese region for POSF-based products[22] (30% to Zone 3 and 70% to Zone 4). The same proportion was used for the latitudinal distribution of emissions from the use and disposal of these Chinese products. The relevant emissions of C_6 and C_{10} substances released (as impurities) from POSF-based products (see our previous study[3]) and from the PHxSF- and PDSF-based emission inventories here were also included in the emissions for the model.

S3.3. Substance properties

Degradation rates, partition coefficients, and fractions of formation were defined in the model for PHxSF, PDSF, PFHxS, PFDS, xFHxSAs, xFHxSEs, xFDSAs, xFDSEs, and intermediates (INT). These were defined at higher and lower levels to cover the range of potential values and support the creation of the higher (fast) and lower (slow) scenarios. Table S15 shows the half-lives used to define the slow and fast degradation rate constants in the model runs, respectively, as well as their corresponding literature references, with details elaborated below. We applied many of the same partition coefficients and degradation rate constants for the substances as used in the model runs focusing on POSF-based homologue compounds from our previous study[3], Schenker et al.[94], and Armitage et al.[17]. However, where information on specific PHxSF and PDSF-based compounds were available, we made adjustments to reflect these specific findings. The degradation rate constants of PFOS and its precursors were often used to represent their C_6 and C_{10} homologues based on previous empirical studies showing that the length of perfluoroalkyl chains has limited influence on the overall degradation.[95,96]

1) The hydrolysis half-lives of POSF/PHxSF/PDSF to PFOS/PFHxS/PFDS are unknown. An early study shows that only 10% of POSF underwent hydrolysis after being heated with water at 180 °C for three days.[58] Hence, it is likely that the half-life in the environment is much longer than three days. We assumed a half-life of 0.5 (fast degradation) and 5 years (slow degradation) for PHxSF and PDSF across all compartments, respectively.

2) PFHxS and PFDS were assumed to not degrade under natural conditions[97] (the half-life was set towards infinity at a value of 10^{19} days).

3) A long half-life of one year in soil was set for xFHxSAs and xFDSAs based on xFOSAs, following the assumption in Gilljam et al., [27] and a short half-life of 13.9 days was set based on measurements in aerobic soil by Avendaño et al. [98] To our best knowledge, studies on the degradation of xFHxSAs or xFDSAs in water were not identified; however, this process was assumed negligible given the substances' tendencies to partition to air and organic matter. The assumed short and long half-lives of xFHxSAs and xFDSAs in air were estimated as a range of 20 to 40 days based on the reported average value of 28.6 days from Martin et al.[99] for xFOSAs.

4) The short and long half-lives used for xFHxSEs and xFDSEs in soil are based on the upper and lower bound experimental results obtained in marine sediments on xFOSEs by Benskin et al.[44] The half-lives of xFHxSEs and xFDSEs in water were taken from two studies completed by 3M on xFOSEs.[100,101] The half-life of xFHxSEs and xFDSEs in air were taken from the results of D'eon et al.[74]

5) Given the inconclusive results of recent studies regarding the ability of PFASs to be metabolized by vegetation,[102,103] we took the possibility into account by assuming vegetative degradation is equal to the degradation rate in water for the fast degradation scenario (Table S16).

6) The half-lives for the intermediate compound (INT) were taken from Schenker et al.[94] and are based on the reaction pathways for the C_8 homologues.

7) Second order rate constants for atmospheric degradation are calculated from these half-lives assuming an OH radical concentration of 7.5×10^5 molecules/cm^3.

Table S15. Half-lives ($t_{1/2}$) in days used to define the slow degradation rate constant set in the model for each substance and compartment. Corresponding references are shown as superscripts. 1.00E+19 = 10^{19}.

Substance	$t_{1/2}$ soil [d]	$t_{1/2}$ water [d]	$t_{1/2}$ air [d]	$t_{1/2}$ vegetation [d]
PHxSF/PDSF	1825	1825	1825	1.00E+19
PFHxS/PFDS	1.00E+19	1.00E+19	1.00E+19	1.00E+19
xFHxSAs/xFDSAs	365 [27]	1.00E+19	40 [99]	1.00E+19
xFHxSEs/xFDSEs	160 [44]	2665 [100,101]	1.8 [74]	1.00E+19
INT	1.00E+19 [94]	1.00E+19 [94]	28.6 [94]	1.00E+19

Table S16. Half-lives ($t_{1/2}$) in days used to define the fast degradation rate constant set in the model for each substance and compartment. Corresponding references are shown as superscripts. 1.00E+19=10^{19}.

Substance	$t_{1/2}$ soil [d]	$t_{1/2}$ water [d]	$t_{1/2}$ air [d]	$t_{1/2}$ vegetation [d]
PHxSF/PDSF	180	180	180	180
PFHxS/PFDS	1.00E+19	1.00E+19	1.00E+19	1.00E+19
xFHxSAs/xFDSAs	13.9 [98]	1.00E+19	20 [99]	1.00E+19
xFHxSEs/xFDSEs	44 [44]	2300 [100,101]	1.8 [74]	2300
INT	1.00E+19 [94]	1.00E+19 [94]	28.6 [94]	1.00E+19

Table S17 shows the partition coefficients and activation energies used as inputs for each substance:

1) The partition coefficients for PHxSF were calculated using COSMOtherm following the method in Wang et al.[73] Results published in Wang et al.[73] were used to define the partition coefficients for PFHxS, as well as for xFHxSEs and xFHxSAs, which were defined by averaging the published values for MeFHxSE and EtFHxSE and of MeFHxSA and EtFHxSA, respectively. The partition coefficients for xFDSEs and xFDSAs were linearly estimated from the reported values of the lower C_4-C_8 homologues as in Wang et al. [73] (all R^2 linear regression coefficient values were greater than 0.98, thus this was taken to be a reasonable approach). Following Armitage et al. in regards to PFOS, PFHxS and PFDS were set to have very low air-water partition coefficients as the sulfonic acids are expected to be in their non-volatile anionic forms in the environment. These values were set to -8, a value at which CliMoChem has been tested previously to handle before causing numerical instability.[17] The octanol-water partition coefficient values for PFHxS and PFDS were

estimated based on a QSAR derived linear regression equation for predominantly hydrophobics published in EU technical guidance documentation on risk assessment (see Table 4 in the EU guidance document[104]) and using experimentally derived values of the sediment organic carbon partition coefficient (K_{oc}) published by Higgins et al. (using an extrapolated value of K_{oc} for PFHxS extrapolated)[105]. Properties for the intermediate substance (INT) were taken from Schenker et al.[94] and as used in the calculations by Armitage et al.[17] for the C_8 homologues. Given a lack of available information and COSMOtherm's inability to complete the estimation calculations, the partition coefficients for PDSF were linearly estimated from the values of the lower C_6 and C_8 homologues calculated by COSMOtherm.

