Global Emission Inventories for C_4–C_{14} Perfluoroalkyl Carboxylic Acid (PFCA) Homologues from 1951 to 2030, Part I: Production and Emissions from Quantifiable Sources

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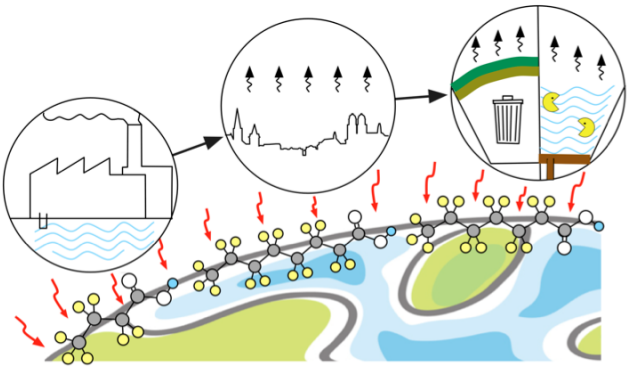


Graphical abstract

In press for *Environment International* (2014)

Abstract

We quantify global emissions of C_4–C_{14} perfluoroalkyl carboxylic acid (PFCA) homologues during the life-cycle of perfluorooctanoic acid (PFOA)-, perfluorononanoic acid (PFNA)-perfluorooctane sulfonyl fluoride (POSF)- and fluorotelomer-based products. We estimate emissions of 2610–21400 tonnes of C_4–C_{14} PFCAs in the period from 1951 to 2015, and project 20–6420 tonnes to be emitted from 2016 to 2030. The global annual emissions steadily increased in the period 1951–2002, followed by a decrease and then another increase in the period 2002–2012. Releases from fluoropolymer production contributed most to historical PFCA emissions (e.g. 55–83% in 1951–2002). Since 2002, there has been a geographical shift of industrial sources (particularly fluoropolymer production sites) from North America, Europe and Japan to emerging Asian economies, especially China. Between PFCA homologues, sources differ, sometimes considerably, and the relative contributions of each source change over time. For example, whereas 98–100% of historical (1951–2002) PFOA emissions are attributed to direct releases during the life-cycle of products containing PFOA as ingredients or impurities, a much higher historical contribution from PFCA precursor degradation is estimated for some other homologues (e.g. 9–78% for PFDA). We address the uncertainties of the PFCA emissions by defining a lower and a higher emission scenario, which differ by approximately a factor of eight.

Key words

Perfluoroalkyl carboxylic acids (PFCAs), global emission inventory, geographical shift of industrial sources, per- and polyfluorinated alkyl substances, PFOA

Terminology

1. The emission inventory of C_4–C_{14} perfluoroalkyl carboxylic acid (PFCA) homologues is arranged by investigating the fate of certain chemical species during the life-cycle of relevant products. The products are grouped and named after the major ingredients therein, e.g. products containing perfluorooctanoic acid (PFOA) and its derivatives that have the same functional moiety (i.e. the perfluoroalkane carbonyl moiety, $C_nF_{2n+1}C(O)$–; including salts, esters, etc.; hereafter *derivatives* only) as major ingredients are categorized as PFOA-based products. The same terminology is used for other products, including fluorotelomer-based products and products based on perfluorononanoic acid (PFNA) and perfluoroalkane sulfonyl fluoride (POSF). In addition to those species that are intentional ingredients in products, [i] PFCAs and their derivatives present in products as undesired byproducts (hereafter *impurities*) and [ii] (POSF- and fluorotelomer-based) present in products as unreacted raw materials (hereafter *residuals*) are also accounted for in the inventory.

2. PFCA sources are divided into two categories. *Direct* sources include PFCA emissions from the life-cycle of [i] PFCA-based products that contain PFCAs or their derivatives as major ingredients and [ii] other products in which PFCAs are present as impurities. *Indirect* sources refer to formation of PFCAs from degradation of precursors such as POSF- and fluorotelomer-based substances in the environment and biota. For details and examples of POSF- and fluorotelomer-based precursors of PFCAs, see Frömel and Knepper (2010), Liu and Avendaño (2013) and Young and Mabury (2010) and the references therein. In this work we adopt the terminology proposed by Buck et al. (2011), which is slightly different from that used by Prevedouros et al. (2006), regarding whether PFCA impurities in other products are considered as direct (here) or indirect sources (by Prevedouros et al., 2006). Details on terminology are provided in *Section S0* in the *Supplementary Data*.

3. PFCAs and their POSF- and fluorotelomer-based precursors belong to the chemical class known as poly- and perfluorinated alkyl substances (PFASs). PFASs are chemicals that contain one or more perfluoroalkyl moieties, $-C_nF_{2n+1}$ (Buck et al., 2011). In the past, PFASs were often referred to as "PFCs" (per- and polyfluorinated chemicals), but this acronym is also commonly used for perfluorocarbons; perfluorocarbons contain only carbon and fluorine and have properties and functionalities different from those of PFASs.

1. Introduction

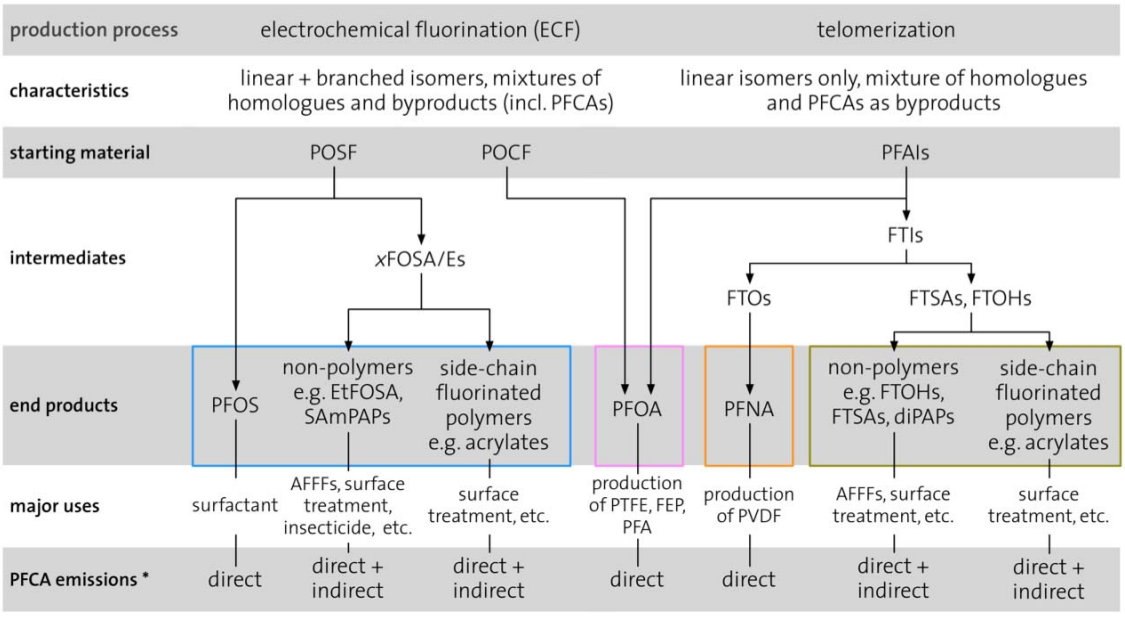
Long-chain perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$, n ≥ 7), including perfluorooctanoic acid (PFOA or C_8 PFCA) and perfluorononanoic acid (PFNA or C_9 PFCA), are recognized as global contaminants of high concern, since they are highly persistent (Parons et al., 2008; Frömel and Knepper, 2010; Young and Mabury, 2010), bioaccumulative

(Conder et al., 2008; ECHA, 2013), and have been detected globally in the abiotic environment (Rayne and Forest, 2009), biota (Giesy and Kannan, 2001), food items (Picó et al., 2011) and humans (Vestergren and Cousins, 2009). In the European Union (EU), C_{11}–C_{14} PFCAs were identified as very persistent and very bioaccumulative (vPvB) substances and PFOA and its ammonium salt (APFO) were identified as persistent, bioaccumulative and toxic (PBT) substances (ECHA, 2013). These PFCA homologues have therefore been added to the Candidate List of Substances of Very High Concern (SVHCs) for Authorisation under the European Chemical Regulations, REACH (EG 1907/2006) (ECHA, 2013).

In order to characterize human and environmental exposure to PFCAs, it is important to understand their levels and trends in the environment, starting with source identification and quantification. Only fragmented information was available until Prevedouros et al. (2006) compiled available information and estimated the total global historical emissions of PFCAs (1951–2004) during the life-cycle of fluorotelomer-based products and prodcuts based on PFOA, PFNA and perfluorooctane sulfonyl fluoride (POSF). General information on the production, major uses and relevance to PFCA emissions of these four product groups is compiled in Fig. 1; for details on each product group, see *Section S1* in the *Supplementary Data*. The work by Prevedouros et al. (2006) highlighted the significance of historical direct sources to the overall presence of PFCAs in the environment, in particular from production of certain fluoropolymers where PFOA- or PFNA-based products have been used as processing aids (Prevedouros et al., 2006). Prior to Prevedouros et al. (2006), indirect sources, in particular atmospheric degradation of residuals in POSF- and fluorotelomer-based products, had been postulated to be the major source of PFCAs in the environment (Ellis et al., 2004). Precursor degradation may well be the dominant source of PFCAs in remote inland environments such as the high Arctic or alpine lakes that are impacted only by atmospheric inputs (Benskin et al., 2011; Schenker et al., 2008; Young et al., 2007), but indirect sources are probably not dominant for other environments (e.g. open oceans) or the globe as a whole (Armitage et al., 2006, 2009a,b).

The availability of emission data made it possible to employ environmental fate models in order to elucidate the global fate of PFCAs and, in particular, their transport pathways to remote areas (Armitage et al., 2006, 2009a,b; Schenker et al., 2008; Stemmler and Lammel, 2010; Wania, 2007). These modeling studies were recently reviewed (Cousins et al., 2011) and were found to support the notion that direct uses of PFOA- and PFNA-based derivatives as processing aids in certain fluoropolymer production are the dominant historical global sources for these PFCA homologues (Prevedouros et al., 2006). The same review also concluded that PFCA homologue patterns in monitoring data indicate that *indirect* sources may become proportionally more important for PFCA homologues with nine or more perfluoroalkyl carbons (Cousins et al., 2011). Hence, the major sources of other PFCA homologues may differ from those of PFOA and PFNA, and need to be assessed individually.

However, Prevedouros et al. focused mainly on PFOA and PFNA; a detailed breakdown of PFCA emissions on a homologue basis was not provided (Prevedouros et al., 2006).



PFCA = perfluoroalkyl carboxylic acid; POSF = perfluorooctane sulfonyl fluoride; POCF = perfluorooctane carbonyl fluoride; *x*FOSA/Es = (N-methyl/etheyl) perfluorooctane sulfonamide / sulfonamidoethanol; SAmPAPs = EtFOSE-based diphosphate; PFAI = perfluoroalkyl iodide; FTI = fluorotelomer iodide; FTO = fluorotelomer olefins; FTSA = fluorotelomer sulfonic acid; FTOH = fluorotelomer alcohol; PFOS = perfluorooctane sulfonic acid; PFOA = perfluorooctanoic acid; PFNA = perfluorononanoic acid; diPAP = fluorotelomer diphosphate; AFFF = aqueous film-forming foam; PTFE = polytetrafluoroethylenee; FEP = perfluorinated ethylene-propylene copolymers; PFA = perfluoroalkoxyl polymers; PVDF = polyvinylidene fluoride

Fig. 1. General information on the production and uses of perfluorooctanoic acid (PFOA)-, perfluorononanoic acid (PFNA)-, perfluorooctane sulfonyl fluoride (POSF)- and fluorotelomer-based products as well as their relevance to the emissions of C_4–C_{14} PFCAs.

When historical PFCA emissions are characterized, it is important to account for changes in industrial practices of PFASs that have occurred over time. There has been a trend amongst global producers to replace chemicals containing long perfluoroalkyl chains (e.g. PFCAs with ≥7 perfluoroalkyl carbons or perfluoroalkane sulfonic acids with ≥6 perfluoroalkyl carbons as defined by OECD, Buck et al., 2011) with their shorter-chain homologues (Ritter, 2010; Wang et al., 2013) or with other fluorinated and non-fluorinated substances (Buck et al., 2011; Wang et al., 2013). These industry initiatives began in 2000 when 3M announced a global phase-out of its products based on C_6, C_8 and C_{10} perfluoroalkane sulfonyl fluoride (PASF)-based chemistry and replaced them with products based on C_4 chemistry such as perfluorobutane sulfonic acid (Ritter, 2010; 3M, 2000a). In 2006, eight major PFCA, fluoropolymer and fluorotelomer manufacturers joined the global US EPA 2010/15 Stewardship Program (US EPA, 2006) to work towards the elimination of long-chain PFCAs and their precursors from emissions and products by 2015. While long-chain PFCAs and

their precursors are being phased out in a series of steps by the major producers in Japan, Western Europe and the United States (US) (US EPA, 2006), new producers (largely in continental Asia) have begun to produce long-chain PFCAs and their precursors (for details and references, see *Section 3.3, Analysis of industrial sources*). Thus, emission sources have changed since the review by Prevedouros et al. (2006) was published.

