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Toward a Comprehensive Global Emission Inventory of C_4–C_{10} Perfluoroalkanesulfonic Acids (PFSAs) and Related Precursors: Focus on the Life Cycle of C_8-Based Products and Ongoing Industrial Transition

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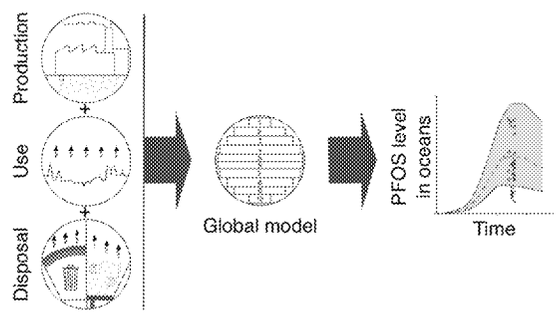
Supporting Information

ABSTRACT: Here a new global emission inventory of C_4–C_{10} perfluoroalkanesulfonic acids (PFSAs) from the life cycle of perfluorooctanesulfonyl fluoride (POSF)-based products in 1958–2030 is presented. In particular, we substantially improve and expand the previous frameworks by incorporating missing pieces (e.g., emissions to soil through land treatment, overlooked precursors) and updating parameters (e.g., emission factors, degradation half-lives). In 1958–2015, total direct and indirect emissions of perfluorooctanesulfonic acid (PFOS) are estimated as 1228–4930 tonnes, and emissions of PFOS precursors are estimated as 1230–8738 tonnes and approximately 670 tonnes for *x*-perfluorooctanesulfonamides/sulfonamido ethanols (*x*FOSA/Es) and POSF, respectively. Most of these emissions occurred between 1958 and 2002, followed by a substantial decrease. This confirms the positive effect of the ongoing transition to phase out POSF-based products, although this transition may still require substantial time and cause substantial additional releases of PFOS (8–153 tonnes) and *x*FOSA/Es (4–698 tonnes) in 2016 to 2030. The modeled environmental concentrations obtained by coupling the emission inventory and a global multimedia mass-balance model generally agree well with reported field measurements, suggesting that the inventory captures the actual emissions of PFOS and *x*FOSA/Es for the time being despite remaining uncertainties. Our analysis of the key uncertainties and open questions of and beyond the inventory shows that, among others, degradation of side-chain fluorinated polymers in the environment and landfills can be a long-term, (potentially) substantial source of PFOS.



INTRODUCTION

Long-chain perfluoroalkanesulfonic acids (PFSAs, $C_nF_{2n+1}SO_3H$, $n \geq 6$), in particular perfluorooctanesulfonic acid (PFOS, C_8 PFSA), and their precursors have been produced in large amounts with widespread use in numerous consumer and industrial applications since the 1950s.[1–4] Since the late 1990s, they have attracted attention as global contaminants for being highly persistent,[5–7] bioaccumulative,[8] toxic,[9] and ubiquitously present in the global abiotic environment,[10] biota,[11] and humans.[12] Due to increasing public concern about their hazardous properties, 3M (the then major global producer) phased out its production of products containing C_6, C_8 and C_{10} PFSAs and their precursors in 2000–2002.[13] Following 3M's phase-out and other regulatory efforts such as the European Union (EU) Directive on restricting the marketing and use of PFOS,[14] there has been an ongoing industrial transition worldwide: while producers in developed countries started phasing out PFOS and related chemicals, some producers in China and Brazil scaled up production to fill in the market gaps remaining.[1] In 2009, PFOS and perfluorooctanesulfonyl fluoride (POSF) were listed in Annex B (restriction of production and use) of the Stockholm Convention on Persistent Organic Pollutants. Consequently, the parties to the Convention have been working toward a global phase-out of PFOS and related chemicals, although a clear timeline has not yet been set.[15]

In order to characterize human and environmental exposure to long-chain PFSAs over time and to assess the effectiveness of phase-out programs, it is important to understand their levels and trends in the environment. This can be achieved via long-term environmental monitoring, including biomonitoring. However, these programs are resource intensive (including manpower and finances), and the results cannot always be easily interpreted and extrapolated, both retro- and prospectively. For example,

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Table 1. Overview of the Methodology and Data Sources Considered in the Present Study and by Paul et al.[3] and Armitage et al.[4]

		present study	Paul et al. (2009)[3]	Armitage et al. (2009)[4]
production before 3M's phase-out	period	1958–2002	1970–2002	1957–2002
	data source	3M's reports	3M's reports	3M's reports
production after 3M's phase-out	period	2003–2015 and post 2015	2003–2012	2003–2010
	data source	peer-reviewed articles + national reports + assumptions	assumptions	national reports + assumptions
emissions from production	POSF	included	not included	not included
	PFOS	air, wastewater, and land treatment	air and wastewater	air and wastewater
	precursors	air, wastewater, and land treatment	air and wastewater	air and wastewater
	data source	3M's reports	3M's reports	3M's reports
emissions from product use and disposal	PFOS	intentional use + impurities + degradation of precursors	impurities only	intentional use + impurities + degradation of some precursors
	precursors	intentional use + residuals (degradation of polymers not included)	residuals (degradation of polymers not included)	residuals (degradation of polymers not included)
	product life span	included	not included	included
	data source	peer-reviewed articles +3M's reports + assumptions	3M's reports + assumptions	3M's reports + assumptions
calculation on homologue basis		included	not included	not included

although human biomonitoring data show downward trends for PFOS following 3M's phase-out,[16,17] abiotic environmental media and wildlife biomonitoring data show no clear temporal trends for PFOS and related substances.[18] Recently, it has been recommended that long-term (bio)monitoring programs should be accompanied by complementary assessments using, for example, environmental fate models.[19]

A comprehensive data set of historic and possible future emissions is a key model input for estimating environmental concentrations that can then be compared with monitoring data. In 2009, two first emission inventories of PFOS (and its precursors) from the life cycle of products based on POSF derivatives (i.e., C_8-based products, hereafter referred to as "*POSF-based products*") were published by Paul et al.[3] and Armitage et al.[4] Both studies are based on reported and assumed production volumes and self-estimated emission factors throughout the product life cycle, with some differences in assumptions (for a methodology comparison, see Table 1). Following the new information and knowledge published in the literature and reported to the Stockholm Convention after 2009, the methodology and content of these two previous inventories[3,4] are no longer complete and up-to-date.