2) The energy of activation (EA) for the degradation reaction is defined by compartment (soil, water, air, and vegetation (veg)). The energy of activation for the degradation reaction in soil, water, and vegetation was set to 30000 J/mol following Armitage et al.[17] for the C_8 homologues. The energy of activation for degradation in air for PHxSF and PFHxS follow Armitage et al. for POSF and PFOS,[17] whereas a value of 5000 for xFOSAs is taken from Wang et al.[106] and is assumed to also represent xFHxSA/Es and xFDSA/Es.

3) The internal energy of phase change between octanol and water (ΔU_{OW}) of -20000 J/mol as well as the values for internal energy of phase change between air and water (ΔU_{AW}) were calculated for the C_8 homologue substances based on the method from MacLeod et al.[107] and assumed to be representative also for the C_6 and C_{10} substances.

Table S17. Model partition coefficients and activation energies for each substance.

Substance	$\log K_{AW}$	$\log K_{OW}$	EA_{SOIL} [kJ]	EA_{WATER} [kJ]	EA_{AIR} [kJ]	EA_{VEG} [kJ]	ΔU_{AW} [J/mol]	ΔU_{OW} [kJ/mol]
PHxSF	3.65	5.77	30	30	15	30	11612	-20
PDSF	5.17	0.23	30	30	15	30	11612	-20
PFHxS	-8	1.98	30	30	15	30	84442	-20
PFDS	-8	4.40	30	30	15	30	84442	-20
xFHxSAs	-1.27	5.17	30	30	5[96]	30	48863	-20
xFHxSEs	-2.94	5.04	30	30	5	30	63069	-20
xFDSAs	0.26	7.69	30	30	5[96]	30	48863	-20
xFDSEs	-1.65	7.47	30	30	5	30	63069	-20
INT	-0.5	5.94	30	30	2.5	30	45213	-20

S3.4. Degradation fractions of formation

We defined the fractions of formation (i.e. yields) from degradation of the substances in the model separately for each environmental compartment (see Table S18):

1) For the air compartment, we follow the simplified atmospheric degradation scheme proposed by Schenker et al.[94] for C_8 homologues as shown in Figure S7. The approach only explicitly considers compounds that are stable for several hours, and it groups similar substances into "blocks", which are defined by an average set of physicochemical properties. In this study, we used the xFOSE, xFOSA, and intermediate (INT) block homologues to represent degradation of xFHxSEs and xFHxSAs to PFHxS, and of xFDSEs and xFDSAs to PFDS. The simplified degradation scheme is shown in part B of Figure S7. The path to PFOS begins with degradation of xFOSE, which leads either to a radical that can further transition to PFOS or to xFOSA that can then degrade to PFOS

via a radical or the INT. The fractions along each step of the pathways are defined in the figure. The overall yield from xFOSE to PFOS ranges and is based on two smog chamber studies on the OH radical oxidation of EtFBSA and MeFBSE, respectively.[74,108] D'Eon et al. reported that after 50% consumption of MeFBSE, a large amount of MeFBSA formed and the concentrations of C_2–C_4 PFCAs and PFBS accounted for approximately 10% and 1% of the loss of MeFBSE, respectively.[74] Martin et al. reported 45% of the EtFBSA transferred into C_2–C_4 PFCAs.[108] Based on this, we used a lower and upper bound of 1% and 4.5% for the overall yields of PFOS from the degradation of xFOSEs, respectively. Using this scheme, the upper and lower yields of degradation from each parent compound to its daughter compound were mathematically solved for this overall range (see Table S18).

2) For the soil compartments (soil and vegetative soil), the yield range for xFHxSE/xFDSE to xFHxSA/ xFDSA and PFHxS/PFDS is based on empirical observations in active marine sediments at 4°C and 25°C after 120 days by Benskin et al.[44] for the C_8 homologues. The higher yield for xFHxSA/ xFDSA to PFHxS/PFDS is based on empirical observation in aerobic soil after 182 days by Avendaño et al.[98] for C_8 homologues, whereas a lower yield of 0.1% was assumed given the lack of any empirical studies.

3) For the snow and ice compartments, all yields were set to zero since degradation is assumed to not occur therein. For the water compartment, we used the same yields as those for the air compartment, as degradation in both media involve OH-radical-mediated pathways with possible, unknown differences. For the vegetation compartment, the higher yield was set equal to that of water following the uncertainty regarding degradation in vegetation that was discussed previously. All degraded PHxSF and PDSF was set to yield PFHxS and PFDS, respectively.

Figure S7. The degradation scheme of FTOH and POSF-based precursors in the atmosphere. (A) a summary of the key reactions with intermediate degradation products, (B) the simplified degradation scheme applied in the model of the present study. Substances in parentheses were not explicitly modeled. Substances in rectangles have direct emissions into the environment. Numbers next to an arrow represent fractions of formation. Adapted with permission from reference 94. Copyright 2008, American Chemistry Society.
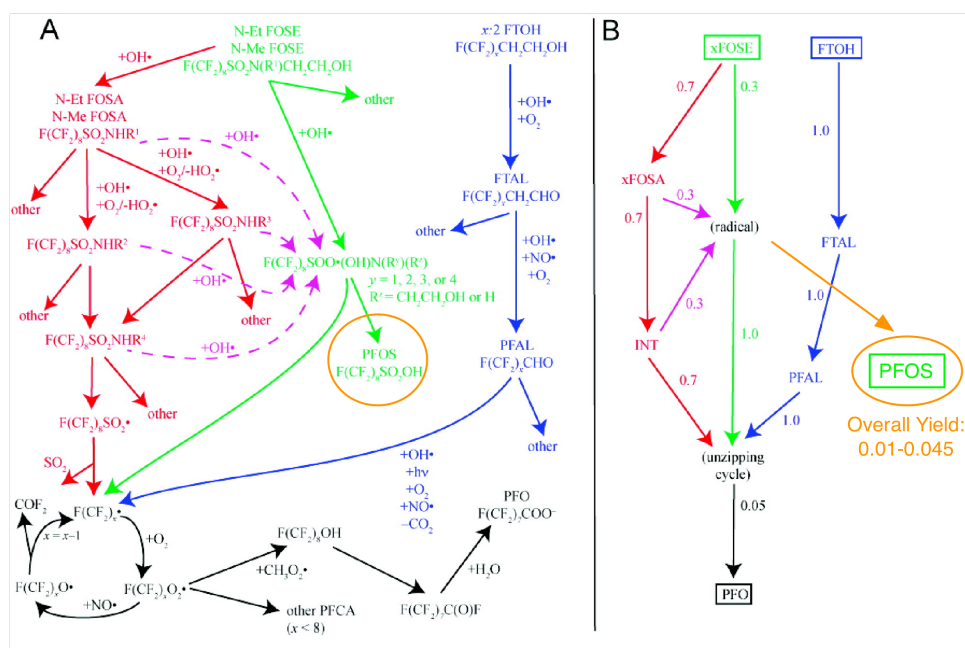
Table S18. Estimated fractions of formation (i.e. yields in mol%) for degradation of each parent compound to its daughter compound.