This study aims to re-evaluate and expand on the work presented by Prevedouros et al. (2006). To this end, an extensive literature research was conducted including all but not limited to the sources summarized in Prevedouros et al. (2006). As a result, a new, more comprehensive set of PFCA sources were identified and efforts were made to quantify emissions from as many sources as possible. Due to a lack of data (on production, use, and disposal, and in some cases also degradation half-lives and yields), not all sources can be quantified. Hence, we divide this study into two parts. In this paper, we focus on the sources that can be quantified, whereas information on those sources that are known to exist but can currently not be quantified is summarized and presented in a companion paper (Wang et al., 2014).

In the *Results* section, we present global emission estimates of C_4–C_{14} PFCA homologues from the life-cycle of PFOA-, PFNA-, POSF- and fluorotelomer-based products in three periods (1951–2002, before the phase-out by 3M; 2003–2015, transition toward alternatives after the phase-out by 3M; 2016–2030, projection). In addition, we assess the geographical distribution of emissions from industrial sources and the receiving environmental media as a function of time with special attention given to the macroeconomic trend of production moving to continental Asia. In the *Discussion* section, we evaluate our estimates by comparing them to (i) several studies that estimated POSF- and fluorotelomer-based precursor emissions with different methods, and (ii) estimated amounts of PFCA homologues in open ocean surface water derived from monitoring studies. Also, we discuss accuracy, uncertainties and limitations of the emission estimates presented here and highlight areas where there are key uncertainties. It should be noted that our estimates (such as levels or homologue patterns) cannot be directly compared to measurements at a single site or source because they represent aggregated emissions from different sources on a global basis. Finally, the fate and behavior of PFCA homologues after being released into the environment (e.g., reactions with OH radicals; Hurley et al., 2004) is beyond the scope of this study and thus not included.

2. Methods

2.1. Identification of PFCA sources

We conducted an extensive literature review of over 4500 documents in the public domain,

including peer-reviewed scientific articles, books, theses, monographs, conference abstracts, industrial studies, patents, as well as databases and technical reports from international bodies. In addition to the sources reviewed by Prevedouros et al. (2006) (i.e., emissions from PFOA-, PFNA-, POSF- and fluorotelomer-based products), we identified several other sources that (may) contribute to the presence of PFCAs in the environment (see Fig. 2, left). For most of the newly identified sources there is a general lack of information on [i] the production, use and disposal of relevant products and [ii] the degradation half-lives and yields (in the cases of indirect sources), preventing these sources from being quantified. Therefore, all identified sources were divided into two groups based on data availability. Quantifiable sources include PFOA-, PFNA-, POSF- and fluorotelomer-based products (see Fig. 2, right); for these sources the PFCA emissions were quantified as explained below and in the *Supplementary Data*. For the other sources, we reviewed available information and highlight the critical knowledge gaps in a companion paper (Wang et al., 2014).

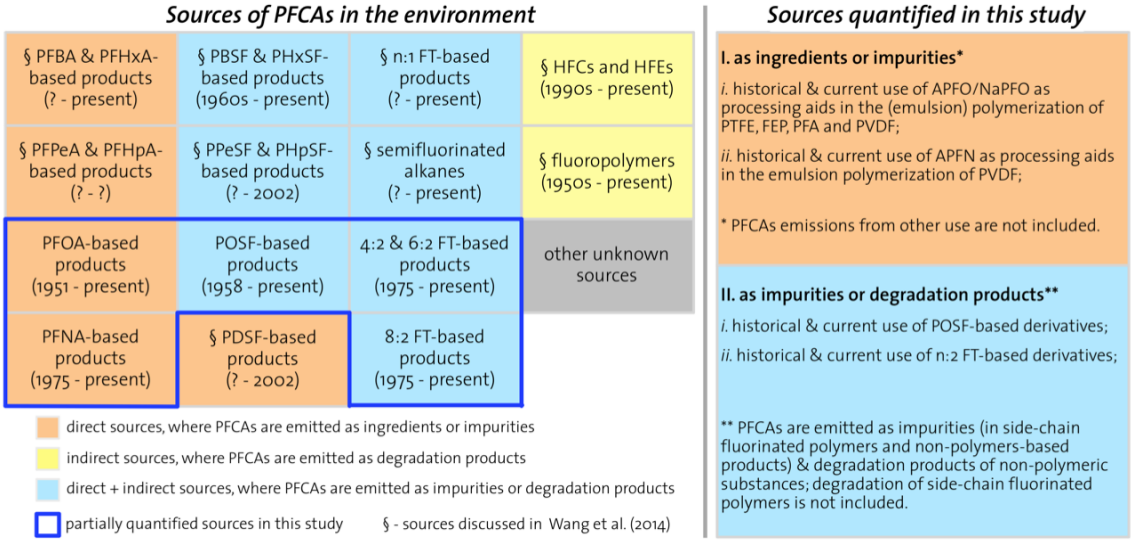


Fig. 2. Left: sources of perfluoroalkyl carboxylic acids (PFCAs) in the environment and their likely time span; right: sources quantified in this study. PFBA = perfluorobutanoic acid, PFHxA = perfluorohexanoic acid, PFPeA = perfluoropentanoic acid, PFHpA = perfluoroheptanoic acid, PFOA = perfluorooctanoic acid, PFNA = perfluorononanoic acid, PBSF = perfluorobutane sulfonyl fluoride, PHxSF = perfluorohexane sulfonyl fluoride, PPeSF = perfluoropentane sulfonyl fluoride, PHpSF = perfluoroheptane sulfonyl fluoride, POSF = perfluorooctane sulfonyl fluoride, PDSF = perfluorodecane sulfonyl fluoride; FT = fluorotelomer, HFC = hydrofluorocarbon, HFE = hydrofluoroether. APFO/NaPFO = ammonium/sodium salts of PFOA, APFN = ammonium salt of PFNA, PTFE = polytetrafluoroethylene, FEP = fluorinated ethylene-propylene copolymers, PFA = perfluoroalkoxyl polymers, PVDF = polyvinylidene fluoride.

2.2. Quantification through the product life-cycle

Due to limited space, here we only report the general approach; *Section S1* in the *Supplementary Data* provides details on all parameters (including data treatment and

202 references). In general, we combined data (retrieved from our literature search) on products
203 containing PFCAs and/or their precursors (including manufacturing processes, production
204 volumes as a function of time, and use patterns) with estimated or empirically derived
205 emission factors during each stage in the product life-cycle (see Fig. 3).

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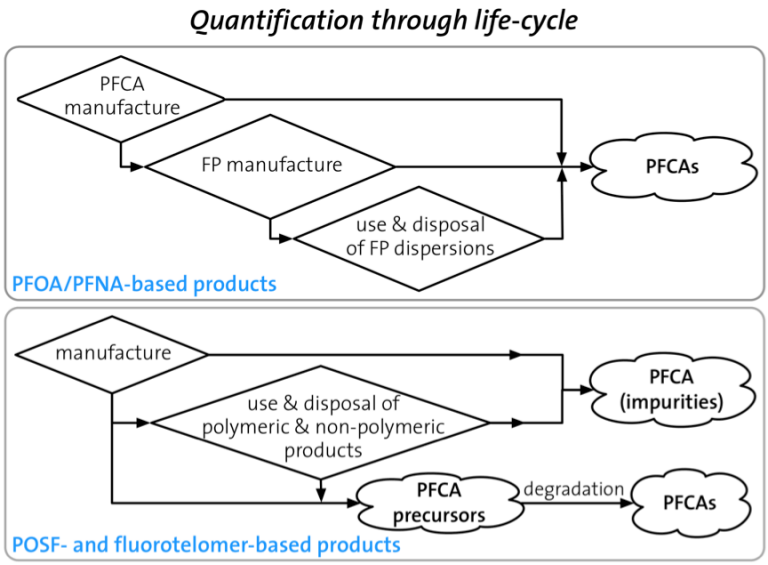

207 **Fig. 3.** Schematic diagram of PFCA emission quantification through the life-cycle of PFOA-, PFNA-,
208 POSF- and fluorotelomer-based products. (FP = fluoropolymers)

209 In comparison to Prevedouros et al. (2006), we updated parameters such as emission factors
210 (see Tables S66 to S68 in the *Supplementary Data*) and also improved the quantification in
211 the following six respects:

212 i. ***Average life-cycle duration.*** Instead of the earlier assumption that PFCA emissions occur
213 in the year when a "source" substance is produced (Prevedouros et al., 2006), we assigned
214 an average duration to each stage in the product life-cycle; this ranges from immediate
215 (production and disposal phase) up to ten years (use phase; duration was set based on
216 product type and use pattern (polymers vs. non-polymers); see *Sections S1.1.1.5, S1.3.1.3.2*
217 *and S1.4.1.3.2* in the *Supplementary Data*). This improves the understanding of temporal
218 trends in emissions during use and disposal of products, particularly for the post phase-out
219 period.

220 ii. ***Two country groups.*** In order to track the possible geographical shift of industrial
221 sources, we conducted our estimation separately, wherever possible, for two country
222 groups: I (Japan, Western Europe and the US) and II (Russia, China, India and Poland).

223 iii. ***New estimates of PFCAs used in fluoropolymer production.*** Due to limited information
224 provided in the *Supporting Information* of Prevedouros et al. (2006), it was not possible to
225 verify the previously reported amounts of relevant fluoropolymers produced and of PFOA-

and PFNA-based products used as processing aids in fluoropolymer production. Hence, we estimated the amounts of PFOA- and PFNA-based derivatives used as fluoropolymer processing aids, based on [i] reported and estimated production volumes of relevant fluoropolymers (i.e., polytetrafluoroethylene or PTFE; perfluorinated ethylene-propylene copolymers or FEP; perfluoroalkoxyl polymers or PFA; and polyvinylidene fluoride or PVDF) in country group I and II, and [ii] use rates of PFOA- and PFNA-based products in various fluoropolymer production processes documented in patents. Details of these new calculations are provided in *Sections S1.1.1 and S1.2.1* in the *Supplementary Data*.

Use rates of PFCAs as fluoropolymer processing aids in patents are often reported as wide ranges (for examples, see Tables S7 and S8 in the *Supplementary Data*). Therefore, one of the consequences of this new approach is that the estimated amounts of PFOA-based products applied have a wider range than in Prevedouros et al. (2006). Because there is little information on actual industrial practice in the literature, we decided not to arbitrarily narrow down the range of use rates, but to set an additional so-called "plausible" scenario. In this scenario, the use rate was set at 0.3 wt% of all relevant fluoropolymers produced, derived from [i] the APFO consumption (ca. 200 tonnes) in 1999 reported by the Fluoropolymer Manufacturers Group (FMG) (Pinchot, 2004) and [ii] the estimated production volume of relevant fluoropolymers by the FMG in 1999 (ca. 67 kt) (Will et al., 2005; Kählin et al., 2012). Thus, this use rate is likely close to the actual industrial practice and used as a reference value.

iv. ***Separation of non-polymeric and polymeric species***. A large proportion of POSF- and fluorotelomer-based PFCA precursors are chemically bound in side chains in so-called side-chain fluorinated polymers where the side chains are fluorinated but the backbone consists of non-fluorinated hydrocarbons, e.g., fluorinated (meth)acrylate polymers (Buck et al., 2011). The side chains of these fluorinated polymers are likely not readily degradable (i.e., not readily detached from the backbone) (Russell et al., 2008, 2010a,b; Washington et al., 2009, 2010). PFCA precursors present in non-polymeric form, in contrast, may be transformed into PFCA homologues within days or weeks (Frömel and Knepper et al., 2010; Young and Mabury, 2010). Hence, we divided PFCA precursors into two groups, polymers and non-polymers. To do so, we introduced non-polymeric:polymeric ratios of different PFCA precursors and varied these ratios as a function of time (see *Sections S1.3.1.3.1 and S1.4.1.3.1* in the *Supplementary Data*).

For non-polymeric species, we included not only residuals in products (e.g., surface-treated textiles or papers; Buck et al., 2011 and Martin et al., 2010) as in Prevedouros et al. (2006), but also species that were not included there, i.e. [i] substances with simple structures including N-ethyl perfluorooctane sulfonamide (EtFOSA) (Martin et al., 2010) or fluorotelomer sulfonic acids (FTSAs) (Buck et al., 2011; Lehmler, 2005) that are used as

ingredients in products; and [ii] substances with complex structures such as phosphate diesters based on N-ethyl perfluorooctane sulfonamide ethanol (EtFOSE) [SAmPAPs, e.g., $(C_8F_{17}SO_2N(C_2H_5)CH_2CH_2O)_2PO_2^-$] and their fluorotelomer-based analogues [diPAPs, e.g., $(C_8F_{17}CH_2CH_2O)_2PO_2^-$] that can break down into substances such as EtFOSE or FTOHs through biodegradation in activated sludge (Lee et al., 2010) or sediment (Benskin et al., 2012a, 2013) and thus form a source of PFCA precursors (Schultz et al., 2006). This degradation behavior has also been observed for other substances, e.g. breakdown of 8:2 fluorotelomer stearate monoester (8:2 FTS, $C_8F_{17}C_2H_4OOCC_{17}H_{35}$) in soil (Dasu et al., 2010, 2012) and of 6:2 fluorotelomer sulfonamide alkylbetaine [6:2 FTAB, $C_6F_{13}C_2H_4SO_2NHC_3H_6N^+(CH_3)_2CH_2COO^-$] in biota or through photolysis (Moe et al., 2012). For degradation half-lives and yields, see sections S1.3.3 and S1.4.3 in the *Supplementary Data*.