Here, in light of new knowledge and data, we aim to improve on and expand the understanding of emissions of C_4–C_{10} PFSAs and their precursors from previous studies,[3,4] including a focus on better quantifying emissions during the ongoing industrial transition. In particular, we adopt a new methodology[1] recently developed for the global emissions of perfluoroalkylcarboxylic acids (PFCAs), and we conduct a new, thorough evaluation of relevant information. In brief, new elements include (1) revised production and use volumes, (2) expanded emission factors (e.g., new inclusion of emissions of POSF and emissions to soil), (3) expanded estimation regarding PFOS precursors (e.g., new inclusion of those precursors used as intentional ingredients and new degradation schemes considered), and (4) calculation of emissions on a homologue basis. For an overview of major differences in the current methodology compared to the previous studies, see Table 1.

Our new emission inventory is presented in the section Estimated global sum emissions from POSF-based products. We further evaluate the inventory by combining it with a global multimedia mass-balance model, CliMoChem,[20–23] and by comparing modeled environmental concentrations/fluxes of PFOS and its precursors with reported field measurements (see sections on modeled vs measured environmental concentrations/fluxes). The present study focuses on POSF-based products only, whereas emissions of C_4–C_{10} PFSAs and their precursors from the life cycle of other products based on chemicals derived from perfluoro-butane, -hexane and -decane sulfonyl fluorides (i.e., C_4-, C_6-, and C_{10}-based products)[2] cannot currently be estimated due to a lack of public, quantitative information. This has a negligible impact on our estimates of PFOS and its precursors, but it may be relevant to other homologues; thus, estimates of homologues other than PFOS and its precursors presented here are a minimum scenario and cannot be directly used to compare with field measurements.

We evaluate key uncertainties and open questions in our emission inventory and make recommendations to address them. In particular, we perform a scenario analysis to evaluate the potential scales of (1) waste stocks in landfills and (2) emissions from degradation of side-chain fluorinated polymers in the environment and landfills, which can currently not be accurately estimated. Furthermore, we discuss the implications of our inventory and modeling results, highlighting future research needs regarding the global environmental fate and trends of PFSAs and their precursors.

MATERIALS AND METHODS

Our calculations consist of three steps (see Figure 1; for details on nomenclature, see Section S1.1 of the Supporting Information, (SI)). In a first step, we quantified direct emissions of C_4–C_{10} PFSAs and their direct precursors throughout the life

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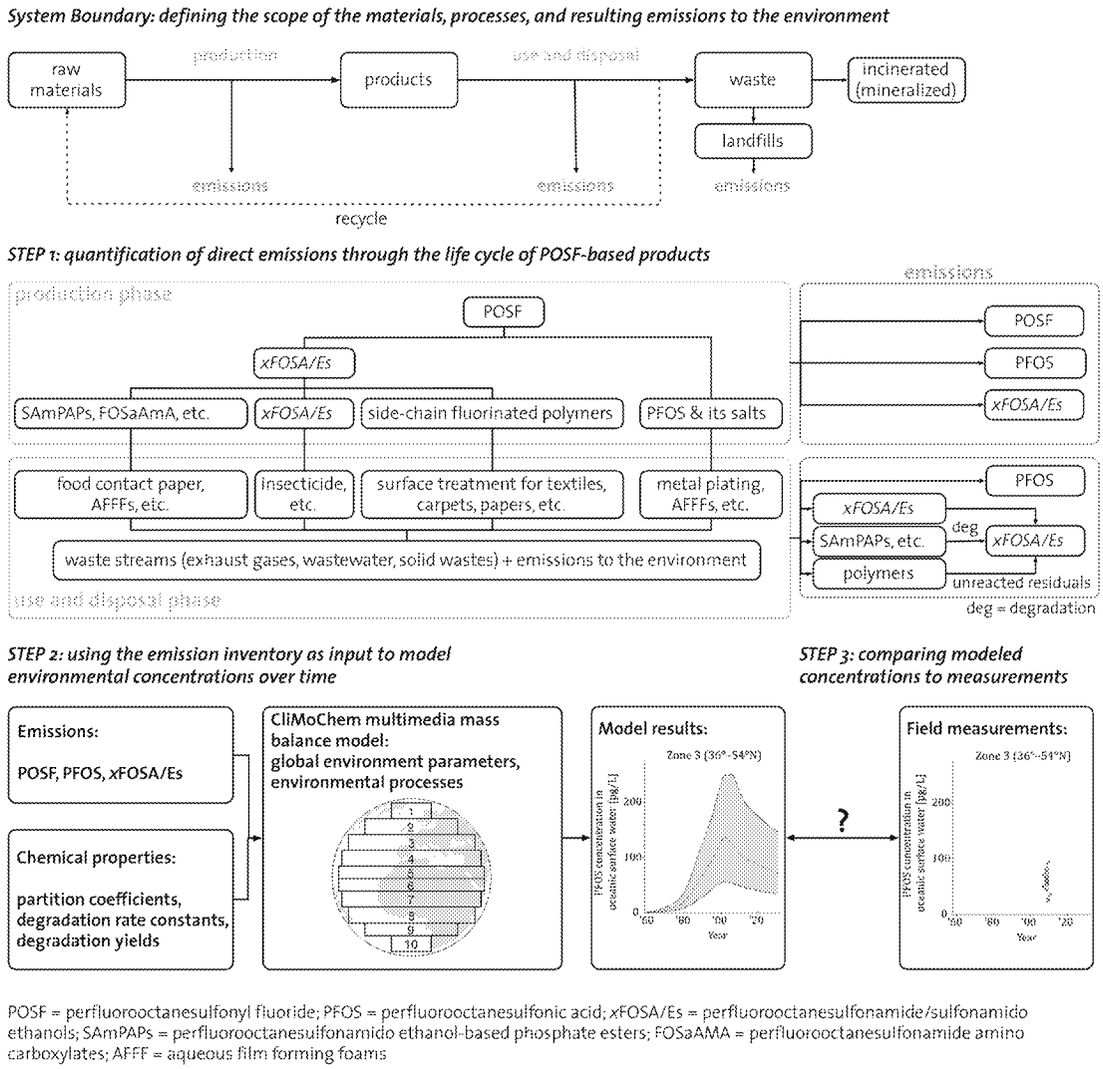