Environmental Compartment	Parent Compound	Daughter Compound	Lower Yield	Higher Yield
Air	*x*FHxSA/*x*FDSA	INT	0.7	0.7
Air	*x*FHxSA/*x*FDSA	PFHxS/PFDS	0.00456	0.02055
Air, Water	*x*FHxSE/*x*FDSE	*x*FHxSA/*x*FDSA	0.7	0.7
Air, Water	*x*FHxSE/*x*FDSE	PFHxS/PFDS	0.00456	0.02055
Air	INT	PFHxS/PFDS	0.00456	0.02055
Soil	*x*FHxSA/*x*FDSA	PFHxS/PFDS	0.001	0.04
Soil	*x*FHxSE/*x*FDSE	PFHxS/PFDS	0.0044	0.12
Soil	*x*FHxSE/*x*FDSE	*x*FHxSA/*x*FDSA	0.017	0.064
Vegetation	*x*FHxSE/*x*FDSE	*x*FHxSA/*x*FDSA	0	0.7
Vegetation	*x*FHxSE/*x*FDSE	PFHxS/PFDS	0	0.02055
Vegetation	PHxSF/PDSF	PFHxS/PFDS	0	1
Air, Soil, Water	PHxSF/PDSF	PFHxS/PFDS	1	1

S3.5. Model runs

In order to identify the potential ranges of modelled environmental concentrations, model runs with different combinations of parameters were conducted taking each substance and environmental compartment into account. Table S19 describes the make-up of the combinations of the higher and lower emission inventory scenarios with the faster or slower degradation and lower or higher yields needed to create the higher and lower bounds of modeled environmental concentrations. In addition, these scenarios were each run twice to consider the uncertain non-polymeric:polymeric ratios for PHxSF-based products in CG1 (20%:80% and 80%:20%) (see Section S2.1.3.1).

The lower emissions inventory was developed using the lower range of all input variables assuming that 10% are released during the use and disposal phase. The higher emission inventory was developed using the higher range of all input variables and assuming that 100% of the produced compounds are released into the environment during the use and disposal phase.

Table S19: Combinations of model parameter sets used to define the higher and lower scenarios of modeled environmental concentrations for PFHxS and PFDS.

Modeled Scenarios	For PFHxS	For PFDS
Higher	higher inventory (20% or 80% polymeric in CG1), faster degradation of precursors, higher yield	higher inventory, faster degradation of precursors, higher yield
Lower	lower inventory (20% or 80% polymeric in CG1), slower degradation of precursors, lower yield	lower inventory, slower degradation of precursors, lower yield

S4. Comparison to field measurements

To evaluate the emission inventory, modeled environmental concentrations of PFHxS and PFDS in ocean water were compared to reported ocean water measurements in literature. The field measurements included in the comparison cover multiple regions of the world, and many were completed during sea sampling campaigns on research vessels. Only measured sites that are representative of background concentrations were considered. Sites on industrialized land, surrounded by industrialized land (e.g., the North, Baltic, and South China Seas), near known point sources, or suspected to have been affected by abnormal events were not considered. Abnormal events, such as floods, have been previously reported to affect measured concentrations.[109] One study[110] found extraordinarily high concentrations of PFHxS in oceanic surface water during a sampling cruise in the Southern Atlantic Ocean. Given that these measurements were anomalously magnitudes larger than concentrations reported by other studies in the same area, these sampling points were not considered for our model evaluation.

Generally, very limited published information regarding measured concentrations of PFHxS and PFDS in the environment were found, and only one study was identified that reports concentrations of PFDS in background ocean water. All studies reporting potentially representative background concentrations were considered, but only reported measurements above the reported limit of detection (LOD) and, where reported, limit of quantification (LOQ) of the study were plotted for comparison with the model. The field studies considered for PFHxS[111–120] and PFDS[121] are listed in the references.

One study[122] provides atmospheric field measurements for PFHxS concentrations across various sampling sites, including a few background sites, within the Global Atmospheric Passive Sampling (GAPS) network. PFDS was also targeted by this study, however concentrations were found to be below the limit of detection at all sites. Although they are a promising tool, passive air samplers are still in development with sampling and analytical methods still being significantly improved and revised[123]. Compared to measurements from active air samplers, which have a known air sampling rate and are not influenced by meteorological conditions, passive air sampling "may be acceptable to identify large differences in concentration gradients on global scales (e.g., semi-quantitative/order of magnitude differences), however they are not able to provide accurate concentrations for a broad set of PFASs."[123] They are therefore not yet seen as an accurate source for comparison with the emission inventory model results presented here. However, as an exercise, the modeled atmospheric concentrations from the developed inventory were compared with sites from this field study, and these results are included in Section S5.2.

There is some additional uncertainty with regard to the amount of PFASs that have been transported into the deep ocean from the surface ocean. However, this amount cannot yet be quantified, as suggested by a recent study.[124] This is a topic for further research. Inland reservoirs are noted to also potentially delay a fraction of emitted chemicals in the inventory from reaching the oceans. However, the fraction of emissions that could enter these reservoirs is unknown, and the resulting delay this could have on global background concentrations is also unclear. Given the low geographical resolution of the CliMoChem model and the widespread use of the various types of related chemical products with different life cycles of several decades (and insufficient information available in the public domain to provide an overview on this), this potential delay cannot explicitly be taken into account by the model.