For polymeric species, due to large uncertainties associated with their degradation half-lives and yields, we did not account for polymer degradation, but did account for degradation of residuals (e.g., FTOHs or FOSEs) in products into account as in Prevedouros et al. (2006). In the companion paper, we investigated if degradation of these side-chain fluorinated polymers could be a relevant source of PFCAs (Wang et al., 2014).

v. ***PFCA emissions on a homologue basis***. PFCAs, as ingredients or impurities, and their precursors are manufactured as homologue mixtures (Buck et al., 2011). To break down the PFCA emissions on a homologue basis, we associated total PFCA emissions with information on homologue compositions of PFCAs and/or PFCA precursors in commercial products. To fill data gaps, assumptions sometimes had to be made; assumed or estimated homologue compositions and explanations are provided in Tables S40, S46, S55, S56, S59, S61 and S62 in the *Supplementary Data*.

vi. ***Industrial transition period (2002–2015)***. Since 2002, major global PFCA, fluoropolymer and fluorotelomer producers have implemented techniques to reduce industrial emissions as well as impurity and residual levels in products (US EPA, 2006), and have started to replace long-chain PFCAs and their precursors with shorter-chain homologues or other fluorinated and non-fluorinated substances (Buck et al., 2011; Ritter, 2010; Wang et al., 2013). In order to capture changes in PFCA emissions caused by these technological transitions, we incorporated information on the transition process (e.g. ,progress reports of the US EPA 2010/15 Stewardship Program; US EPA, 2006, 2008a,b, 2009a, 2010, 2011, 2012, 2013a) for the period 2002–2015 by [i] reducing the relevant emission factors (see Tables S29, S31, S35, S44, S45, S49 and S58 in the *Supplementary Data*); [ii] reducing the corresponding production volumes (see Tables S16, S22, S27, S43, S47 and S48 in the *Supplementary Data*); [iii] changing the homologue compositions (see Table S39, S51 and S59 in the *Supplementary Data*).

To project emissions in 2016–2030, we assumed that long-chain PFCAs and their precursors will no longer be produced in country group I based on the companies' commitment to the US EPA Stewardship Program (US EPA, 2006), but may still be contained in products in these regions due to global trade. In contrast, only qualitative but no quantitative data on emission reductions are available for producers in country group II such as China (for details and references, see *Section 3.3, Analysis of industrial source* section). Hence, we set up two scenarios for producers in country group II: (i) a lower scenario in which producers cease production and use of long-chain PFCAs and their precursors in line with global transition trends and (ii) a higher scenario in which the emission scenario in 2015 is assumed to remain constant until 2030. For details, see Sections S1.1.1, S1.2.1, S1.3.1 and S1.4.1 in the *Supplementary Data*.

In order to evaluate our results, we compared our estimated emissions of PFCA precursors to air with three other studies that made their estimates using different methods. Also, we compared our PFCA emission estimates to the inventory of PFCAs in open ocean water, which is the largest global reservoir of PFOA, PFNA and likely other PFCA homologues (Cousins et al., 2011). The ocean inventory was calculated by multiplying background levels of PFCAs in open ocean surface water (derived from monitoring studies) by the volume of the global ocean surface mixed layer (assuming 100–200 m depth with a median value of 150 m) (Prevedous et al., 2006; Armitage et al., 2009a). Comparisons are presented in the *Discussion* section. For details, see *Sections S2.4 and S2.5* in the *Supplementary Data*.

2.3. Analysis of industrial sources

In order to provide information on emission reduction potential, we developed profiles of the environmental media (air, water and land) receiving emissions and of the geographical distributions of industrial sources (including those industrial sites where PFOA-, PFNA-, POSF- and fluorotelomer-based products are manufactured and used as well as industrial waste treatment facilities). Each profile was derived from publicly accessible information on industrial sites (such as locations and on-site mass flows), technical expert knowledge, and our own estimates. In all cases, the mode of emission was assumed to be constant with time and homologue, whereas temporal changes were considered for geographical distributions. All profiles are provided in the *Supplementary Data* (see *Section S2.2*) and summarized in the *Results* section.

2.4. Uncertainty analysis

The methods in this study rest on various assumptions derived from limited empirical studies, which introduce uncertainties into the estimates. Using Monte Carlo simulation to

quantify the uncertainties is currently not possible, because for most of the parameters there is insufficient information on the range and/or distribution of their values. Instead, in those cases where the data were sufficient, parameters such as emission factors or levels of PFCA impurities in products were estimated in two scenarios (lower and higher) (Morgan, 2001; Refsgaard et al., 2007). Some other uncertainties introduced by using default values cannot be reliably quantified due to a lack of data. For instance, we might overestimate the amounts of PFCAs formed from precursors by using yields measured in laboratory experiments conducted with zero or low levels of NO (high levels of NO, especially in urban air, can lead to further degradation, shortening the perfluoroalkyl chain and ultimately leading to the formation of COF_2) (Young and Mabury, 2010). However, an adjustment factor to extrapolate data from laboratory studies to field conditions is not available. As there are different levels of uncertainties attributed to the various parameters, we introduced a scoring system to indicate for each parameter the level of uncertainty: 0–1 represents low uncertainty (reported estimates and/or measured emissions which have been evaluated for accuracy); 1–2 represents medium uncertainty (expert estimates or measured emissions which have not been (fully) evaluated); 2–3 represents high uncertainty (crude estimates or extrapolated emissions). Details are provided in *Section S3* in the *Supplementary Data* and summarized in the *Discussion* section.

3. Results

3.1. Estimated total global emissions of C_4–C_{14} PFCAs from quantified sources

Fig. 4 and Table 1 display the estimated total global annual and the cumulative emissions of C_4–C_{14} PFCAs from all quantified sources, respectively. The annual emissions show a steady increase in 1951–2002, followed by a decrease and then another increase between 2002 and 2012. This recent re-increase is caused by the industrial transition in opposite directions in country groups I (decrease) and II (increase), which is elucidated in detail further below in *Section 3.3. Analysis of industrial sources*. After 2012, a further decline of PFCA emissions from industrial sites in country group I is expected based on the companies' commitments to the US EPA 2010/15 PFOA Stewardship Program (US EPA, 2006) and the on-going transition to replacements of long-chain PFCAs and their precursors (for details and examples, see Wang et al., 2013). Similar emission reduction actions by major producers in country group II have been reported, but in a rather qualitative manner with no clear timeline given (for details and references, see *Section 3.3. Analysis of industrial sources*). Therefore, it is likely that the emissions of long-chain PFCAs in country group II are being reduced and will be eliminated in the foreseeable future. However, due to a lack of quantitative data, it is unclear how rapidly emissions will be discontinued. In total, we estimate 2610–21400 tonnes of C_4–C_{14} PFCAs are emitted globally from 1951 to 2015 and project 20–6420 tonnes to be emitted

from 2016 to 2030. Releases during the life-cycle of PFOA- and PFNA-based products contribute most to the emissions of C_4–C_{14} PFCAs before 2015. Thereafter, the potential contributions from possible continuing production and use of PFOA-based products in certain fluoropolymer production in China and Russia as well as degradation of fluorotelomer-based substances may well be the dominant emissions.

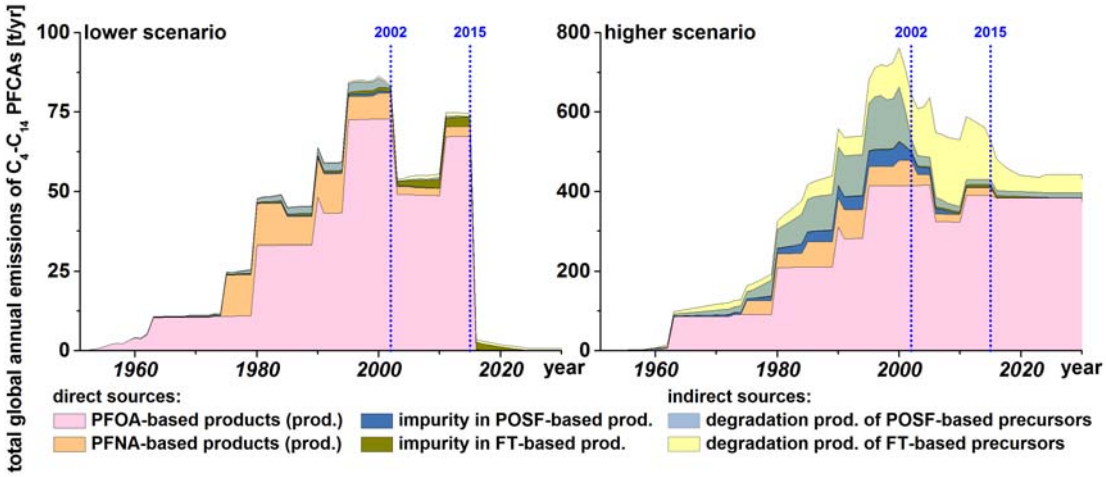

Fig. 4. Estimated total global annual emissions of C_4–C_{14} PFCAs (1951–2030) from six quantified sources (left: lower scenario; right: higher scenario). PFOA – perfluorooctanoic acid; PFNA – perfluorononanoic acid; POSF – perfluorooctane sulfonyl fluoride; FT– fluorotelomer.

In Table 1, we compare our estimates of the total historical releases of PFCAs from 1951 to 2002 to the estimates by Prevedouros et al. (2006). In most cases, both estimates for total PFCA emissions agree well, particularly when the plausible scenario (i.e. assuming a use rate of 0.3 wt% PFOA-based products in fluoropolymer production) is used. A notable difference is that we obtain much higher PFCA emissions from the life-cycle of POSF- and fluorotelomer-based products, as impurities or degradation products. The causes of these higher estimates are elucidated in the *Discussion* section.

Table 1. Estimated global cumulative emissions of total C_4–C_{14} PFCAs from 1951 to 2030 in this study and from 1951 to 2002 in Prevedouros et al. (2006). Figures in brackets represent estimates based on a use rate of 0.3 wt% (of relevant fluoropolymers produced) PFOA-based products as processing aids in fluoropolymer production (i.e. the plausible scenario).

	Quantified emission source category	Prevedouros et al. 1951–2002 [t] min.–max.	This study 1951–2002 [t] lower	1951–2002 [t] higher	2003–2015 [t] lower	2003–2015 [t] higher	2016–2030 [t] [a] lower	2016–2030 [t] [a] higher
Direct sources	***PFOA-based products***							
	1. PFOA manufacture	400–700	90 (200)	970 (570)	30 (90)	430 (280)	0	630 (440)
	2. Fluoropolymer (FP) manufacture with PFOA	2000–4000	1220 (2790)	6560 (3850)	660 (1700)	3870 (2430)	0	4520 (3130)
	3. Use & disposal of FP dispersions containing PFO	200–300	90 (210)	490 (290)	50 (140)	320 (200)	1 (3)	320 (220)
	PFNA-based products							
	4. PFNA manufacture	70–200	20	180	0	50	0	0
	5. PVDF manufacture with PFNA	400–1400	270	1270	30	220	0	0
	6. Use & disposal of PVDF dispersions containing PFN	10–20	10	20	0	0	0	0
	POSF-based products, as impurities							
	7. Manufacture phase	20–130 [b]	1	30	0	0.1	0	0
	8. Use & disposal phase		12	746	1.5	101	0	20
	fluorotelomer-based products, as impurities							
	9. Manufacture phase	0.3–30 [b]	0	0	0	0	0	0
	10. Use & disposal phase		17	34	30	61	10	20
Indirect	***Degradation of POSF-based products***							
	11. Manufacture, use & disposal	1–30	50	2400	6	226	0	180
	Degradation of fluorotelomer-based products							
	12. Manufacture, use & disposal	6–130	9	1518	13	1902	11	726
	Total direct sources [c]	3200–6900	1730 (3530)	10300 (6990)	800 (1990)	5050 (3340)	10 (10)	5510 (3830)
	Total indirect sources [c]	30–350	60	3920	20	2130	10	910
	Total emissions (direct + indirect) [c]	3200–7300	1790 (3590)	14220 (10910)	820 (2010)	7180 (5470)	20 (20)	6420 (4740)

[a] Two scenarios for country group II were set up: (i) a lower scenario in which producers cease production and use of long-chain PFCAs and their precursors in line with global transition trends and (ii) a higher scenario in which the emissions in 2015 is assumed to remain constant until 2030.

[b] The emission estimates in Prevedouros et al. (2006) include emissions both from manufacture and from use and disposal.

[c] The figures are rounded to the nearest 10.

3.2. Estimated global emissions of individual homologues from quantified sources

Fig. 5 shows the relative contribution of each source to the total estimated global emissions of individual PFCA homologues from all quantified sources in two periods (1951–2002 and 2003–2015). The dominant sources differ (sometimes considerably) between PFCA homologues. In 1951–2002, PFCA homologues can be divided into three groups: (i) the majority of C_8, C_9, C_{11} and C_{13} PFCAs were emitted from PFOA- and PFNA-based products, (ii) >50% of the C_5–C_7 PFCAs were released to the environment as degradation products of POSF- and fluorotelomer-based precursors, and (iii) for C_4, C_{10}, C_{12} and C_{14} PFCAs, the dominant source differs in the lower and higher scenarios. Moreover, the relative contribution of each source changes over time. After 2002, emissions from PFOA- and PFNA-based products are less relevant than before for almost all PFCA homologues, whereas emissions from fluorotelomer-based products, as impurities or as degradation products, are the dominant sources for most of the PFCA homologues after 2002.