POSF = perfluorooctanesulfonyl fluoride; PFOS = perfluorooctanesulfonic acid; xFOSA/Es = perfluorooctanesulfonamide/sulfonamido ethanols; SAmPAPs = perfluorooctanesulfonamido ethanol-based phosphate esters; FOSaAMA = perfluorooctanesulfonamide amino carboxylates; AFFF = aqueous film forming foams

Figure 1. Schematic illustration of the methodology employed.

cycle of POSF-based products. Following the approach introduced by Armitage et al.,[4] we used *x*-perfluorooctanesulfonamides (*x*FOSAs) and *x*-perfluorooctanesulfonamido ethanols (*x*FOSEs) as surrogates to represent direct PFOS precursors, because most, if not all, other PFOS precursors are derived from these substances (see Figure S3 in the SI), and we refer to them collectively as "*x*FOSA/Es". We additionally estimated the emissions of POSF, another direct precursor, separately. Then, we input these emission estimates into the global multimedia mass-balance model, CliMoChem, to calculate environmental concentrations of PFOS and *x*FOSA/Es over time and to assess the contribution of the degradation of *x*FOSA/Es and POSF to the overall presence of PFOS in the environment. Finally, we compared modeled environmental concentrations with reported field measurements as an external evaluation of the emission inventory. All data were retrieved in an extensive review of publicly available literature. Here we report the methods employed in this study, highlighting the improvements in comparison to the previous studies.[3,4] Details on the structure and parameter settings of the emission inventory, parameter settings for the CliMoChem model, and collected field measurements are provided in the SI.

Quantification of Direct Emissions Throughout the Product Life Cycle. In establishing our emission inventory, we adopted the methodology recently developed for the new global emission inventory of PFCAs[1] with specific refinements for PFSAs and their precursors. In brief, we combined data on POSF-based products (e.g., production and use volumes as a function of time) with empirically derived or estimated emission factors during each stage in the product life cycle (see Figure 1); for details, see Section S2 in the SI. Compared to the previous inventories,[3,4] we have considered new elements in both the methodology and input values, in particular the following:

i. *Realistic production and use volumes during the ongoing transition.* Instead of the assumptions used previously,[3,4] new information from industrial surveys by the OECD[24,25] and in China[26−31] and Brazil[32] was used as the production and use volumes of POSF-based products in 2003−2015 (see Section S2.1.1 in the SI). New production volumes were much lower than those assumed by Paul et al.[3] and on the same order of magnitude as those assumed by Armitage et al.[4] with some temporal variations. A large portion of POSF produced in China has been exported to Brazil to synthesize *N*-ethyl FOSA (EtFOSA) as the active ingredient in Sulfluramid, an insecticide that has been widely applied across Brazil to control leaf-cutting ants since the early 1990s.[33] We used values from a recent study on Sulfluramid sales and exports in Brazil[32] to adjust our

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inventory (see Section S2.1.3.5 in the SI). For the period after 2015, we assumed two scenarios of a linear phase-out based on China's recently initiated efforts to reduce and phase out PFOS,[30] i.e. by 2018 (lower scenario), or by 2025 (higher scenario).

ii. *Expanded emissions from production sites.* Before 3M began transporting sludge from their wastewater processing to hazardous waste and industrial landfills in 1998, the sludge was deposited directly onto open lands for land treatment.[34,35] This served as an additional emission pathway for POSF-based substances that was not considered previously.[3,4] 3M's reports[34,36−45] were used to estimate relevant emission factors for this pathway of emissions to soil (see Section S2.1.2 in the SI). In addition, according to another 3M report,[34] a small portion of POSF was released to air, soil and water from its production sites; these data were used to define emission factors of POSF into these compartments from production sites, which were not considered previously.

iii. *Revised and expanded estimation of PFOS precursors.* Following Wang et al.,[1] products based on polymers and non-polymers were separated in the inventory with different data treatment for each as summarized here (for further details, see Section S2.1.3.1 in the SI). Similarly to Armitage et al.,[4] polymeric products were accounted for containing both PFSA impurities and unreacted residual PFSA precursors that are steadily released over a generic product lifetime of 10 years. Due to a lack of data on the types and quantities of polymers produced and released, and on their degradation half-lives, degradation of polymers cannot be included in the inventory. Instead, a scenario analysis was performed to evaluate the potential relevance of polymer degradation to the overall emissions of PFOS precursors under different combinations of key parameters (see see Section S5.7 in the SI), and the outcomes are discussed in the section Uncertainties and Open Questions: In brief, we considered that polymers degrade during an assumed, generic time frame (as a surrogate of total time available for degradation) with a first-order rate constant derived from an assumed degradation half-life in each scenario. Polymers released into the environment during the use and disposal phase were assumed to have an unlimited time available for degradation, and all remaining polymers were assumed to become waste (and either landfilled or incinerated) following a lifetime of 10 years. We then compared the estimated *x*FOSA/Es emissions from the scenarios of polymer degradation to estimates of emissions from all other sources. Similarly to Paul et al. and Armitage et al.,[3,4] non-polymeric products were accounted for containing both PFSA impurities and unreacted residual precursors that are steadily released over a generic product lifetime of two years. Additionally, we incorporated the emissions of all intentionally used non-polymers such as EtFOSA in Sulfluramid and EtFOSE-based phosphate esters (SAmPAP) such as $(C_8F_{17}SO_2N(C_2H_5)\text{-}CH_2CH_2O)_2PO_2^-$ in paper packaging (see Figure S3 in the SI) over the generic product lifetime of two years, as well as their degradation (e.g., the hydrolysis of SAmPAP to EtFOSE).[46,47] For details, see Section S2.1.3.5 in the SI.