However, the authors believe that the current set up of the inventory and model does provide an adequate range of results that likely covers this uncertainty. This is primarily due to the very wide applied fractional emission range of 10% (lower bound) to 100% (higher bound) representing the use and disposal phase. For example, if only a small fraction (10%) is assumed to be emitted from a product, some part of the remaining 90% may represent a certain amount of the chemical that has been released but significantly

delayed or permanently trapped in such reservoirs. This could certainly be improved when further details are known from future research, particularly with regard to a better regional/local resolution of emissions.

Using the inventory, the CliMoChem model could potentially also be run to predict environmental concentrations of the C_9 homologue perfluorononanesulfonic acid (PFNS; CAS number 68259-12-1) based on its emissions as an impurity in C_{10} products. A single literature study was found that reports PFNS concentrations in the Arctic Ocean off the coast of Greenland; however, the study mentions that these detected levels were likely due to applications in Iceland and therefore not representative of background levels. Analytical standards for PFNS were also reported to not have been available for use at the time of the study. Therefore, this comparison with potential PFNS model results could not be made at this time.

S5. Additional results that supplement those included in the main publication

S5.1. Calculation on a homologue basis

Table S20. Global emissions of C$_4$–C$_{10}$ PFSAs, *x*FASA/Es, and PASFs from the life cycle of PHxSF-based products in the years 1958-2002, 2003-2015 and post 2015 in tonnes. Also shown is the total amount of emissions when including the emissions (as impurities) from PDSF-based products (from the developed emission inventory in this study) and also from emissions (as impurities) from Sulfluramid pesticide products in Brazil (from the developed emission inventory in our previous study[3]). Where applicable, the different results assuming 20% of manufactured PHxSF-based products in CG1 are polymers are shown, and results associated with the assumption that 80% of manufactured products in CG1 are polymers are shown in parentheses. All results are rounded to the nearest tonne.

PFSAs (In PFHxS equivalents)

C$_n$ PFSA	1958-2002 [t]		2003-2015 [t]		2016-2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C$_4$ PFBS	2	24	0	0	0	0	2	24
C$_5$ PFPeS	1	19	0	0	0	0	1	19
C$_6$ PFHxS	92	393	5	33	1	22	98	448
C$_6$ PFHxS*	92	401	5	33	1	22	98	456
C$_7$ PFHpS	0	5	0	0	0	0	0	5
C$_8$ PFOS	0	5	0	0	0	0	0	5
C$_9$ PFNS	0	5	0	0	0	0	0	5
C$_{10}$ PFDS	0	5	0	0	0	0	0	5

_x_FASA/Es (In _x_FHxSA/Es equivalents)

C$_n$ _x_FASA/Es	1958-2002 [t]		2003-2015 [t]		2016-2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C$_4$ FBSA/Es	2 (3)	521 (320)	1 (3)	43 (159)	1 (3)	19 (74)	4 (9)	583 (553)
C$_5$ FPeSA/Es	3 (4)	447 (274)	1 (4)	37 (136)	1 (5)	16 (64)	5 (13)	500 (474)
C$_6$ FHxSA/Es	299 (437)	7364 (4521)	112 (425)	707 (2342)	118 (458)	339 (1128)	529 (1320)	8410 (7991)
C$_6$ FHxSA/Es*	300 (438)	7372 (4529)	113 (427)	732 (2367)	118 (458)	373 (1163)	531 (1323)	8477 (8059)
C$_7$ FHpSA/Es	3 (5)	74 (46)	1 (5)	6 (23)	1 (5)	3 (11)	5 (15)	83 (80)
C$_8$ FOSA/Es	0 (1)	74 (46)	0 (1)	6 (23)	0 (1)	3 (11)	0 (1)	83 (80)
C$_9$ FNSA/Es	0 (1)	74 (46)	0 (1)	6 (23)	0 (1)	3 (11)	0 (1)	83 (80)
C$_{10}$ FDSA/Es	0 (1)	74 (46)	0 (1)	6 (23)	0 (1)	3 (11)	0 (1)	83 (80)

PASFs (In PHxSF equivalents)

C$_n$ PASF	1958-2002 [t]		2003-2015 [t]		2016-2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C$_4$ PBSF	2	5	0	0	0	0	2	5
C$_5$ PPeSF	1	4	0	0	0	0	1	4
C$_6$ PHxSF	78	78	4	4	0	2	82	84
C$_6$ PHxSF*	78	78	4	4	0	2	82	84
C$_7$ PHpSF	0	1	0	0	0	0	0	1
C$_8$ POSF	0	1	0	0	0	0	0	1
C$_9$ PNSF	0	1	0	0	0	0	0	1
C$_{10}$ PDSF	0	1	0	0	0	0	0	1

* Also including emissions with regard to those contained in PDSF-based products and EtFOSA in Brazil as impurities.

Table S21. Global emissions of C$_4$–C$_{10}$ PFSAs and PASFs from the life cycle of PDSF-based products in the years 1958-2002, 2003-2015 and post 2015 in tonnes. Also shown is the total amount of emissions when including the emissions (as impurities) from PHxSF-based products (from the developed emission inventory in this study) and also from emissions (as impurities) from Sulfluramid pesticide products (from the developed emission inventory in our previous study[3]). Where applicable, the different results assuming 20% of manufactured PHxSF-based products in CG1 are polymers are shown, and results associated with the assumption that 80% of manufactured PHxSF-based products in CG1 are polymers are shown in parentheses. All results are rounded to the nearest tonne.