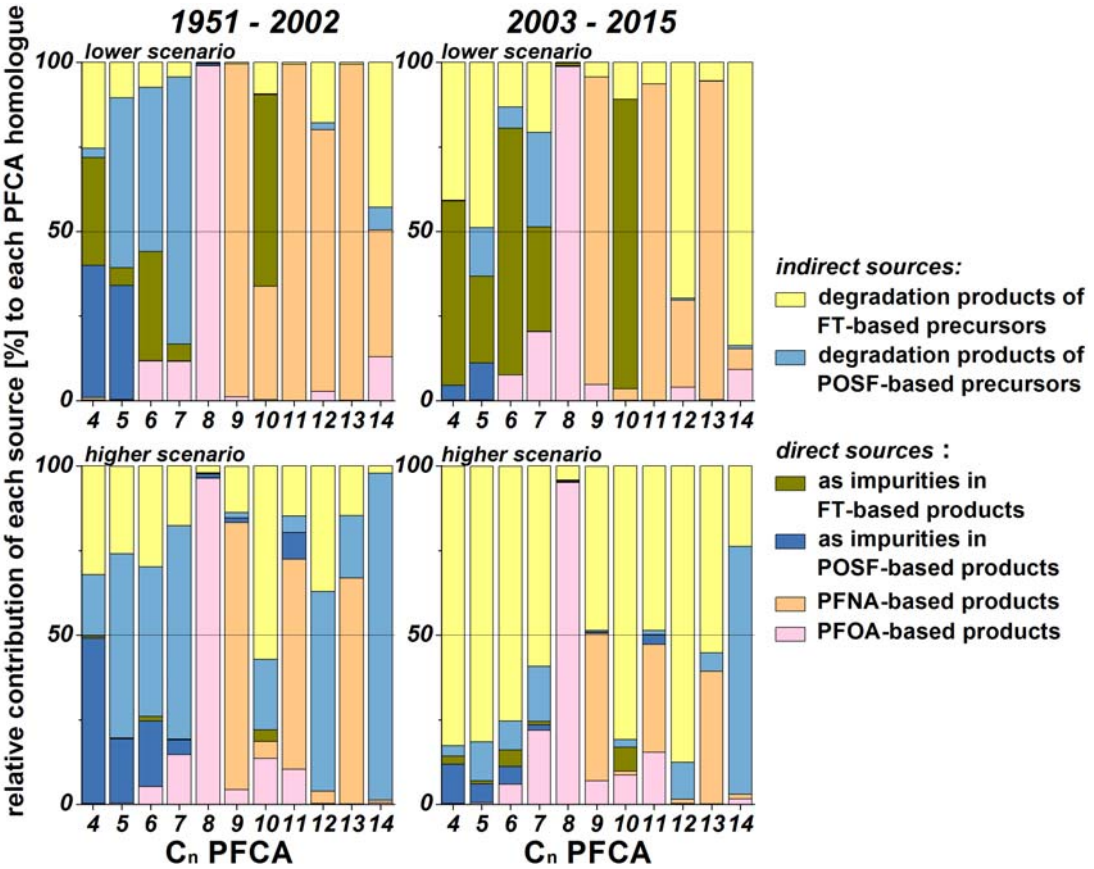

Fig. 5. Relative contributions of each source to estimated total global emissions from all quantified sources for individual C_4–C_{14} PFCA homologues in 1951–2002 (pre-phase-out) and 2003–2015 (transition after phase-out).

Table 2 lists the estimated global cumulative emissions of individual PFCA homologues from all quantified sources in 1951–2002, 2003–2015 and 2016–2030. C_8 and C_9 PFCAs are the homologues released in largest amounts, followed by C_4 and C_5 PFCAs. PFCAs with ten or more carbons are emitted in relatively low amounts compared to other homologues.

Table 2. Estimated global cumulative emissions of C_4–C_{14} PFCA homologues (1951–2030) from quantified sources in tonnes. Numbers in brackets indicate the percentage of emissions from direct sources. The percentage of emissions from indirect sources can be calculated as 100% minus these percentages. N.A. – not applicable.

C_n PFCA	1951–2002 [t]		2003–2015 [t]		2016–2030 [t]		Total [t]	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
C_4	5 (72%)	402 (50%)	5 (58%)	220 (14%)	6 (17%)	293 (3%)	15 (47%)	915 (26%)
C_5	14 (39%)	690 (20%)	5 (37%)	305 (7%)	7 (8%)	382 (2%)	26 (31%)	1377 (12%)
C_6	16 (26%)	1061 (26%)	17 (80%)	513 (16%)	5 (98%)	117 (48%)	39 (59%)	1691 (24%)
C_7	44 (17%)	2123 (19%)	13 (51%)	774 (24%)	2 (94%)	358 (64%)	59 (26%)	3264 (26%)
C_8	1344 (100%)	8184 (98%)	730 (100%)	4773 (96%)	3 (100%)	5408 (100%)	2078 (100%)	18366 (98%)
C_9	222 (100%)	1371 (85%)	28 (96%)	469 (51%)	0 (0%)	62 (72%)	250 (99%)	1901 (76%)
C_{10}	3 (91%)	109 (22%)	4 (89%)	93 (17%)	1 (100%)	20 (66%)	8 (91%)	222 (24%)
C_{11}	59 (99%)	471 (80%)	7 (93%)	173 (50%)	0 (N.A.)	45 (83%)	67 (99%)	689 (73%)
C_{12}	0 (80%)	40 (4%)	0 (0%)	20 (1%)	0 (N.A.)	3 (0%)	0 (63%)	63 (3%)
C_{13}	15 (99%)	109 (67%)	2 (94%)	35 (39%)	0 (N.A.)	3 (0%)	17 (99%)	147 (59%)
C_{14}	0 (0%)	16 (1%)	0 (0%)	2 (0%)	0 (N.A.)	1 (0%)	0 (0%)	19 (1%)

3.3. Analysis of industrial sources

As shown in Table 1, most of the historical PFCA emissions from quantified sources occurred at industrial point sources where PFCA-based products were produced or used (sources 1, 2, 4 and 5 in Table 1). Here, we take a closer look at these industrial sites, focusing on the mode of entry into the environment of emissions and on their geographical distribution (illustrated for PFOA-based products in Fig. 6), so as to provide information for future emission prevention or reduction measures. Major industrial events regarding PFCA, PASF- and fluorotelomer-based products that have likely resulted in increases or decreases in PFCA emissions since the 1950s are summarized in a timeline (see Figure S9 in the *Supplementary Data*).

Among all PFAS-related industrial sites, production sites of PFOA-based products and fluoropolymer production sites where PFOA-based products were used as processing aids are best studied. At these sites, most of the emissions occurred with wastewater streams, whereas small amounts were emitted with exhaust gases or solid wastes (see pie charts in Fig. 6). Since PFNA and its derivatives have physicochemical properties similar to those of PFOA and its derivatives, it is expected that a similar mode of entry occurred at sites where PFNA-based products were produced or processed. This is consistent with recent observations of high PFNA levels in industrial effluents from a metal-plating factory (US EPA, 2009b) and a textile factory (Clara et al., 2008). For POSF- and fluorotelomer-based derivatives, in contrast, a generalized mode of entry of emissions from industrial sites cannot be determined, because (i) at the primary production sites studied, only selected (but not all) substances were monitored in one or more (but not all) environmental compartments (3M, 2000b,c,d,e,f,g,h,i; Dauchy et al., 2012; Ruan et al., 2010) (ii) no mass

444 flow study is yet available at downstream industrial sites such as textile or paper factories
445 where products containing POSF- or fluorotelomer-based products are used.

446 A trend in the geographical distribution of major industrial sites is that production of PFCAs,
447 fluoropolymers and other PFAS products has shifted from Japan, Western Europe and the US
448 to the emerging economies in continental Asia (e.g., China and India), suggesting that the
449 proportion of global PFCA emissions originating from continental Asia has increased.
450 Detailed analyses for each product group (including references) are provided as follows.

451 i. ***PFOA-based products.*** There has been a rapid increase in domestic demand and
452 production of PTFE in China since the late 1990s (from 6.6 kt/yr in 1999 to about 64 kt/yr in
453 2012) (Kälin et al., 2012; Fang, 2004; Wang, 2006; Cai, 2009). Thus, the amounts of PFOA-
454 based products produced in China (initiated in the 1960s in Shanghai; Huang et al., 2010)
455 increased accordingly from a negligible amount before the 1990s to an annual production
456 capacity of about 50–80 tonnes in 2009, with at least five production sites now in China
457 (Mei, 2008). Similarly, PTFE production increased in India after 2010 (ca. 2.3 kt in 2011 and
458 7.5 kt in 2012; Kälin et al., 2012), resulting in a likely increase in use of PFOA-based products
459 as fluoropolymer processing aids. Thus, releases of PFCAs from these production sites of
460 PFOA-based products and fluoropolymer production sites in China and India have likely
461 increased (Fig. 6, orange areas). In contrast, after 2000, major PFOA producers in Japan,
462 Western Europe and the US subsequently ceased PFOA production (e.g. 3M in 2002 (3M,
463 2000a); Dyneon in 2004 and Miteni in 2010 (OECD, 2009); Daikin in 2012 (Daikin, 2013);
464 and DuPont in 2013 (DuPont, 2013)), and the remaining production was/is mostly
465 conducted in closed processes with marginal losses only (DuPont, 2005; OECD, 2009; US
466 EPA, 2006). At the same time, major fluoropolymer producers in these regions implemented
467 technologies to recover and reuse PFOA from wastewater streams (3M, 2009; Chapman,
468 1998; OECD, 2009) and started to use PFOA-free alternatives in the polymerization
469 processes (Dyneon uses alternatives only from 2009 (Dyneon, 2011), Asahi from 2011
470 (Asahi, 2009 a,b), Daikin and Solvay from 2013 (Daikin, 2013; Solvay, 2013), and DuPont
471 from mid-2013 (DuPont, 2013)). These actions have led to decreasing PFCA releases from
472 production sites in Japan, Western Europe and the US after 2000 (Fig. 6, purple areas). The
473 increase in PFCA emissions at the manufacturing sites of PFOA-based products and
474 fluoropolymers in country group II is likely much faster than the decline at such sites in
475 country group I in the period 2002–2012, causing a re-increase of global annual PFCA
476 emissions as illustrated in Fig. 4. It should be noted that several major Chinese
477 fluoropolymer producers have also developed technologies to recycle PFOA from waste
478 streams (Feng, 2007; Tang et al., 2009) or industrialized production with alternative
479 substances replacing PFOA-based products (Wang et al., 2010; Xie et al., 2011; Xu et al.,
480 2011); however, due to a lack of quantitative data, the corresponding reduction of PFCA
481 releases from these sites in China cannot be quantified and has not been included here. In

addition to these industrial activities, regulatory activities have been undertaken in China. In 2011, PFOA-relevant technology and products were added to the *Catalogue for the Guidance of Industrial Structure Adjustment* (NDRC, 2011), including that new installation of PFOA production facilities shall be restricted and that PFOA-containing paints and fluoropolymers that use PFOA in the polymerization shall be eliminated. In 2013, fluoropolymers that use PFOA in the polymerization were recognized as products with high pollution and high environmental risk ("dual-high" products) in the *Comprehensive Catalog for Environmental Protection* (China MEP, 2013). However, it is currently unclear when the producers in regions such as China, India and Russia will phase-out PFOA-based products, as a detailed timeline for the restriction and elimination of PFOA in these regions has not been available.

ii. ***PFNA-based products.*** Reports from the only known producer and major industrial users (i.e., PVDF producers) in Japan, Western Europe and the US show that emissions related to PFNA-based products from their production sites were reduced in the last few years (APFN Work Group, 2003) and PFCA-free alternatives have been developed and partially implemented (Arkema, 2011). Although PVDF production in China started to increase rapidly after 2008 (3F, 2011; Kälin et al., 2012), the producers there have likely used either PFOA-based products or PFCA-free alternatives in the polymerization process, but not PFNA-based products (Arkema, 2008; Zhao et al., 2011). Hence, it is likely that emissions from the life-cycle of PFNA-based products have been reduced worldwide since 2002.

iii. ***POSF-based products.*** The geographical shift has also been observed for the industrial sites that produce and use POSF-based products. After 3M ceased its global production of POSF-based products in 2002, there were still a few producers in Japan and Western Europe: about 50–160 tonnes of POSF-based products were produced in 2003 in Belgium, Germany, Italy and Japan (OECD, 2005); and 73–162 tonnes in 2005 (OECD, 2006). We assumed that production in these regions decreased linearly thereafter and only negligible amounts (for those uses for which exemptions have been defined under the Stockholm Convention) were produced after 2008, due to regulatory efforts under the EU Directive 2006/122/EC and the Stockholm Convention on Persistent Organic Pollutants. Meanwhile, major downstream industrial users in these regions such as hard metal plating started to use alternatives (OECD, 2006; UNEP, 2012; Wang et al., 2013). Hence, there is likely a strong decrease of emissions of PFCA impurities and POSF-based PFCA precursors from these industrial sites in Japan, Western Europe and the US after 2002. In contrast, large-scale production began in China in 2003, with extensive use of polymeric POSF-based products in textile, carpet and leather surface treatments between 2003 and 2008 (in a similar amount to the uses of non-polymeric products) (Zhang et al., 2012). Reported total annual production in China before 2004 was less than 50 t/yr, expanded to about 250 t/yr by 2006, and declined to 100 t/yr in 2008 (Huang, 2010; Lim et al., 2011; China MEP, 2008; Zhang et al., 2012). The remaining uses are mainly in metal plating, aqueous film-forming foams

(AFFF) synthesis and sulfluramid (insecticide) formulation (Zhang et al., 2012). Recently, Chinese manufacturers have developed or are developing alternative substances to replace PFOS and related chemicals (UNEP, 2012; Wang et al., 2013). Furthermore, POSF-based products have been added by Chinese regulators to China's domestic *Catalogue for the Guidance of Industrial Structure Adjustment* (NDRC, 2011) so that new installations of POSF production facilities shall be restricted and paints containing POSF-based substances shall be eliminated. However, a detailed phase-out plan is not yet available.

iv. ***Fluorotelomer-based products.*** It is currently unclear how the geographical distribution of emissions from industrial sites where fluorotelomer-based products are manufactured and used change with time (our estimates represent production and emissions on a global scale without regional resolution). Historically, production of fluorotelomer-based products was located in Japan, Western Europe and the US (Banks, 1994; Prevedouros et al., 2006). Recently, manufacturers in China also started the production of fluorotelomer-based substances at a minimum of two sites (Fuxin, 2013; Ruan et al., 2010) and one manufacturer may have initiated production in India (AFT, 2013). Thus, it is likely that emissions of fluorotelomer-based products from industrial sites have increased in China and India. The relative weight of emissions at industrial sites between regions, however, cannot be determined due to scarce information regarding the amounts produced and used in all regions.