iv. *Consideration of waste stocks.* Our inventory includes emissions during the production, use and disposal phases, but not emissions from waste stocks after disposal (e.g., in landfills). We acknowledge that waste stocks are available for eventual release into the environment, for example, via landfill leachate[48−50] and outgassing.[51] However, as wastes have been managed very differently around the world and over time, there is a lack of data to make estimates with reasonable uncertainties. Instead, we performed a simplified scenario analysis to calculate possible maximum and minimum volumes of waste stocks, as an indication of their potential relevance for emissions (see Section S5.6 in the SI): The remaining, non-released substances after disposal were either landfilled or incinerated; those landfilled were considered as waste stocks, whereas those incinerated were considered to be completely destroyed. The outcomes are discussed in the section Uncertainties and Open Questions.

v. *Emissions on a homologue basis.* The emission inventory was calculated on a homologue basis by considering both POSF-based substances as well as their shorter- and longer-chain homologues that are present as impurities in products. This was done using reported homologue compositions in various commercial products (see Section S2.1.4 in the SI).

Modeling Environmental Concentrations and Fluxes over Time. The CliMoChem model was used to estimate environmental concentrations and fluxes of PFOS and *x*FOSA/Es over time, including tracking the degradation of *x*FOSA/Es and POSF to PFOS. The model divides the Earth into latitudinal zones, and for this study five zones per hemisphere were used with each spanning 18° of latitude. Each zone includes compartments representing tropospheric air, bare and vegetation-covered soil, vegetation, oceanic surface water, snow, and ice. The model can simultaneously simulate multiple compounds including transformation products. Details on the model setup of environmental parameters and processes are provided in previous studies[20−22] and are therefore not repeated here. Details on the input parameters and modeling scenarios are available in Section S3 of the SI.

The model was run at a monthly resolution from 1958 until the year 2030. The estimated yearly emission inputs of PFOS, POSF, *x*FOSAs, and *x*FOSEs were equally distributed over each year, and they were assigned to latitudinal zones based on reported and estimated geographical distributions of production, use, and disposal locations. For example, 50% of the production emissions from the United States, Western Europe and Japan were assigned to Zone 3 (36°−54°N) and the other 50% to Zone 4 (18°−36°N) based on the location of the two main 3M production facilities in Antwerp, Belgium and Decatur, U.S., as similarly done by Armitage et al.[4] Emissions from POSF-based product manufacture in China were assigned 30% to Zone 3 and 70% to Zone 4 based on estimated emissions by Chinese regions.[52] Further details are available in Section S3.2 of the SI.

Partition coefficients as well as degradation pathways, rate constants, and reaction yields in individual compartments were defined for PFOS, POSF, *x*FOSAs, *x*FOSEs, and a hypothetical substance (INT) that is used as a surrogate of degradation intermediates from *x*FOSA/Es to PFOS (see Section S3.3 in the SI). For partition coefficients, we updated the values used by Armitage et al.[4] with more recent estimates.[53] For degradation pathways, we followed the simplified atmospheric degradation

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scheme proposed by Schenker et al.[22] for the atmosphere, and we made use of additional studies for soil[46,54] and water,[55,56] which had not been considered by Armitage et al.[4] For the degradation rate constants and yields of *x*FOSAs and *x*FOSEs to PFOS, we reviewed and expanded the values used by Armitage et al.[4] Due to the lack of a hydrolysis rate constant for POSF in the environment, we cannot assess the transformation from POSF to PFOS with accurate time resolution, although POSF released will ultimately all transform to PFOS. Instead, for POSF, we assumed hydrolysis half-lives of 0.5 and 5 years as the fast and slow scenarios, respectively.

Comparison with Field Measurements. As an evaluation of the emission inventory, modeled environmental concentrations and fluxes (i.e., PFOS concentrations in oceanic surface water, concentrations of *x*FOSAs and *x*FOSEs in air, and atmospheric deposition fluxes of PFOS to the Arctic (65−90°N latitude)) were compared to field measurements from the literature or from recent sampling campaigns[57−72] (for details on the field measurements, see Section S4 in the SI). Given that the CliMoChem model predicts average concentrations within a zone, it can be expected that the model results for PFOS and *x*FOSA/Es are similar to measured background concentrations from the field,[73] but much lower than measurements close to sources. Therefore, only measurements from sites representing background concentrations were considered. For example, sites on industrialized land, surrounded by industrialized land (e.g., the North, Baltic, and South China Seas), near known sources (e.g., inhabited islands), measurements that may have been influenced by abnormal natural events (e.g., large floods), or anomalously high measurements were not considered.

Uncertainty Analysis. The emission inventory in this study depends on various inputs derived from a wide range of studies and reports. This introduces uncertainties into the estimates, and using Monte Carlo simulation to quantify them is currently not possible since there is a lack of adequate information on the range and/or distribution of most input parameters. Instead, wherever possible, we defined higher and lower bounds for parameters including production volumes, emission factors, and degradation rate constants and yields to capture the potential variability and uncertainties, as suggested by Morgan[74] and Refsgaard et al.[75] The CliMoChem model was run multiple times, once for each combination of individual emission scenarios (low, medium and high) coupled with either fast or slow degradation and high or low yields (for details, see Section S3.4 in the SI). These combinations were used to estimate ranges of modeled environmental concentrations (or fluxes) for each chemical and compartment. As there are different levels of uncertainties attributed to the various parameters, we introduced a scoring system to indicate the level of uncertainty for each parameter (for details, see Section S5.8 in the SI). Lessons learned from the uncertainty analysis are highlighted below in the section Uncertainties and Open Questions.