PFSAs (In PFDS equivalents)

C$_n$ PFSA	1958-2002 [t]		2003-2015 [t]		2016-2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C$_4$ PFBS	0	4	0	0	0	0	0	4
C$_5$ PFPeS	0	4	0	0	0	0	0	4
C$_6$ PFHxS	0	13	0	0	0	0	0	13
C$_7$ PFHpS	0	16	0	0	0	0	0	16
C$_8$ PFOS	1	20	0	0	0	0	1	20
C$_9$ PFNS	2	48	0	1	0	0	2	49
C$_{10}$ PFDS	37	363	0	6	0	1	37	370
C$_{10}$ PFDS**	37 (37)	370 (370)	0 (0)	6 (6)	0 (0)	1 (1)	38 (38)	377 (377)

xFASA/Es (In xFDSA/Es equivalents)

C$_n$ xFASA/Es	1958-2002 [t]		2003-2015 [t]		2016-2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C$_4$ FBSA/Es	0	0	0	0	0	0	0	0
C$_5$ FPeSA/Es	0	0	0	0	0	0	0	0
C$_6$ FHxSA/Es	0	0	0	0	0	0	0	0
C$_7$ FHpSA/Es	0	0	0	0	0	0	0	0
C$_8$ FOSA/Es	0	0	0	0	0	0	0	0
C$_9$ FNSA/Es	0	0	0	0	0	0	0	0
C$_{10}$ FDSA/Es	0	0	0	6	0	5	0	11
C$_{10}$ FDSA/Es**	1 (1)	110 (68)	1 (2)	20 (44)	0 (0)	12 (12)	2 (3)	142 (124)

PASFs (In PDSF equivalents)

C$_n$ PASF	1958-2002 [t]		2003-2015 [t]		2016-2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C$_4$ PBSF	0	0	0	0	0	0	0	0
C$_5$ PPeSF	0	0	0	0	0	0	0	0
C$_6$ PHxSF	0	0	0	0	0	0	0	0
C$_7$ PHpSF	0	0	0	0	0	0	0	0
C$_8$ POSF	0	0	0	0	0	0	0	0
C$_9$ PNSF	0	1	0	0	0	0	0	1
C$_{10}$ PDSF	4	4	0	0	0	0	4	4
C$_{10}$ PDSF**	4 (4)	6 (6)	0 (0)	0 (0)	0 (0)	0 (0)	4 (4)	6 (6)

** Also including emissions with regard to those contained in PHxSF-based products and EtFOSA in Brazil as impurities.

S5.2. Additional modeled environmental concentrations

Figure S8, Figure S9, and Figure S10 show modeled environmental concentrations of PFHxS and PFDS in ocean water in comparison to reported field concentrations for modeled zones and scenarios not included in the main publication. Table S22 shows details regarding the number of field measurements within the modeled range.
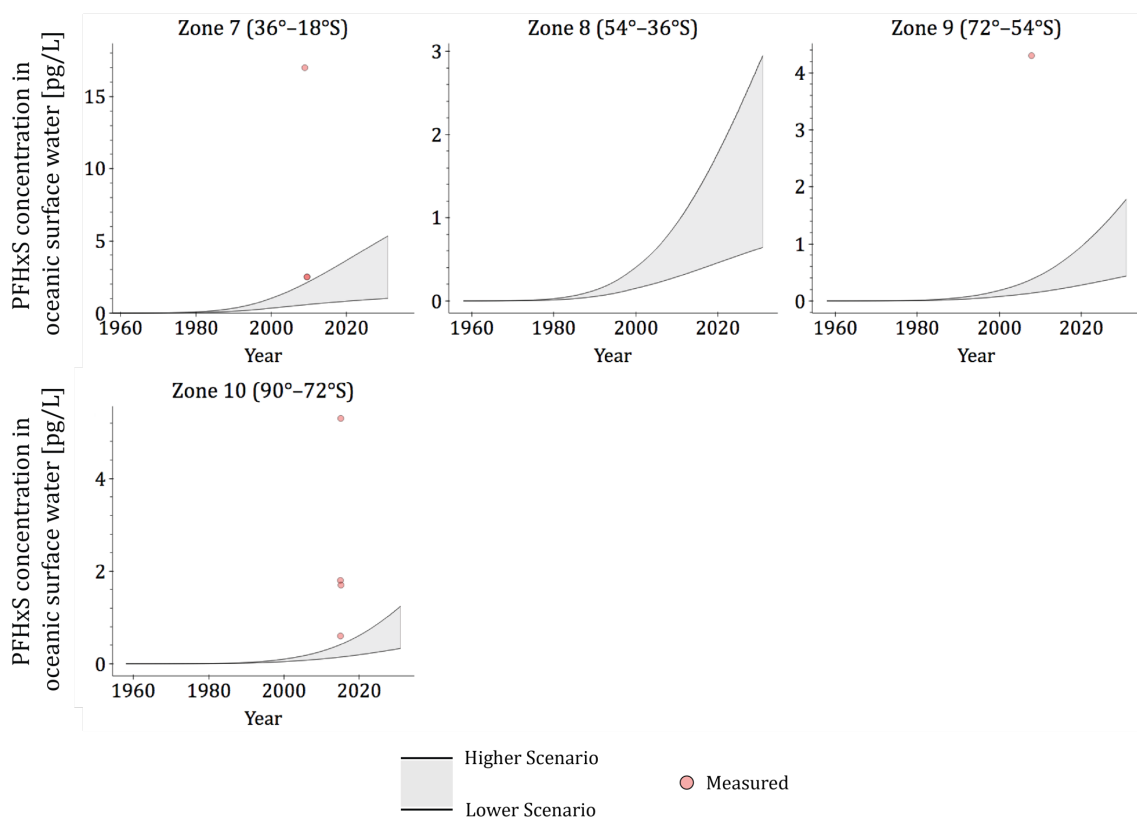