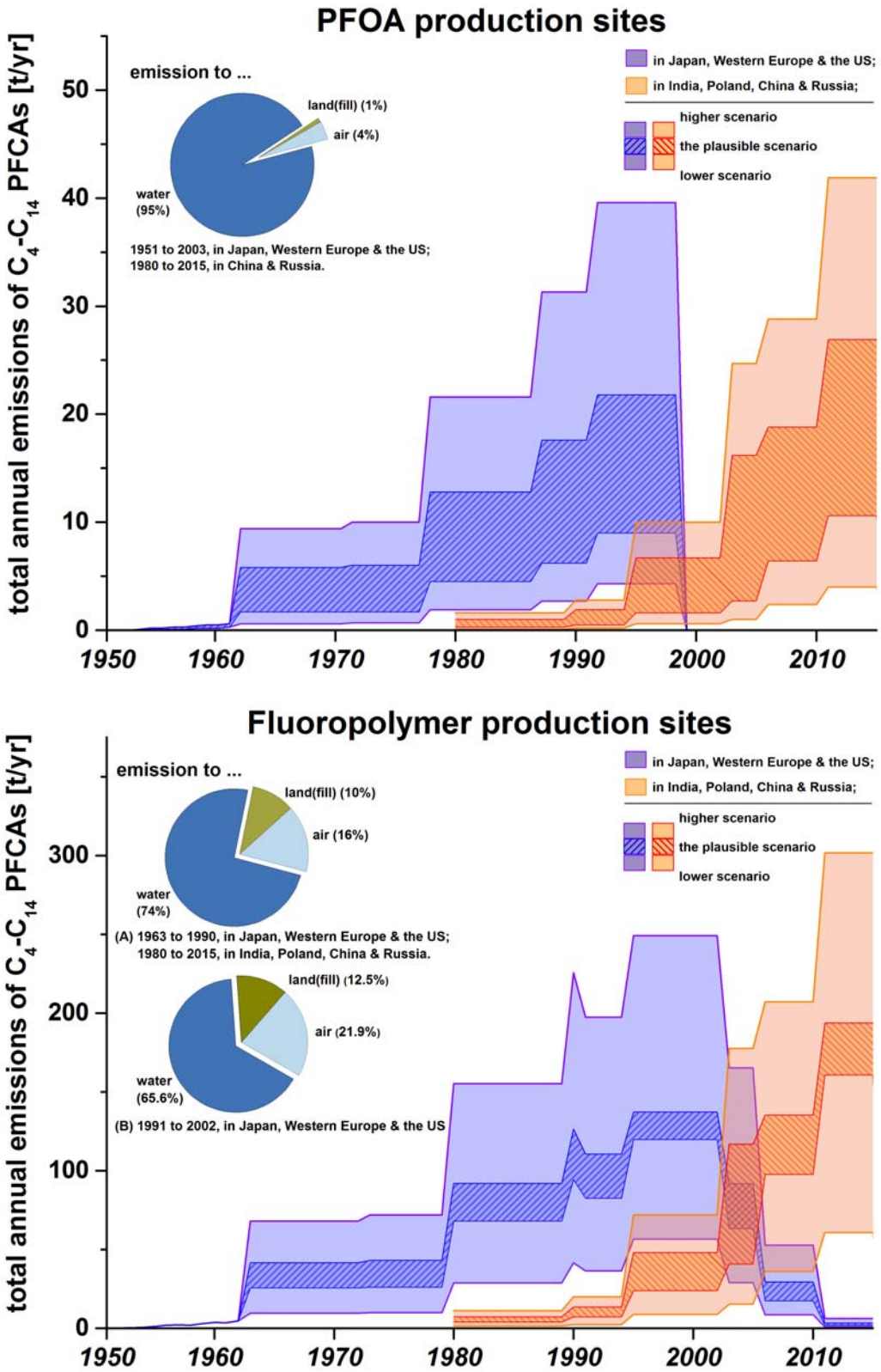

Fig. 6. Estimated annual releases of PFCAs from PFOA production sites (top) and fluoropolymer (FP) production sites (bottom) in the United States (US), Western Europe and Japan (purple) as well as in China, Russia, Poland and India (orange). The pie charts show fractions of emissions to different environmental media. The colored areas represent the estimated ranges of annual emissions based on the full ranges of the APFO/NaPFO use rates from patents; the areas shaded in dark represent the estimated ranges of annual releases based on the APFO/NaPFO use rate of 0.3 wt% of relevant fluoropolymers produced (plausible scenario).

546 # 4. Discussion

547 ## 4.1 Comparison to Prevedouros et al. and other literature

548 In estimating emissions from PFCA precursors, we have modified the approach of
549 Prevedorous et al. (2006) as described in the *Methods* section. Here we focus on the
550 evaluation of our newly estimated emissions that occur during the life-cycle of POSF- and
551 fluorotelomer-based products.

552 We estimated considerably higher releases of PFCAs as impurities in POSF-based products
553 than Prevedorous et al. (2006) (ca. 5 times in our higher scenario; sources 7 and 8 in Table
554 1). This higher estimate is caused by the fact that the levels of PFCA impurities (200–1600
555 ppm) in Prevedorous et al. (2006) represent only the PFOA content in products (3M, 2003),
556 whereas we include impurity levels of all C_4–C_{14} homologues (400–13300 ppm) based on
557 four recent studies (3M, 2003; Naile et al., 2010; Reagen et al., 2007; Seacat et al., 2003; for
558 details see *Section S1.3.2* in the *Supplementary Data*). It is possible that these estimated
559 levels of PFCA impurities are still underestimated because in an early study, a 1% (10000
560 ppm) yield of solely perfluorooctanoyl fluoride formed in the electrochemical fluorination to
561 produce POSF was reported (Gramstad and Haszeldine, 1957). In addition, measurements of
562 PFCAs in a few technical products show that the levels of PFCA impurities vary considerably
563 within a production line and among products (Jackson et al., 2013a; Naile et al., 2010;
564 Reagen et al., 2007; Seacat et al., 2003). Hence, further studies on PFCA impurities in POSF-
565 based products are needed to improve the understanding of this historical source. Note that
566 part of the PFCA impurities formed during the production of POSF can react with the
567 substances added in the subsequent reactions of POSF and form derivatives such as
568 perfluorooctanamides ($C_7F_{15}CONH(R)$, R = CH_3 or C_2H_5) and their homologues (Jackson et al.,
569 2013a). Similar to their sulfonamide analogues, these perfluoroalkane carboxamides can be
570 transformed back into the corresponding PFCA (and its shorter-chain homologues) through
571 OH-radical mediated reactions in air (Jackson et al., 2013b) and enzymatic hydrolysis in
572 biota (Seacat, 2004) and thus act as sources of PFCAs. Therefore, in addition to C_4–C_{14} PFCA
573 homologues, their derivatives in technical products (e.g. perfluoroalkane carboxamides, see
574 Jackson et al., 2013a; methyl esters, see Hanari et al., 2014) should be considered in future
575 studies. Given that these historical POSF-based products are no longer manufactured,
576 obtaining samples for future studies is problematic.

577 Two changes made in this study contribute to the higher estimates of PFCAs released from
578 degradation of POSF- and fluorotelomer-based precursors (Table 1, sources 11 and 12).
579 First, in addition to residuals, which were treated as the only source of PFCA precursors in
580 Prevedouros et al. (2006), we take two more sources into account, namely [i] PFCA
581 precursors such as EtFOSAs and FTSAs that are present in products as ingredients, and [ii]
582 substances with complex structures that may break down to PFCA precursors such as

583 EtFOSE or FTOHs. Second, we used updated degradation yields in the calculations that were
584 derived from recent studies showing that a wide range of PFCA homologues can be formed
585 from precursors under varied conditions. For example, N-ethyl perfluorobutane sulfonamide
586 (EtFBSA) may transform into C_2–C_4 PFCAs through OH radical oxidation (Martin et al., 2006),
587 and 8:2 FTOH ($C_8F_{17}C_2H_4OH$) can degrade into C_6–C_8 PFCAs biotically (Liu et al., 2007; Wang
588 et al., 2005) or C_5–C_9 PFCAs through OH radical oxidation (Ellis et al., 2004). Details on
589 emissions of POSF- and fluorotelomer-based PFCA precursors and degradation yields of
590 PFCAs are provided in *Sections S1.3.3* and *S1.4.3* in the *Supplementary Data*.

591 To evaluate our estimates for emissions of POSF- and fluorotelomer-based PFCA precursors,
592 we compared our results for 8:2–14:2 FTOHs as well as perfluorooctane sulfonamides and
593 sulfonamidoethanols (*x*FOSA/Es, x = CH_3 and C_2H_5) with three studies conducted with
594 different approaches (Buser and Morf, 2009; Müller et al., 2012; Wang et al., 2012; Yarwood
595 et al., 2007) (see Fig. 7 and Table S65 in the *Supplementary Data*). Yarwood et al. (2007)
596 estimated emissions of 8:2–14:2 FTOHs in North America in 2004 and 2007, based on
597 DuPont's sales data and reduction plan, respectively. Using the emission estimates in 2004
598 as input data, a North America-based air quality model predicted FTOH levels in air that
599 were in agreement with monitoring data, suggesting that the 2004-emission scenario is
600 plausible (Yarwood et al., 2007). Buser and Morf (2009) reported emission estimates for 8:2
601 and 10:2 FTOHs into air in Switzerland in 2007, based on a substance flow analysis for
602 residual contents of FTOHs detected in samples including aqueous dispersions of
603 fluorotelomer-based polymers and other fluorinated surfactants. Wang et al. (2012) used a
604 multimedia mass-balance model that describes the day-night cycle of (semi-)volatile organic
605 chemicals in air to interpret day-night measurements of FTOHs (8:2 and 10:2) and *x*FOSAs
606 performed in summer 2010 in Zurich, Switzerland (Müller et al., 2012). They estimated the
607 source strength of these PFCA precursors released during the use and disposal of consumer
608 products from Zurich, where there is no PFAS-related industry. To compare our emission
609 estimates to these other studies, all estimates were normalized to global annual emissions
610 based on per-capita emissions (data are listed in Table S65 in the *Supplementary Data*),
611 since: (i) FTOHs and *x*FOSA/Es are primarily emitted from use of household consumer
612 products; (ii) uses and levels of FTOHs and *x*FOSA/Es are broadly similar in households in
613 industrialized regions throughout the industrialized world, as observed in air monitoring
614 studies (Shoeib et al., 2011).

615 For *x*FOSA/Es, our emission estimates are ca. 14–29 t/yr higher than the range of *x*FOSAs
616 emissions in Wang et al. (2012) (Fig. 7, left). This is likely caused by the different scope of
617 these two studies. Estimates in Wang et al. (2012) represent only emissions during the use
618 and disposal of consumer products such as paper, textiles and carpets that were treated with
619 POSF-based products, whereas estimates in the present study also include use of EtFOSA in
620 insecticides in Brazil (ca. 30 t/yr; assuming 50–100% emitted) (UNEP, 2007). Thus, our

621 "bottom-up" estimates of *x*FOSA/Es emissions are in good agreement with the combined
622 modeling and monitoring studies (Müller et al., 2012; Wang et al., 2012).

623 For 8:2 and 10:2 FTOHs, the higher bounds of the estimates in this paper are slightly higher
624 than the median value of the 2004-emission scenario (by less than a factor of 3) and much
625 higher than the median value of the 2007-emission scenario in Yarwood et al. (2007) (Fig. 7,
626 middle and right). This finding is consistent with a monitoring study (Shoeib et al., 2010)
627 reporting that levels of 8:2 FTOH in air samples collected on the Gulf of Mexico and East
628 Coast Carbon Cruise in 2007 are close to the model results of Yarwood et al. (2007) based on
629 the 2004-emission scenario. In addition, our estimated emission ranges are well within the
630 range of emissions estimated by Buser and Morf (2009) and slightly higher (by factors of 3
631 and 6 for 8:2 and 10:2 FTOH in the higher scenario, respectively) than the emission ranges
632 estimated by Wang et al. (2012). Similarly to xFOSA/Es, emission estimates in Wang et al.
633 (2012) represent solely diffusive releases from use and disposal of consumer products,
634 whereas our estimates also take production and processing by downstream industrial users
635 into account. For 12:2 FTOH, the median value of the 2004-emission scenario in Yarwood et
636 al. (2007) is within the range of our estimates; the median value of 14:2 FTOH from the
637 2004-emission scenario in Yarwood et al. (2007) is slightly higher than our estimates (see
638 Table S65 in the *Supplementary Data*).