RESULTS AND DISCUSSION

Estimated Global Sum Emissions from POSF-Based Products. Table 2 shows the lower and upper bounds of estimated global sum emissions of PFOS, *x*FOSA/Es, and POSF from the individual source categories considered between 1958−2002, 2003−2015, and 2016−2030. Most of the PFOS emissions were estimated to have occurred between 1958−2002, followed by a substantial decrease after 2002. Similar trends are also observed for *x*FOSA/Es and POSF. This confirms the positive effect of existing measures to restrict POSF-based products, although the transition may still require substantial time and cause substantial additional releases of PFOS and its precursors in 2016−2030 (8−153 tonnes and 6−707 tonnes, respectively). The relative uncertainty range of the estimates of PFOS emissions for individual source categories followed the sequence: from production < from degradation of POSF < from use and disposal < from degradation of *x*FOSA/Es.

Table 2. Global Emissions of PFOS, *x*FOSA/Es and POSF from the Life Cycle of POSF-Based Products in This Study (in Tonnes)

	1958−2002 [t]	2003−2015 [t]	2016−2030 [t]	total [t]
PFOS				
1. emissions from production (to water and soil)[a]	714−716	27−28	2−10	743−754
2. emissions from use and disposal (to water)	267−2677	48−628	6−113	321−3418
3. emissions from degradation of *x*FOSA/Es[b]	5−337	1−36	0−25	6−398
4. emissions from degradation of POSF[b]	160−491	6−17	0−5	166−513
total	1146−4221	82−709	8−153	1236−5083
*x*FOSA/Es				
1. emissions from production (to air, water, and soil)	557−689	21−26	2−10	580−725
2. emissions from use and disposal (to air and excluding Sulfluramid)[c]	175−6950	13−500	2−78	190−7528
3. emissions from application of Sulfluramid (to air and soil)	114−141	350−432	0−610	464−1183
total	846−7780	384−958	4−698	1234−9436
POSF				
1. emissions from production (to air and soil)[a]	652−653	24−25	2−9	678−687

[a]Ranges of calculated PFOS and POSF emissions from production are often small due to the use of single emission factors and production volumes as well as a small uncertainty range of the homologue composition of products (see Sections S2.1.2 and S2.1.4 in the SI). [b]These values were estimated by the CliMoChem model. Part of the initial amounts of POSF and *x*FOSA/Es released into the environment were predicted by the model to become trapped in permanent ice. Snow and ice were added in the most recent version of the CliMoChem model,[23] which was not considered in Armitage et al.[4] (see Section S5.4 in the SI). [c]These values do not include the potential emissions from the degradation of side-chain fluorinated polymers or additional non-polymeric precursors with unclear fates (see the section Uncertainties and Open Questions).

Furthermore, we estimated the global sum emissions of individual C_4−C_{10} PFSAs and their precursors from POSF-based products (see Table S19 in the SI). The C_8 homologues were predominant, as the non-C_8 homologues were present only as low-level impurities in POSF-based products (see Section S2.1.4 in the SI). However, C_4, C_6 and C_{10}-based products were also commercialized in the past,[2] and some are still being produced as replacements to POSF-based products.[76] Therefore, the actual emissions of these homologues are expected to be (much) higher than our estimates, however emissions from C_4, C_6, and C_{10}-based products are beyond the scope of this study.

Modeled vs Measured Environmental Concentrations of PFOS and Its Precursors. Figures 2 and 3 illustrate modeled concentrations of PFOS in oceanic surface water from zones 1

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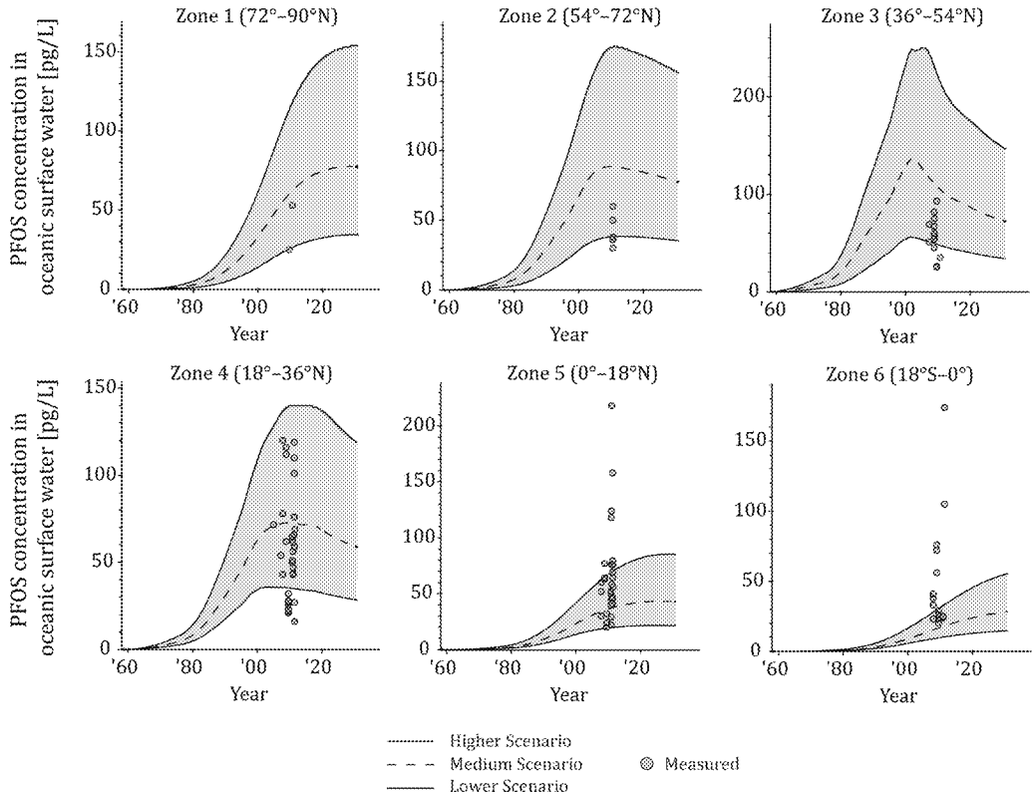