Figure S8. Modeled vs. measured field concentrations[111–120] for PFHxS in oceanic surface water between 1958–2030 in Zones 7–10. Results from the higher and lower model scenarios are shown. Results shown here and in the figure in the main text assume that 80% of manufactured PHxSF-based products in CG1 are polymers. See Fig. 1 in the main text for results from Zones 1-6.
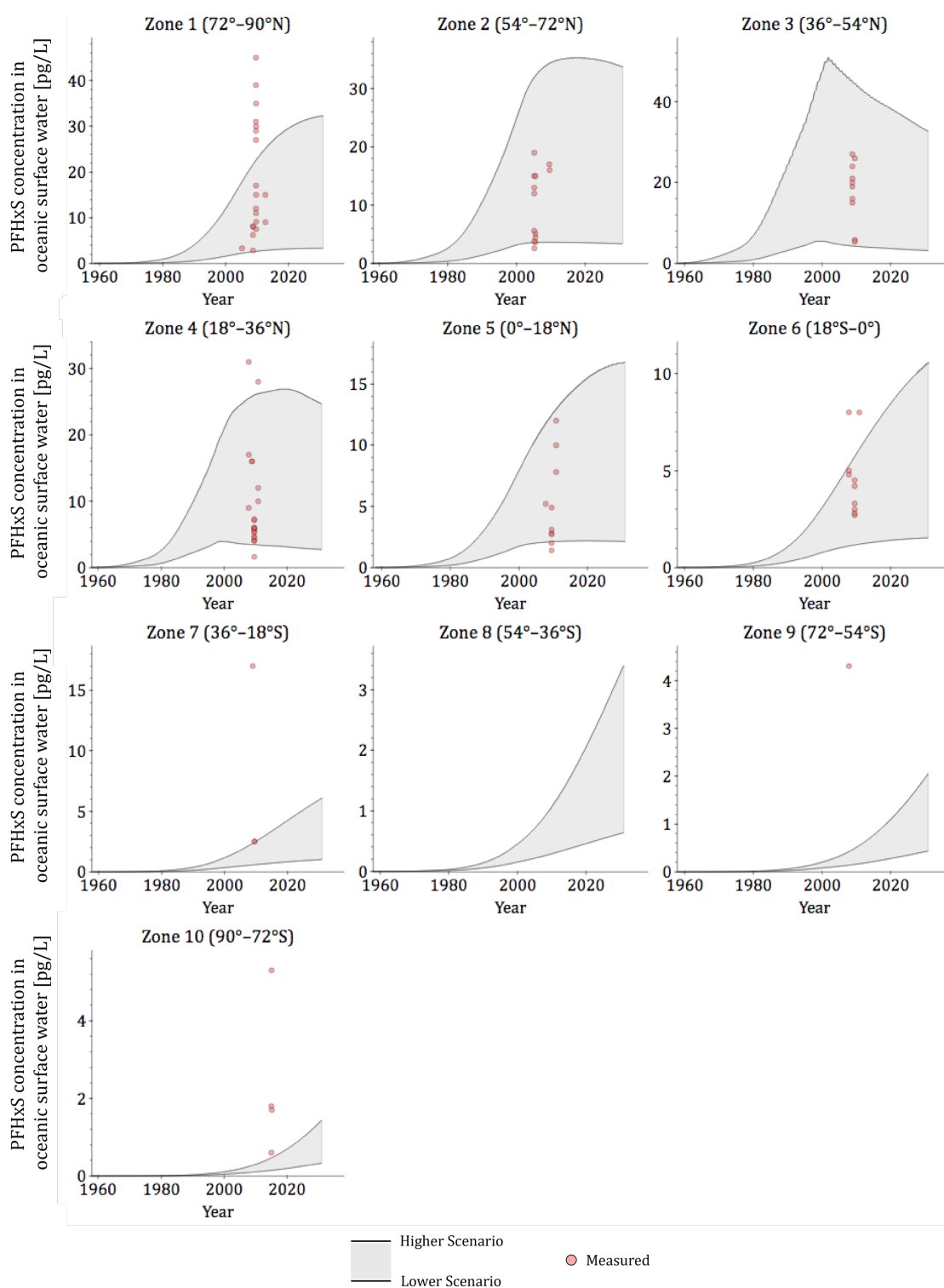
Figure S9. Modeled vs. measured field concentrations[111–120] for PFHxS in oceanic surface water between 1958–2030 in Zones 1–10. Results from the higher and lower model scenarios are shown. Results shown here assume that 20% of manufactured PHxSF-based products in CG1 are polymers.
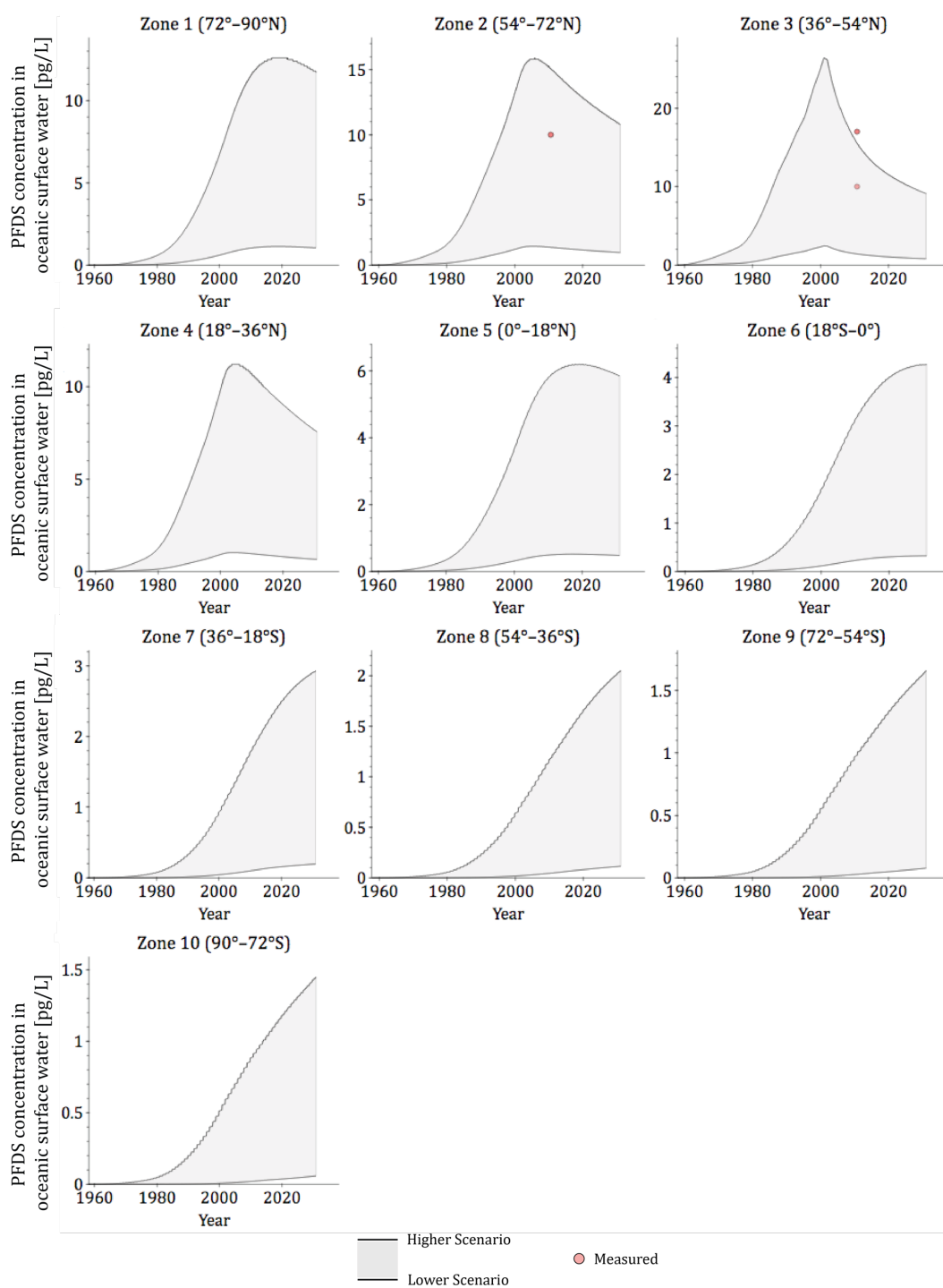
Figure S10. Modeled vs. measured field concentrations[121] for PFDS in oceanic surface water between 1958–2030 in Zones 1–10. Results from the higher and lower model scenarios are shown. Results assume that 80% of the included C$_{10}$ emissions from impurities in PHxSF-based products in CG1 are polymers (80% polymer scenario). Emissions of C$_{10}$ impurities in PHxSF-based products assuming that 20% of the products in CG1 are polymers differ by less than 1% from the 80% polymer scenario. This influence on the model results is therefore much less than that caused by other input uncertainties, and the results from this scenario are consequently not included here.