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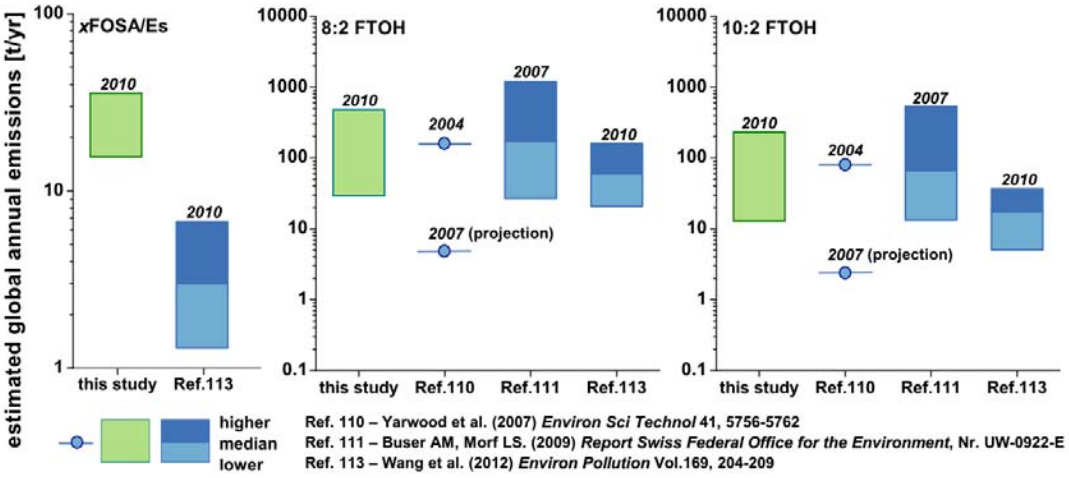

640 **Fig. 7.** Estimated emission ranges of *x*FOSA/Es, 8:2 FTOH and 10:2 FTOH in 2010 in this study
641 (green boxes) and estimated emission ranges in 2004 and 2007 from Yarwood et al. (2007), in
642 2007 from Buser and Morf (2009) and in 2010 from Wang et al. (2012) (blue boxes).

643 In summary, our improvements on the emission quantification of PFCA precursors (8:2–14:2
644 FTOHs and *x*FOSA/Es) are reasonable; but there are still important data gaps, as indicated in
645 the *Uncertainty Analysis* section. The ongoing high emissions of 8:2 and 10:2 FTOHs instead
646 of a sharp decrease as projected by Yarwood et al. (2007) are likely caused by one or a
647 combination of the following factors: (i) not all fluorotelomer producers and/or downstream

industrial users follow a similar emission reduction plan as projected by Yarwood et al. (2007); (ii) despite the reduction of the relative emissions (per kg of products), the absolute emissions have not decreased due to increasing amounts of products being produced and used; (iii) new producers started to manufacture and process fluorotelomer-based products, for example, in China (Fuxin, 2013; Ruan et al., 2010) and India (AFT, 2013); (iv) Yarwood et al. (2007) assumed that emissions occur only in the year when 8:2 and 10:2 FTOHs were produced, thus a lag time of emissions during the use and disposal that occurs in reality was not considered.

4.2. Comparison to estimated ocean inventory

Since ocean water is the major global reservoir of PFOA, PFNA and likely the other PFCA homologues (Cousins et al., 2011), we used an inventory of C_4–C_{14} PFCA homologues in open ocean surface water (denoted as the "ocean inventory" in the following) derived from monitoring studies (Ahrens et al., 2009, 2010; Benskin et al., 2012b,c; Cai et al., 2012a,b; Wei et al., 2007; Yamashita et al., 2005, 2008; Zhao et al., 2012) for another independent evaluation of our results. We have made two changes in estimating the ocean inventory in comparison to Prevedouros et al. (2006): (i) we extended the ocean inventory in the Northern Hemisphere to a global ocean inventory by taking monitoring studies from the Southern Hemisphere into account; (ii) instead of using the range of measured PFCA levels, we used the software "ProUCL 4.1" from US EPA to perform a statistical analysis that includes "non-detect" samples (i.e. those that are measured above the detection limit, but below the quantification limit) to calculate the 95% upper confidence limit of the background level. For details on raw data and data analysis, see section 2.5 in the *Supplementary Data.* The comparison of our estimated emissions and the ocean inventory is shown in Fig. 8.

The higher values of our emission inventories of C_7–C_9 and C_{11} PFCAs show a good agreement with the ocean inventories based on the median oceanic mixed layer depth (150m); they are within or close to a factor of 1.5. This indicates that the major sources of these PFCA homologues have been covered in this study (see also Fig. 5 and Table 2). For the other PFCA homologues, particularly C_4, C_5, C_{10}, C_{12}–C_{14} PFCAs, the ocean inventory substantially exceeds our emission inventory and there thus appear to be missing sources.

Despite the large uncertainty associated with the ocean inventory caused by limited measurements (in the case of C_4 and C_5 PFCAs, about 80% of measurements are "non-detect" samples; Ahrens et al., 2010b, Cai et al., 2012a,b), the huge discrepancy between the ocean inventory and the emission inventory for the C_4, C_5, C_{10}, C_{12}–C_{14} PFCAs could have the following plausible explanations. First, the newly identified but currently unquantifiable

sources shown in Fig. 2 may have contributed significantly to the presence of these PFCA homologues in the environment. For example, PFCAs may be emitted as ingredients, impurities and/or degradation products during the life-cycle of C_4–C_7 PFCA- as well as C_4–C_7 and C_{10} PASF-based products that were already in use in the US in the 1980s or even earlier (>4.5 t/yr) (US EPA, 2013). In addition, some other commercially available substances such as hydrofluoroethers (HFEs) or odd-carbon-numbered fluorotelomer alcohol (n:1 FTOH or $CF_3(CF_2CF_2)_nCH_2OH$, n = 1 or 2) may undergo atmospheric transformation and form short-chain PFCAs (Bravo et al., 2010). Details on these new sources are presented in the companion paper (Wang et al., 2014). Second, the levels of PFCA homologues as impurities in POSF- and fluorotelomer-based products may have been underestimated, since they are derived from very limited measurements (see sections S1.3.2 and S1.4.2 in the *Supplementary Data*). Third, emissions of long-chain fluorotelomer-based precursors (e.g. 14:2 FTOH) may have been underestimated.

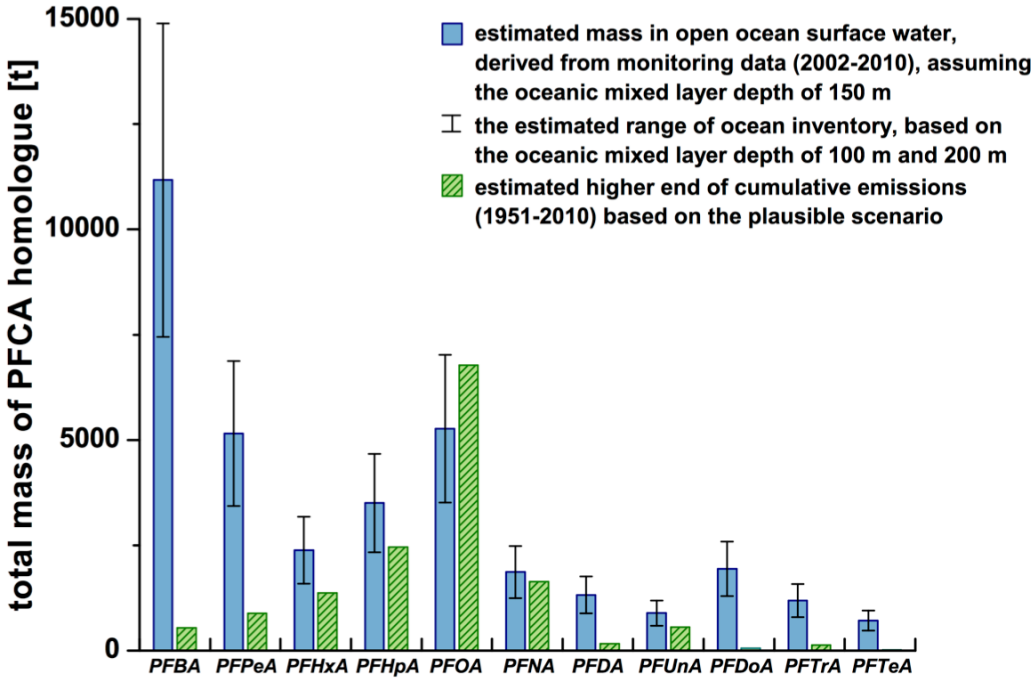

Fig. 8. Blue: estimated ocean inventories of C_4–C_{14} PFCAs derived from monitoring studies[117-126] based on the median oceanic mixed-layer depth of 150 m. Green: higher values of our cumulative emissions of C_4–C_{14} PFCA homologues until 2010, based on the use rate of 0.3 wt% PFOA-based products as processing aids in fluoropolymer production (i.e. the plausible scenario). The error bars represent the range of ocean inventory based on oceanic mixed layer depths from 100 to 200 m).

4.3. Uncertainty analysis

In Tables S66 to S68 in the *Supplementary Data*, we provide for all parameters their origin (estimated or assumed), estimated uncertainty level indicated by their uncertainty score, and location of details in the *Supplementary Data.* In general, the uncertainty levels increase

709 in the order: [i] PFOA-based products ≤ PFNA-based products < POSF-based products <
710 fluorotelomer-based products; [ii] production phase < use and disposal phase; [iii]
711 emissions from 1951 to 2015 < emissions from 2016 to 2030.

712 For PFOA-based products, the estimated amounts used in fluoropolymer production have
713 the largest uncertainty, due to: [i] the use rates are reported in wide ranges; and [ii] the
714 transition process to non-PFCA alternatives after 2002 has only been roughly reported. To
715 address the first uncertainty, we proposed a plausible scenario that is likely to be close to
716 actual industrial practice; regarding the second uncertainty, we may have overestimated the
717 amounts used in recent years, which can only be corrected with new information. For PFNA-
718 based products, the composition of PFCA homologues in products is the most uncertain
719 parameter, since only one measurement is available. For POSF- and fluorotelomer-based
720 products, only little information is available for the use and disposal phase, due to the huge
721 diversity of products involved, leading to wide ranges of emissions estimated in this study.
722 In addition, the estimated production of fluorotelomer-based products is highly uncertain.

723 Furthermore, the projections of PFCA emissions (2016–2030) have much higher
724 uncertainties in comparison to the emission estimates for the period before 2016, due to the
725 large uncertainty associated with the elimination of production and use of long-chain PFASs
726 in country group II. There is evidence that action is being taken in these regions to replace
727 long-chain PFASs with alternatives substances (for references, see *Section 3.3, Analysis of*
728 *industrial sources,* and Wang et al., 2013); therefore, the production, use and emissions of
729 long-chain PFASs are likely being reduced in these regions. However, a quantitative emission
730 reduction strategy has not currently been reported for these regions.

731

732 ## 5. Future prospects

733 In this review we have for the first time provided homologue-specific global emission
734 estimates for C_4–C_{14} PFCAs from 1951 to 2030. Quantified sources of PFCAs include PFOA-,
735 PFNA-, POSF- and fluorotelomer-based products (see Fig. 2). The dominant sources differ (in
736 some cases considerably) between individual PFCA homologues and the relative
737 contributions of different sources changes over time. The emission estimates are possibly
738 too low for some homologues (especially C_4 and C_5 PFCAs), because there are newly
739 identified but currently unquantifiable sources, including (i) historical and current use of
740 products based on C_4–C_7 perfluoroalkane carbonyl fluorides (PACFs) as well as C_4–C_7 and C_{10}
741 PASFs and (ii) potential formation from fluoropolymers, side-chain fluorinated polymers or
742 other unknown precursors (for details on these currently unquantifiable sources, see
743 companion paper; Wang et al., 2014).

744 Our emission estimates are global totals and thus the PFCA homologue pattern in the
745 inventories may differ from those observed in environmental and biota samples taken at
746 specific sites, because (i) environmental and biota samples reflect the influence of various
747 local sources, and (ii) the PFCA homologue source pattern can be significantly transformed
748 between emission and samples taken in environmental or biological media due to
749 differences in the fate and bioaccumulation of individual homologues. Nevertheless, our
750 emission inventory is a further step towards the goal of understanding the variability in
751 PFCA homologue patterns in environmental and biological matrices in different geographical
752 regions. We encourage environmental fate studies to take advantage of the data presented
753 here, particularly in continental Asia where future emissions will predominantly occur.

754

755 **Acknowledgements.** The Swiss Federal Office for the Environment (FOEN) provided
756 funding for this research. We thank US EPA for providing the AR-226 documents, Gai
757 Junchao for providing peer-reviewed articles from Chinese journals and Matthew MacLeod
758 for useful comments.