Figure 2. Modeled vs measured concentrations of PFOS in oceanic surface water in 1958–2030 in Zones 1–6.[57–65] Each measured concentration is represented by a semitransparent circle. For measurements of similar values, the circles overlap and appear progressively darker.

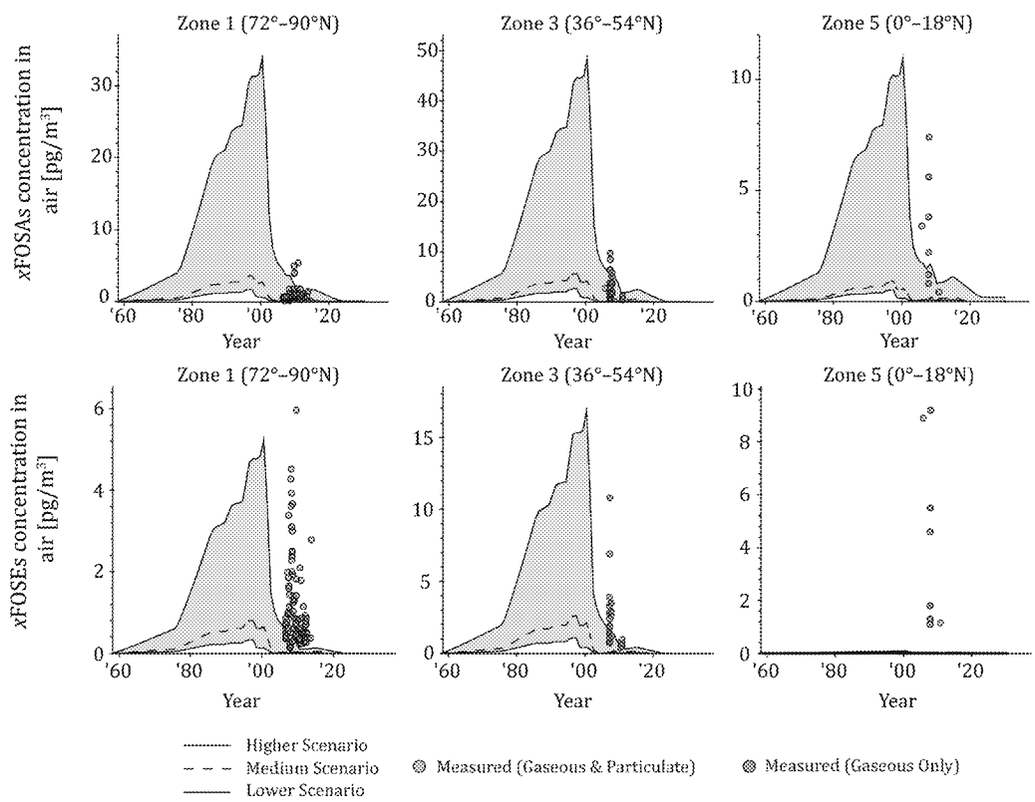

Figure 3. Modeled vs measured concentrations of *x*FOSAs (top) and *x*FOSEs (bottom) in air in 1958–2030 in Zones 1, 3, and 5.[59,60,65,67–70,72] Averaged annual results of modeled concentrations are shown here, and results for all zones are available in Section S5.5 of the SI.

(72°–90°N latitude) to 6 (18°S–0°) and of *x*FOSAs and *x*FOSEs in air in zones 1 (72°–90°N), 3 (36°–54°N), and 5 (0°–18°N) over time in comparison to field measurements. For results from the other zones, see Section S5.5 in the SI. In

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general, we observe a good agreement between modeled and measured concentrations, suggesting that our new emission inventory captures to a large extent the actual emissions from the life cycle of POSF-based products, at least for the time being and despite remaining uncertainties. Some more detailed observations are elaborated in the following.

i. *Observations from modeled concentrations.* In Figure 2, the modeled PFOS concentration in oceanic surface water rises most rapidly in zone 3 following the start of POSF production in 1958 and reaches a peak concentration range of approximately 55−250 pg/L (lower and higher scenarios) in 2002. Concentrations in the zones further to the north or south from source zones 3 and 4 show an increasing delay before concentrations begin to rise. In zone 6, this delay is almost 20 years after emissions in the Northern Hemisphere began. A similar delay in the response for zones without substantive sources is also predicted by the model for the time period following 3M's phase-out in 2000−2002. For example, in zones 1 and 5 through 10, a concentration decrease is not seen within the temporal bounds of the model runs (through 2030), in contrast to source zones 3 and 4. Similarly, the modeled concentrations of *x*FOSAs and *x*FOSEs in air rise quickly following the start of POSF production and reach peak values in 2000 (see Figure 3). In contrast to PFOS, these atmospheric precursor levels react quickly to the phase-out due to the faster mixing of air and shorter degradation half-lives of *x*FOSA/Es.

ii. *Observations from modeled vs measured concentrations.* For PFOS, at least 60% of the field measurements are within the range of the modeled concentrations for zones 3 through 5, whereas the other 40% are outside of the range. In the Southern Hemisphere, modeled concentrations are substantially lower than field measurements, and in zones 7 through 9 all of the field measurements are above the modeled concentrations (see Figure S7 in the SI). This is likely caused by additional emissions from product use and disposal in the Southern Hemisphere[77,78] that cannot be accurately attributed for modeling due to a lack of data. For *x*FOSAs, more than 80% of the field measurements are within the modeled ranges for zones 1 through 3, 8, and 9, whereas the modeled ranges are often lower for zones 4 through 6 (see Figure S8 and Table S22 in the SI). For *x*FOSEs, most of the field measurements in zones 1 through 10 are above the modeled ranges. This could be an indication of underestimation in the emission inventory, although the field measurements are all rather low (>90% are less than 5 pg/m^3). Similarly to PFOS, the modeled concentrations in zones 5−10 are substantially lower than those in zones 1−4.