Table S22. The numbers of reported measurements of PFHxS and PFDS in each zone that were compared with modeled environmental concentrations. The numbers of the measurements that were below the limit of quantification (LOQ) of the corresponding study (i.e. non-detects) are shown in parentheses. The percentage values reflect the fractions of reported measurements above the LOQ (i.e. detects) that are within the range of modeled environmental concentrations in the corresponding zones.

	PFHxS			PFDS	
	Number of measurements (of which non-detects)	Detects within modeled range; 20% polymer CG1	Detects within modeled range; 80% polymer CG1	Number of measurements (of which non-detects)	Detects within modeled range
Zone 1	41 (21)	65%	65%	7 (7)	-
Zone 2	30 (17)	92%	85%	10 (8)	100%
Zone 3	15 (5)	100%	100%	3 (0)	33%
Zone 4	24 (3)	86%	90%	0 (0)	-
Zone 5	15 (5)	80%	70%	0 (0)	-
Zone 6	19 (9)	80%	60%	0 (0)	-
Zone 7	10 (7)	0%	0%	0 (0)	-
Zone 8	15 (15)	-	-	0 (0)	-
Zone 9	24 (23)	0%	0%	0 (0)	-
Zone 10	26 (22)	0%	0%	0 (0)	-

Figure S11 shows atmospheric PFHxS field measurements for background sites included in a recently published study[122] compared to the modeled concentrations over time by our study.

It can be seen that the field measurements are all above the modeled concentrations. Passive air sampling as a measurement tool is still in development with methods still being improved and revised[123]. Measurements from passive air sampling are therefore not yet seen as a source for accurate comparison with the model presented here, and this comparison is therefore not further discussed in this study. For more discussion on this, see Section S4.
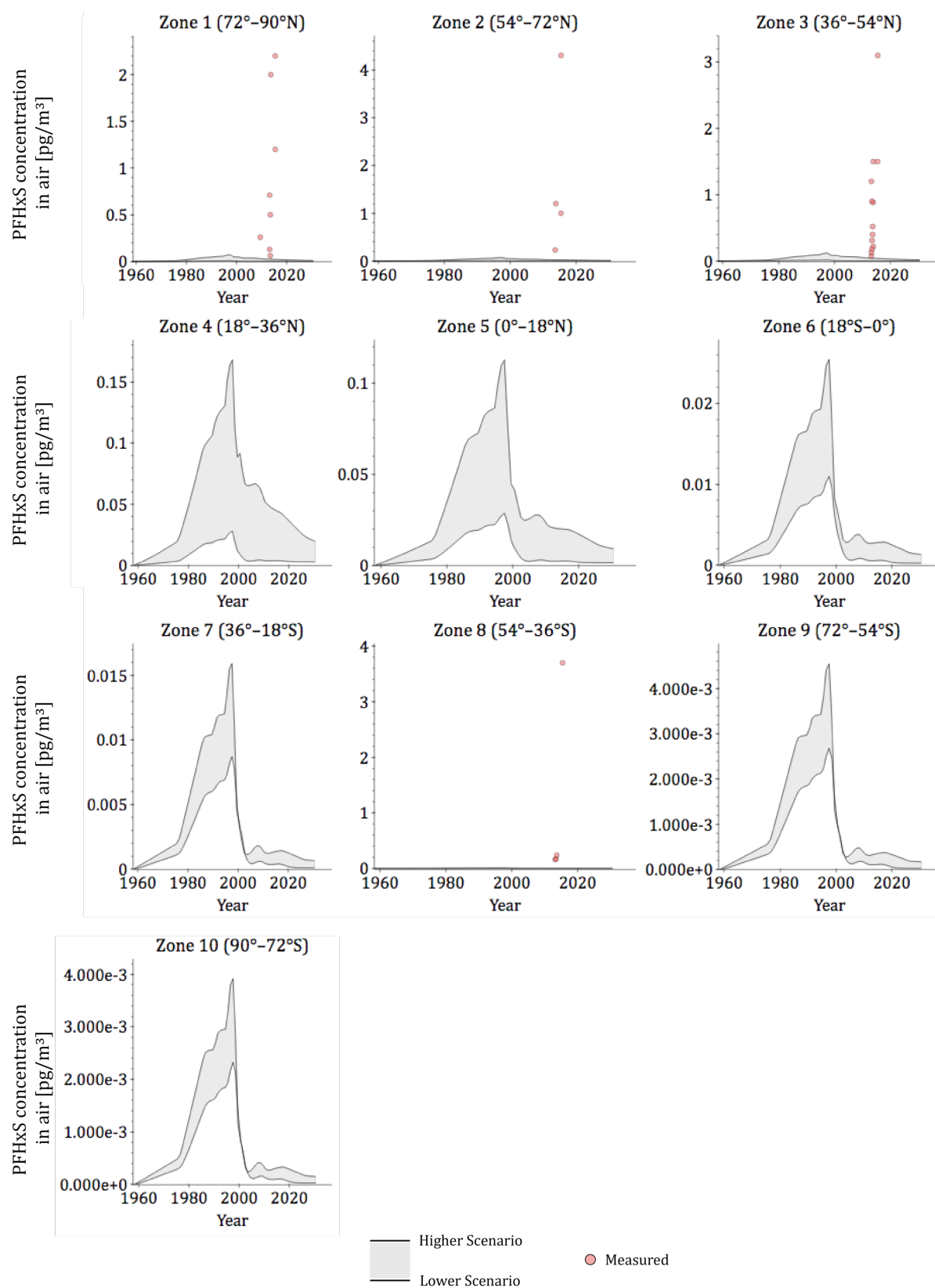
Figure S11. Modeled vs. measured[122] field concentrations for PFHxS in air between 1958–2030 in Zones 1–10. Results are average annual concentrations from the higher and lower model scenarios, and they assume that 80% of the included C_6 emissions from impurities in PHxSF-based products in CG1 are polymers (80% polymer scenario).