759

760 **Conflict of Interest.** R.C. Buck is an employee of E.I. duPont de Nemours and Company,
761 Inc., a global manufacturer of fluoropolymers and flurootelomer-based products.

762

763 **Supplementary Data.** Details on methodologies for estimating emissions from each
764 source as well as additional information, figures and tables as noted in the text are provided
765 in the *Supplementary Data*.

766

References

3F. News: 3F becomes the largest domestic producer and distributor of PVDF. Jiang Su Lu Jian 2011;2. (in Chinese)

3M. Letter to US EPA Re: phase-out plan for POSF-based products (226-0600); US EPA Administrative Record 226 2000a; pp. 1–11.

3M. Voluntary use and exposure information profile: perfluorooctane sulfonamid (226-0577); submitted by 3M in US EPA Administrative Record 226 2000b; pp. 1–14.

3M. Voluntary use and exposure information profile: N-ethyl perfluorooctanesulfonamide (226-0580); submitted by 3M in US EPA Administrative Record 226 2000c; pp. 1–23.

3M. Voluntary use and exposure information profile: N-methyl perfluorooctanesulfonamide (226-0581); submitted by 3M in US EPA Administrative Record 226 2000d; pp. 1–20.

3M. Voluntary use and exposure information profile: N-ethyl perfluorooctylsulfonamido ethanol (226-0582); submitted by 3M in US EPA Administrative Record 226 2000e; pp. 1–24.

3M. Voluntary use and exposure information profile: N-methyl perfluorooctanesulfonamido ethanol (226-0583); submitted by 3M in US EPA Administrative Record 226 2000f; pp. 1–23.

3M. Voluntary use and exposure information profile: N-ethyl perfluorooctylsulfonamido ethyl acrylate (226-0584); submitted by 3M in US EPA Administrative Record 226 2000g; pp. 1–19.

3M. Voluntary use and exposure information profile: N-ethyl perfluorooctanesulfonamido ethyl methacrylate (226-0585); submitted by 3M in US EPA Administrative Record 226 2000h; pp. 1–20.

3M. Voluntary use and exposure information profile: N-methyl perfluorooctanesulfonamido ethyl acrylate (226-0586); submitted by 3M in US EPA Administrative Record 226 2000i; pp. 1–25.

3M. Environmental, health and safety measures relating to perfluorooctanoic acid and its salts (PFOA) - US. EPA EDocket OPPTS-2003-0012-0007; 2003.

3M. Activities at 3M and Dyneon LLC to Develop PFC Alternatives. Contribution to the Workshop on Managing Perfluorinated Chemicals and Transistioning to Safer Alternatives. Geneva Switzerland 12-13 February 2009. p 1–7.

AFT. Product catalogue: telomer; Advanced fluorine technologies Pvt. Ltd. 2013. http://www.aftpl.com/products.htm

Ahrens L, Barber JL, Xie Z, Ebinghaus R. Longitudinal and latitudinal distribution of perfluoroalkyl compounds in the surface water of the Atlantic Ocean. Environ Sci Technol 2009;43:3122–7.

Ahrens L, Gerwinski W, Theobald N, Ebinghaus R. Sources of polyfluoroalkyl compounds in the North Sea Baltic Sea and Norwegian Sea: Evidence from their spatial distribution in surface water. Mar Pollut Bull 2010;60:255–60.

APFN Work Group. presentation to US EPA (226-1298); US EPA Administrative Record 226 2003; pp. 1–10.

Arkema. Arkema eliminates fluorosurfactants from Kynar 500® PVDF. 2008. http://www.arkema.com/en/media/news/news-details/Arkema-eliminates-fluorosurfactants-from-Kynar-500-PVDF/

Arkema. Letter: Arkema Inc. 2010 update reporting for EPA PFOA Stewardship Program; US EPA 2010/2015 PFOA Stewardship Program 2011; pp. 1–4. http://www.epa.gov/oppt/pfoa/pubs/stewardship/Arkema2011.pdf

Armitage J, Cousins IT, Buck RC, Prevedouros K, Russell MH, MacLeod M, Korzeniowski SH. Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. Environ Sci Technol 2006;40:6969–75.

Armitage JM, MacLeod M, Cousins IT. Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model. Environ Sci Technol 2009a;43:1134–40.

Armitage JM, MacLeod M, Cousins IT. Comparative assessment of the global fate and

transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources. Environ Sci Technol 2009b;43:5830–6.
Asahi. Fluon PTFE will be free of PFOA. Sealing Technology 2009a;6:2. DOI: 10.1016/S1350-4789(09)70303-4.
Asahi. PFC activities at Asahi. Contribution to the Workshop on Managing Perfluorinated Chemicals and Transistioning to Safer Alternatives. Geneva Switzerland 12-13 February 2009b, 1–2.
Banks RE, Smart BE, Tatlow JC. Organofluorine chemistry: principles and commercial applications; Plenum Press: New York and London 1994.
Benskin JP, Phillips V, St Louis VL, Martin JW. Source elucidation of perfluorinated carboxylic acids in remote alpine lake sediment cores. Environ Sci Technol 2011;45: 7188–94.
Benskin JP, Ikonomou MG, Gobas FAPC, Woudneh MB, Cosgrove JR. Observation of a novel PFOS-precursor the perfluorooctane sulfonamido ethanol-based phosphate (SAmPAP) diester in marine sediments. Environ Sci Technol 2012a;46:6505–14.
Benskin JP, Ahrens L, Muir DCG, Scott BF, Spencer C, Rosenberg B, Tomy G, Kylin H, Lohmann R, Martin JW. Manufacturing origin of perfluorooctanoate (PFOA) in Atlantic and Canadian Arctic seawater. Environ Sci Technol 2012b;46:677–85.
Benskin JP, Muir DCG, Scott BF, Spencer C, De Silva AO, Kylin H, Martin JW, Morris A, Lohmann R, Tomy G, Rosenberg B, Taniyasu S, Yamashita N. Perfluoroalkyl acids in the Atlantic and Canadian Arctic Oceans. Environ Sci Technol 2012c;46:5815–23.
Benskin JP, Ikonomou MG, Gobas FAPC, Begley TH, Woudneh MB, Cosgrove JR. Biodegradation of N-ethyl perfluorooctane sulfonamido ethanol (EtFOSE) and EtFOSE-based phosphate diester (SAmPAP diester) in marine sediments. Environ Sci Technol 2013;47:1381–89.
Bravo I, Díaz-de-Mera Y, Aranda A, Smith K, Shine KP, Marston G. Atmospheric chemistry of $C_4F_9OC_2H_5$ (HFE-7200), $C_4F_9OCH_3$ (HFE-7100), $C_3F_7OCH_3$ (HFE-7000) and C_3F_7CH2OH: temperature dependence of the kinetics of their reactions with OH radicals atmospheric lifetimes and global warming potentials. Phys Chem Chem Phys 2010;12:5115–25
Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, De Voogt P, Jensen AA, Kannan K, Mabury SA, van Leeuwen SPJ. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology classification and origins. Integr Environ Assess Manag 2011;7:513–41.
Buser A, Morf L. Substance flow analysis for Switzerland: Perfluorinated surfactants perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA); 67; Swiss Federal Office for the Environment (FOEN) 2009; pp. 1–146.
Cai F. Current situation of fluorochemicals and development proposal in our country. Chemical Engineer 2009;23:7. (in Chinese) DOI: 10.3969/j.issn.1002-1124.2009.07.020
Cai M, Yang H, Xie Z, Zhao Z, Wang F, Lu Z, Sturm R, Ebinghaus R. Per- and polyfluoroalkyl substances in snow lake surface runoff water and coastal seawater in Fildes Peninsula King George Island Antarctica. J Hazard Mater 2012a;209-210:335–42.
Cai M, Zhao Z, Yin Z, Ahrens L, Huang P, Cai M, Yang H, He J, Sturm R, Ebinghaus R, Xie Z. Occurrence of perfluoroalkyl compounds in surface waters from the North Pacific to the Arctic Ocean. Environ Sci Technol 2012b;46:661–8.
Chapman G. Meeting notes and charts for the January 6 and 7, 1998 PACE Team Meetings (226-2084); US EPA Administrative Record 226 1998; pp. 1–34.
China MEP (China Ministry of Environmental Protection). Memo to Mr. Donald Cooper, Secretariat of the Stockholm Convention: additional information on production and use of PFOS; Stockholm Convention on Persistent Organic Pollutants 2008.
China MEP (China Ministry of Environmental Protection). Comprehensive Catalog for Environmental Protection. 2013.
http://www.mep.gov.cn/gkml/hbb/bgth/201401/W020140124406842816106.pdf
Clara M, Scheffknecht C, Scharf S, Weiss S, Gans O. Emissions of perfluorinated alkylated substances (PFAS) from point sources - identification of relevant branches. Water Sci Technol 2008;58:59–66.
Conder JM, Hoke RA, De Wolf W, Russell MH, Buck RC. Are PFCAs bioaccumulative? A critical

878 review and comparison with regulatory criteria and persistent lipophilic compounds.
879 Environ Sci Technol 2008;42:995–1003.
880 Cousins IT, Kong D, Vestergren R. Reconciling measurement and modelling studies of the
881 sources and fate of perfluorinated carboxylates. Environ Chem 2011;8:339–54.
882 Daikin. Elimination of PFOA in fluorochemical products; Daikin Industries Ltd. 2013.
883 http://www.daikin.com/chm/pfoa/
884 Dasu K, Royer LA, Liu J, Lee LS. Hydrolysis of fluorotelomer compounds leading to
885 fluorotelomer alcohol production during solvent extractions of soils. Chemosphere
886 2010;81:911–7.
887 Dasu K, Liu J, Lee LS. Aerobic soil biodegradation of 8:2 fluorotelomer stearate monoester.
888 Environ Sci Technol 2012;46:3831–6.
889 Dauchy X, Boiteux V, Rosin C, Munoz JF. Relationship between industrial discharges and
890 contamination of raw water resources by perfluorinated compounds: part II: case study
891 of a fluorotelomer polymer manufacturing plant. B Environ Contam Tox 2012;89:531–6.
892 DuPont. Presentation to EPA: DuPont global PFOA strategy - comprehensive source
893 reduction (226-1914); US EPA Administrative Record 226 2005; pp. 1–43.
894 DuPont. Letter to US EPA OPPT Document Control Office. 2013.
895 http://www2.dupont.com/PFOA2/en_US/assets/downloads/Letter-to-EPA-with-VSP-
896 Submission-Oct-31-2013.pdf
897 Dyneon. PFOA-free fluoropolymer production early complete conversion has paid off. Vision
898 in Plastics 2011;1:26–7.
899 ECHA (European Chemical Agency). Candidate List of Substances of Very High Concern for
900 Authorisation. 2013. http://echa.europa.eu/web/guest/candidate-list-table
901 Ellis DA, Martin JW, De Silva AO, Mabury SA, Hurley MD, Sulbaek Andersen MP, Wallington
902 TJ. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated
903 carboxylic acids. Environ Sci Technol 2004;38:3316–21.
904 Fang X. Current state and trend of fluoropolymer. Silicone and Fluorine Information
905 2004;3:15–19. (in Chinese)
906 Feng D, Su X. Trend on the PFOA in fluorinated applications. New Chemical Materials
907 2007;S1. (in Chinese)
908 Frömel T, Knepper TP. Biodegradation of fluorinated alkyl substances. Rev Environ Contam
909 Toxicol 2010:208:161–77.
910 Fuxin. Product catalogue: fluorinated surfactants. Fuxin Hengtong Fluorine Chemicals Co.
911 Ltd. 2013. (in Chinese) http://www.htfluo.com/FluorinatedSurfactant/10351464.shtml
912 Giesy JP, Kannan K. Global Distribution of Perfluorooctane Sulfonate in Wildlife. Environ Sci
913 Technol 2001;35:1339–42.
914 Gramstad T, Haszeldine RN. 512. Perfluoroalkyl derivatives of sulphur. Part VI.
915 Perfluoroalkanesulphonic acids CF3·[CF2] n· SO3H (n= 1–7). J. Chem Soc 1957;2640–5.
916 Hanari N, Itoh N, Ishikawa K, Yarita T, Numata M. Variation in concentration of
917 perfluorooctanoic acid in methanol solutions during storage. Chemosphere
918 2014;94:116–20.
919 Huang C, Li X, Jin G. Electro fluorination and its fine-fluorine production branches . Chemical
920 Production and Technology 2010;17:1–7. (in Chinese)
921 Hurley M, Andersen M, Wallington T, Ellis D, Martin J, Mabury SA. Atmospheric chemistry of
922 perfluorinated carboxylic acids: Reaction with OH radicals and atmospheric lifetimes. J
923 Phys Chem A 2004;108:615–20.
924 Jackson DA, Mabury SA. Polyfluorinated amides as a historical PFCA source by
925 electrochemical fluorination of alkyl sulfonyl fluorides. Environ Sci Technol
926 2013a;47:382–9.
927 Jackson DA, Wallington TJ, Mabury SA. Atmospheric oxidation of polyfluorinated amides:
928 historical source of perfluorinated carboxylic acids to the environment. Environ Sci
929 Technol 2013b;47:4317–24.
930 Kälin T, Will R, Yamaguchi Y. CEH marketing research report: fluoropolymers; IHS Chemical
931 2012.
932 Lee H, D'eon J, Mabury SA. Biodegradation of polyfluoroalkyl phosphates as a source of
933 perfluorinated acids to the environment. Environ Sci Technol 2010;44:3305–10.