Modeled vs Measured Environmental Fluxes of PFOS to the Arctic. We compared the modeled annual fluxes of PFOS to the Arctic via air between 1995−2005 (with and without POSF emissions considered) with fluxes estimated from snow core measurements at the Devon Ice Cap[71,79] (see Figure S6 in the SI). In general, the measured fluxes are within the range of modeled fluxes with and without POSF emissions considered. However, the lower and medium modeling scenarios substantially underestimate the fluxes in comparison to the measured field values[71] when POSF emissions are not considered. This suggests that POSF emissions may have a substantial role in the long-range transport of PFOS to remote areas, for example, the Arctic. The comparison here is not conclusive due to the potentially high uncertainty of PFOS measurements in snow and ice cores (e.g., postdepositional transport associated with melting events as indicated by the authors[71,79] and others[80]). This limitation in the field measurements is further addressed in the section Implications from Our Study and Future Perspectives.

Uncertainties and Open Questions. In Table S23 in the SI, we provide for all parameters in our inventory their origin (estimated or assumed), estimated uncertainty level as indicated by a score, and location of details in the SI. In general, the uncertainty levels increase in the order: [i] production phase < use and disposal phase; and [ii] emissions from 1951 to 2015 < emissions from 2016 to 2030. Higher uncertainty for the use and disposal phase is due to only limited information available for the enormous diversity of products involved. Here we took a conservative approach by applying a wide range of potential emissions from use and disposal (10−100%) that are uniformly distributed over the product lifetime. To reduce uncertainties, substantial additional product-specific information (including types, quantities and average releases over time) is needed; some has been generated, but it is not yet available to the public.[35] Furthermore, the projections of future emissions also have uncertainties associated with the elimination of production and use of POSF-based products worldwide. Following the 2009 listing under the Stockholm Convention, the production and use of PFOS and POSF are allowed only for remaining "exempted" or "acceptable" uses.[31] However, a global phase-out time plan is not yet available. China has recently initiated a national project to reduce and phase-out PFOS in priority sectors between 2017 and 2021,[30] which forms the basis of our assumptions.

Furthermore, several parameters and processes could not be properly quantified in the emission inventory. Here we qualitatively discuss them and highlight key open questions to be addressed in future studies.

i. *Releases from generated waste stocks.* During the disposal phase, POSF-based products may be released, recycled, incinerated, landfilled or dumped on open sites. Our inventory covers those released (including dumping on open sites) and recycled (partially), but it does not cover those landfilled. Landfills may act as long-term reservoirs (years to decades) with only slow releases[81] via leachate[48−50,82] and outgassing.[51] However, there are little to no data on (1) the quantities of PFOS and individual types of PFOS precursors (both non-polymeric and polymeric) landfilled over time, (2) the quantities and characteristics of relevant landfills around the world over time,[83] and (3) how varying characteristics such as infrastructure (e.g., lining and leachate treatment types) and operating conditions (e.g., aerobic, anaerobic, anoxic, etc.) of landfills influence degradation and/or releases over time. Thus, it is not yet possible to estimate emissions from landfills using a realistic time scale and with reasonable uncertainties, particularly on the global level. As a first indication, our scenario analysis of generated waste stocks indicates that a cumulative amount of 4711−41 934 tonnes of PFOS precursors (*x*FOSA/Es, other non-polymers, and polymers) may have been landfilled between 1958−2015. In contrast, 1230−8738 tonnes of *x*FOSA/Es are estimated to have been cumulatively released during production and use and disposal for the same time period; for details see Section S5.6 in the SI. This indicates that global releases from waste stocks might

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have been minor compared to those from the production and use and disposal phases (assuming fewer than 1% of waste stocks are released annually), but their contributions are becoming increasingly relevant with the ongoing phase-out of POSF-based products. Future empirical studies to understand the fate of PFSAs and their precursors in waste stocks are warranted, and results can be coupled with highly resolved information on product types, quantities, and disposal behavior to expand our inventory to include releases from waste stocks, similar to recent efforts made for polychlorinated biphenyls.[84]

ii. *Degradation of side-chain fluorinated polymers.* A substantial amount of PFOS precursors have been incorporated as side chains in so-called "side-chain fluorinated polymers", and these may be released when the polymers break down, as shown in the cases of structurally similar fluorotelomer-based side-chain fluorinated polymers.[88−93] However, there are little to no data on (1) POSF-based polymers, including types (e.g., acrylate or urethane polymers), characteristics, and quantities subject to degradation, and (2) the degradation half-lives of individual types of polymers, which prevents estimation of emissions. Building upon our previous scenario analyses of the degradation of POSF-based polymers during use and disposal[2] and of waste stocks generated (above), our new scenario analysis considers degradation both during the use and disposal phase and as waste in landfills (see Section S5.7 in the SI). The following key lessons are learned: [i] Huge ranges of emissions result from different scenarios. [ii] A longer time frame for degradation results in higher releases of *x*FOSA/Es via both a longer time period during which degradation occurs and a higher accumulation of polymers available for degradation. [iii] A shorter degradation half-life results in higher releases of *x*FOSA/Es per unit of time. [iv] In a reasonable scenario with a time frame of 50 years and a long degradation half-life of 100 years, the estimated emissions of *x*FOSA/Es from degradation of polymers are much lower than those from all other sources for the time period before 2002, but are still considerable with increasing relevance in the years following (see Figure S13 in the SI). Thus, omitting the degradation of polymers has only limited influence on our inventory through 2015, but it may underestimate substantial future long-term emissions. Studies on the mass flows of these polymers throughout the life cycle and on their fate in the environment and in landfills are needed.