S5.3. Review and uncertainty scores of individual parameters

As there are different levels of uncertainties attributed to the various source categories, we introduced a scoring system to indicate the level of uncertainty of the parameters considered within the inventory calculations and modeling (see Table S23): 0 to 1 represents low uncertainty (reported estimates and/or measured emissions which have been evaluated for their accuracy); 1 to 2 represents medium uncertainty (expert estimates or measured emissions which have not been (fully) evaluated); 2 to 3 represents high uncertainty (crude estimates or extrapolated emissions).

Table S23. Origin of parameters used in this work to estimate PFSA emissions from PHxSF and PDSF-based products. @ = at; ASMP = assumption; CG1 = Japan, Western Europe and the United States; Deg = degradation; Emis = emissions; Extrapol = extrapolation; Fig = Figure; Inconc = inconclusive; Interpol = interpolation; MFG = manufacturing; Prod = production; RPT = reports; SI = Supporting Information; Tab = Table; ($\uparrow$) = overestimation; ($\downarrow$) = underestimation; ($\updownarrow$) = inconclusive. Uncertainty score A/B = uncertainty level in 1995–2002/uncertainty level in 2003–2015.

QUANTIFICATION STEP	PARAMETERS	1951–2002	2003–2030	UNCERTAINTY SCORES	LOCATION IN THIS DOCUMENT
STEP 1.1 PROD VOLUME	Prod volume in CG1	Company's RPT + Extrapol	OECD RPT + ASMP + Extrapol	1.5/2.0	Table S5, Table S6
	Prod volume in China	Not applicable	Company's RPT + articles + ASMP + Extrapol, intentional production unclear and not considered ($\downarrow$)	-/2.5	Table S5, Table S6
STEP 1.2 EMIS @ MFG	Emission factors in CG1	Extrapolation from company's mass flow studies of C_8 ($\downarrow$)	Extrapolation from company's reduction RPT of C_8 ($\downarrow$)	2.5/2.5	Table S7
	Emission factors in China	Not applicable	ASMP: same as before 1998 in CG1 ($\updownarrow$)	-/2.5	Table S7
STEP 1.3 EMIS @ USE & DISPOSAL	Average lifetime of non-polymeric products	ASMP: 2 years	ASMP: 2 years	2.0/2.0	Section S2.1.3.2
	Average lifetime of polymeric products	ASMP: 10 years	ASMP: 10 years	2.0/2.0	Section S2.1.3.2
	Non-polymeric:polymeric ratio in CG1	ASMP	ASMP	3.0/3.0	Section S2.1.3.1
	Non-polymeric:polymeric ratio in China	Not applicable	articles + Extrapol	-/1.5	Section S2.1.3.1
	Unreacted residual levels in products	Company's RPT + Extrapol	Company's RPT + Extrapol	2.5/2.5	Table S10
	Proportions of PFHxS/PFDS in CG1	ASMP: 1-5% (PFHxS), 100% (PFDS)	ASMP: 1-5% (PFHxS), 100% (PFDS)	2.5/2.5	Section S2.1.3.3

Table S23 (continued). Origin of parameters used in this work to estimate PFSA emissions from PHxSF and PDSF-based products.

QUANTIFICATION STEP	PARAMETERS	1951–2002	2003–2030	UNCERTAINTY SCORES	LOCATION IN THIS DOCUMENT
STEP 1.3 EMIS @ USE & DISPOSAL	Proportions of PFHxS/PFDS in China	Not applicable	UNEP RPT+ articles + Extrapol	-/1.5	Section S2.1.3.3
	Emissions factors of PFHxS/PFDS in products to water	ASMP: 10-100%	ASMP: 10-100%	3.0/3.0	Section S2.1.3.5
STEP 2. EMIS OF PFSA IMPURITIES	PFCA impurity levels in products	Articles + Extrapol ($\updownarrow$)	Articles + Extrapol ($\updownarrow$)	2.5/2.5	Section S2.1.3.4
	Emission factors of PFSA impurities	ASMP: 100%	ASMP: 100%	2.5/2.5	-
STEP 3. EMIS OF PRECURSORS	Emission factors of residuals in non-polymeric products	ASMP: 10-100% (during use & disposal), 90-99% (CG1) and 90-95% (China) are complex molecules, range of 27-100% of complex molecules degrade into precursors	ASMP: 10-100% (during use & disposal), 90-99% (CG1) and 90-95% (China) are complex molecules, range of 27-100% of complex molecules degrade into precursors	3.0/3.0	Section S2.1.3.5
	Emission factors of residuals in polymeric products	ASMP: 10-100% to air	ASMP: 10-100% to air	2.5/2.5	-
	Degradation of polymeric products (PHxSF-based) and release of PFHxS precursors	ASMP: degradation half-life range of 10-100 years, precursor release into air (20%), water (40%), and soil (40%)	ASMP: degradation half-life range of 10-100 years, precursor release into air (20%), water (40%), and soil (40%)	3.0/3.0	Section S2.1.3.7
	Homologue distribution of PHxSF/PDSF-based products	Articles + Extrapol ($\updownarrow$)	Articles + Extrapol ($\updownarrow$)	2.5/2.5	Table S12
	Homologue distribution of xFHxSA/E-based products	Articles + Extrapol ($\updownarrow$)	Articles + Extrapol ($\updownarrow$)	2.5/2.5	Table S14
	Degradation rate constants and fractions of formation	Articles + Company's RPT +ASMP: based on C_8 homologues	Articles + Company's RPT +ASMP: based on C_8 homologues	2.0/2.0	Table S15, Table S16, Table S18
	Partition coefficients and activation energies	Articles +ASMP: based on C_8 homologues	Articles +ASMP: based on C_8 homologues	2.0/2.0	Table S17

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