iii. *Incomplete understanding of the fate of non-polymeric precursors to PFOS.* Foremost, likely due to their explorative rather than deterministic nature, none of the existing degradation studies ran experiments to the end when no further reaction occurs.[46,54,94,95] Therefore, using the empirical yields from these studies in our inventory via the CliMoChem model may have been an underestimation of actual yields of PFOS from its precursors. In addition, some existing studies were conducted at conditions that are irrelevant for the environment. For example, the only known hydrolysis study of POSF was conducted with heated water at 180 °C under high pressure for 3 days,[96] which cannot be used to extrapolate a half-life under normal conditions. Furthermore, only a limited number of non-polymeric precursors have been tested, most of which are *x*FOSA/Es and their homologues. Given the high percentage of POSF reported by 3M to have been used for production of *x*FOSA/Es and their ester derivatives (>90%, Figure S3 in the SI), the use of *x*FOSA/Es to represent all other PFOS direct precursors in the model is a reasonable simplification. Nevertheless, this simplification may result in some over- or underestimation in the modeling results given that a small portion of POSF-based products may not form *x*FOSA/Es, but other substances, as intermediates. In contrast, only one precursor with a complex molecular structure has been tested and there were no clear conclusions.[39] Thus, knowledge of degradation half-lives of transformations of complex precursors to *x*FOSA/Es in the real environment is lacking, while the yields can be deduced from theoretical exploration (e.g., the hydrolysis of esters). The currently assumed degradation time frame for complex molecules to *x*FOSA/Es (see Section S2.1.3.5 in the SI) has no influence on the absolute amounts, but might cause a different temporal distribution in comparison to the actual degradation in the environment. In addition to issues related to degradation kinetics and yields, the fate of these complex molecules in compartments other than air (e.g., retarded degradation due to adsorption on soil/sediment particles) remains a knowledge and data gap, and thus, these substances could not be meaningfully included in the inventory. These two points need to be addressed in future studies when new data are made available. As a first step to overcome this data scarcity, future efforts to improve analytical methods and standards are needed. For example, previous efforts to measure POSF via HPLC-MS could not distinguish it from PFOS,[97] and efforts using GC-MS resulted in no signal.[98]

Implications from Our Study and Future Perspectives. This study is a step toward a comprehensive global emission inventory of C_4−C_{10} PFSAs and their precursors. It provides a systematic overview of POSF-based products and a framework that can be expanded for C_4, C_6 and C_{10}-based products, once relevant data are generated and/or made available. It also shows that substantial sources of PFOS and its precursors are still ongoing and may last long into the future. Our study highlights the following needs for future research:

i. *A better understanding of the situation in the Southern Hemisphere.* Many of the measured field concentrations of PFOS and its precursors in the Southern Hemisphere are above the modeled concentrations. This suggests that there have been additional emissions in these regions that were not considered in the modeling. This is reasonable given the high number of POSF-based products that can be expected to make their way into these growing markets. However, there is currently a definite lack of import, use, and emissions data in the Southern Hemisphere, particularly for South America and Africa. The availability of such data that cover these regions would greatly advance the understanding of these emission source areas.

ii. *Consistent, long-term monitoring at more background sites.* The comparison between modeled and measured environmental occurrence of PFOS and its precursors here has been made only for the concentrations in air and water, as well as for fluxes through air (including into snow and ice), with measured data mostly from the Atlantic Ocean and regions near the Poles with few to none in the Pacific and Indian Oceans. Due to a general lack of background

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measurements, comparisons have not been made for other compartments (e.g., soil, vegetation), for zone 10 geographically, and for time periods other than circa 2000–2015. This limited availability of measurements introduces non-measurable uncertainties in the model-to-field comparison. In particular, the temporal development of our modeled environmental concentrations cannot yet be compared with existing field measurements for the following reasons:

(1) Modeled concentrations exhibit a wide range due to the parameter uncertainties and structural uncertainties in the emission inventory and in the environmental fate modeling; they therefore cannot reflect fluctuations observed in the field measurements that are smaller than the uncertainty range of the model results.

(2) It is challenging to measure and interpret temporal trends in the environment. For example, soil/sediment/snow and ice core measurements of PFOS and its precursors reflect not only the temporal changes of deposition, but also changes caused by post-depositional transport and degradation processes.[80,99] In addition, existing "snapshot" measurements at background sites[57−72] and longer-term air monitoring in the Arctic[72,100] do not yet show clear temporal trends. Such a delay in showing clear trends may be caused by a combination of factors including [i] inconsistent sampling and analytical methods by various laboratories, [ii] ongoing production and use of POSF-based products, [iii] delayed releases from landfills, [iv] continuous degradation of side-chain fluorinated polymers, and [v] delayed transport from other regions (as investigated in the Southern Ocean[101] and also seen in our modeling results).

Therefore, consistent, long-term environmental monitoring at various background sites (e.g., through deployment of passive air samplers)[102] is continuously needed as the only reliable tool to track and understand ongoing changes in the global environment and evaluate the effectiveness of measures to phase-out these compounds, in particular in countries with major ongoing production and use such as China and Brazil. Additional measurements in other compartments such as soil and vegetation, as well as retrospective analysis of samples collected in environmental specimen banks, are also encouraged.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b06191.

Detailed methodology for estimating emissions from each source and additional information, figures and tables (PDF)

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Notes

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