Lehmler H. Synthesis of environmentally relevant fluorinated surfactants - a review. Chemosphere 2005;58:1471–96.
Lim TC, Wang B, Huang J, Deng S, Yu G. Emission inventory for PFOS in China: review of past methodologies and suggestions. ScientificWorldJournal 2011;11:1963–80.
Liu J, Lee L. S, Nies L. F, Nakatsu C. H, Turcot R. F. Biotransformation of 8:2 fluorotelomer alcohol in soil and by soil bacteria isolates. Environ Sci Technol 2007;41:8024–30.
Liu J, Avendaño SM. Microbial degradation of polyfluoroalkyl chemicals in the environment: a review. Environ Int 2013;61:98–114.
Martin JW, Ellis DA, Mabury SA, Hurley MD, Wallington TJ. Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. Environ Sci Technol 2006;40:864–72.
Martin JW, Asher BJ, Beesoon S, Benskin JP, Ross MS. PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? J Environ Monit 2010;12:1979–2004.
Mei S. Current state of domestic production and application of PFOS/PFOA as well as domestic and international legislations. Organo-Fluorine Industry 2008;1:21–5. (in Chinese)
Moe MK, Huber S, Svenson J, Hagenaars A, Pabon M, Trümper M, Berger U, Knapen D, Herzke D. The structure of the fire fighting foam surfactant Forafac®1157 and its biological and photolytic transformation products. Chemosphere 2012;89:869–75.
Morgan MG. The neglected art of bounding analysis. Environ Sci Technol 2001;35:162A–4A.
Müller CE, Gerecke AC, Bogdal C, Wang Z, Scheringer M, Hungerbühler K. Atmospheric fate of poly- and perfluorinated alkyl substances (PFASs): I. Day-night patterns of air concentrations in summer in Zurich Switzerland. Environ Pollut 2012;169:196–203.
Naile JE, Khim JS, House JN, Jones PD, Giesy JP. Standard purity and response factors of perfluorinated compounds. Toxicol Environ Chem 2010;92:1219–32.
NDRC (China National Development and Reform Commission). Catalogue for the Guidance of Industrial Structure Adjustment. 2011. www.gov.cn/gzdt/att/att/site1/20110426/001e3741a2cc0f20bacd01.pdf
OECD. Results of survey on production and use of PFOS, PFAS and PFOA related substances and products/mixtures containing these substances. 2005. http://search.oecd.org/officialdocuments/displaydocumentpdf/?doclanguage=en&cote=env/jm/mono%282005%291
OECD. Results of the 2006 OECD survey on production and use of PFOS, PFAS, PFOA, PFCA, their related substances and products/mixtures containing these substances. 2006. http://search.oecd.org/officialdocuments/displaydocumentpdf/?doclanguage=en&cote=env/jm/mono%282006%2936
OECD. SIDS initial assessment report after SIAM 22, Paris, France, 18-21 April 2006 - ammonium perfluorooctanoate & perfluorooctanic acid. 2009; pp. 1–210.
Parsons JR, Sáez M, Dolfing J, de Voogt P. Biodegradation of perfluorinated compounds. Rev Environ Contam Toxicol 2008;196:53–71.
Picó Y, Farré M, Llorca M, Barceló D. Perfluorinated compounds in food: a global perspective. Crit Rev Food Sci Nutr 2011;51:605–25.
Pinchot R. Presentation "APFO use and Exposure peer review" (226-1667); US EPA Administrative Record 226 2004; pp. 1–25.
Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH. Sources fate and transport of perfluorocarboxylates. Environ Sci Technol 2006;40:32–44.
Rayne S, Forest K. Perfluoroalkyl sulfonic and carboxylic acids: a critical review of physicochemical properties levels and patterns in waters and wastewaters and treatment methods. J Environ Sci Health A Tox Hazard Subst Environ Eng 2009;44:1145–99.
Reagen WK, Lindstrom KR, Jacoby CB, Purcell RG, Kestner TA, Payfer RM, Miller JP. Environmental characterization of 3M electrochemical fluorination derived perfluorooctanoate and perfluorooctanesulfonate. SETAC North American 28th Annual Meeting in Milwaukee U.S. 2007; pp. 1–33.

990 Refsgaard JC, van der Sluijs JP, Højberg AL, Vanrolleghem PA. Uncertainty in the
991 environmental modelling process – A framework and guidance. Environ Modell Softw
992 2007;22:1543–56.
993 Ritter SK. Fluorochemicals go short. Chem Eng News 2010; 88 12–17.
994 Ruan T, Wang Y, Wang T, Zhang Q, Ding L, Liu J, Wang C, Qu G, Jiang G. Presence and
995 partitioning behavior of polyfluorinated iodine alkanes in environmental matrices
996 around a fluorochemical manufacturing plant: another possible source for
997 perfluorinated carboxylic acids? Environ Sci Technol 2010;44:5755–61.
998 Russell MH, Berti WR, Szostek B, Buck RC. Investigation of the biodegradation potential of a
999 fluoroacrylate polymer product in aerobic soils. Environ Sci Technol 2008;42:800–7.
1000 Russell MH, Wang N, Berti WR, Szostek B, Buck RC. Comment on "Degradability of an
1001 acrylate-linked fluorotelomer polymer in soil." Environ Sci Technol 2010a;44:848.
1002 Russell MH, Berti WR, Szostek B, Wang N, Buck RC. Evaluation of PFO formation from the
1003 biodegradation of a fluorotelomer-based urethane polymer product in aerobic soils.
1004 Polym Degrad Stabil 2010b;95:79–85.
1005 Schenker U, Scheringer M, MacLeod M, Martin JW, Cousins IT, Hungerbühler K. Contribution
1006 of volatile precursor substances to the flux of perfluorooctanoate to the Arctic. Environ
1007 Sci Technol 2008;42:3710–6.
1008 Schultz MM, Higgins CP, Huset CA, Luthy RG, Barofsky DF, Field JA. Fluorochemical mass
1009 flows in a municipal wastewater treatment facility. Environ Sci Technol 2006;40:7350–
1010 7.
1011 Seacat AM, Thomford PJ, Hansen KJ, Clemen LA, Eldridge SR, Elcombe CR, Butenhoff JL. Sub-
1012 chronic dietary toxicity of potassium perfluorooctanesulfonate in rats. Toxicology
1013 2003;183:117–31.
1014 Seacat AM. Toxicokinetic screen of FC methyl carboxamide (T-7483) in rats; 3M Medical
1015 Department: St. Paul, MN, 2004;
1016 http://www.epa.gov/oppt/tsca8e/pubs/8ehq/2004/sep04/8ehq_0904_15847a.pdf
1017 Shoeib M, Vlahos P, Harner T, Peters A, Graustein M, Narayan J. Survey of polyfluorinated
1018 chemicals (PFCs) in the atmosphere over the northeast Atlantic Ocean. Atmos Environ
1019 2010;44:2887–93.
1020 Shoeib M, Harner T, M Webster G, Lee SC. Indoor sources of poly- and perfluorinated
1021 compounds (PFCS) in Vancouver Canada: implications for human exposure. Environ Sci
1022 Technol 2011;45:7999–8005.
1023 Solvay. Solvay Solexis announces substitute for PFOA. 2013.
1024 http://www.solvayplastics.com/sites/solvayplastics/EN/news/Pages/Solexis_09_11_0
1025 6_Solvay_Solexis_announces_substitute_for_PFOA.aspx
1026 Stemmler I, Lammel G. Pathways of PFOA to the Arctic: variabilities and contributions of
1027 oceanic currents and atmospheric transport and chemistry sources. Atmos Chem Phys
1028 Discuss 2010;10:11577–614.
1029 Tang Y, Xu P, Zhou X. Recovery and application of perfluorooctanoic acid (PFOA). Organo-
1030 Fluorine Industry 2009;4:43–7. (in Chinese)
1031 UNEP. Risk management evaluation on perfluorooctane sulfonate (UNEP-POPS-POPRC.3-20-
1032 Add.5); Secretariat of the Stockholm Convention on Persistent Organic Pollutants 2007;
1033 pp. 1–22.
1034 UNEP. Technical paper on the identification and assessment of alternatives to the use of
1035 perfluorooctane sulfonic acid in open applications (UNEP/POPS/POPRC.8/INF/17).
1036 Secretariat of the Stockholm Convention on Persistent Organic Pollutants 2012.
1037 US EPA (United States Environmental Protection Agency). 2010/15 PFOA Stewardship
1038 Program. 2006 http://www.epa.gov/oppt/pfoa/pubs/stewardship
1039 US EPA (United States Environmental Protection Agency). EPA's baseline year summary
1040 report; US EPA 2010/2015 PFOA Stewardship Program 2008a.
1041 http://www.epa.gov/oppt/pfoa/pubs/stewardship/sumrpt.html
1042 US EPA (United States Environmental Protection Agency). US EPA's summary tables for
1043 2007 Company Progress Reports; US EPA 2010/2015 PFOA Stewardship Program
1044 2008b. http://www.epa.gov/oppt/pfoa/pubs/stewardship/preports.html#summary
1045 US EPA (United States Environmental Protection Agency). US EPA's summary tables for

2008 Company Progress Reports; US EPA 2010/2015 PFOA Stewardship Program 2009a. http://www.epa.gov/oppt/pfoa/pubs/stewardship/preports2.html#summary
US EPA (United States Environmental Protection Agency). Final report: PFOS chromium electroplater study; US EPA - Region 5 2009b. pp. 1–31. http://www.epa.gov/opptintr/pfoa/pubs/pfoschromeplaterstudypdf_final.pdf
US EPA (United States Environmental Protection Agency). US EPA's summary tables for 2009 Company Progress Reports; US EPA 2010/2015 PFOA Stewardship Program 2010. http://www.epa.gov/oppt/pfoa/pubs/stewardship/preports3.html#summary
US EPA (United States Environmental Protection Agency). US EPA's summary tables for 2010 Company Progress Reports; US EPA 2010/2015 PFOA Stewardship Program 2011. http://www.epa.gov/oppt/pfoa/pubs/stewardship/preports4.html#summary
US EPA (United States Environmental Protection Agency). US EPA's summary tables for 2011 Company Progress Reports; US EPA 2010/2015 PFOA Stewardship Program 2012. http://www.epa.gov/oppt/pfoa/pubs/stewardship/preports5.html#summary
US EPA (United States Environmental Protection Agency). US EPA's summary tables for 2012 Company Progress Reports; US EPA 2010/2015 PFOA Stewardship Program 2013a. http://www.epa.gov/oppt/pfoa/pubs/stewardship/preports6.html#summary
US EPA (United States Environmental Protection Agency). US EPA chemical data reporting (CDR) database (former Inventory Update Reporting (IUR) database); 2013b. http://epa.gov/cdr/
Vestergren R, Cousins IT. Tracking the pathways of human exposure to perfluorocarboxylates. Environ Sci Technol 2009;43:5565–75.
Wania F. A global mass balance analysis of the source of perfluorocarboxylic acids in the Arctic Ocean. Environ Sci Technol 2007;41:4529–35.
Wang N, Szostek B, Buck RC, Folsom PW, Sulecki LM, Capka V, Berti WR, Gannon JT. Fluorotelomer alcohol biodegradation-direct evidence that perfluorinated carbon chains breakdown. Environ Sci Technol 2005;39:7516–28.
Wang J. Current state and trend of fluoropolymer in China . Organo-Fluorine Industry 2006;4:28–31. (in Chinese)
Wang H, Fang J, Li W, Li X, Hao H. Patent: Fluorine-containing emulsifier for fluoropolymer emulsion polymerization and preparation thereof. CN 101745338, 2010.
Wang Z, Scheringer M, MacLeod M, Bogdal C, Müller CE, Gerecke AC, Hungerbühler K. Atmospheric fate of poly- and perfluorinated alkyl substances (PFASs): II. Emission source strength in summer in Zurich Switzerland. Environ Pollut 2012;169:204–209.
Wang Z, Cousins IT, Scheringer M, Hungerbühler K. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs) perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. Environ Int 2013;60:242-8.
Wang Z, Cousins IT, Scheringer M, Buck RC, Hungerbühler K. Global emission inventories for C_4–C_{14} perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030 part II: the remaining pieces of the puzzles. Environ Int 2014. (submitted)
Washington JW, Ellington J, Jenkins TM, Evans JJ, Yoo H, Hafner SC. Degradability of an acrylate-linked fluorotelomer polymer in soil. Environ Sci Technol 2009;43:6617–23.
Washington JW, Ellington JJ, Jenkins TM, Yoo H. Response to comments on "Degradability of an acrylate-linked fluorotelomer polymer in soil." Environ Sci Technol 2010;44:849–50.
Wei S, Chen LQ, Taniyasu S, So MK, Murphy MB, Yamashita N, Yeung LWY, Lam PKS. Distribution of perfluorinated compounds in surface seawaters between Asia and Antarctica. Mar Pollut Bull 2007;54:1813–8.
Will R, Kälin T, Kishi A. CEH marketing research report: fluoropolymers; IHS Chemical 2005.
Xie X, Qu J, Bai R, Zhang J, Yang X. Patent: Peroxidic fluoropolyether and its use in emulsion polymerization of fluorin-containing monomer. US 2011/0207880 A1, 2011.
Xu Y, Zhao M, Li H, Lu W, Su X, Han Z. A novel fluorocarbon surfactant: synthesis and application in emulsion polymerization of perfluoroalkyl methacrylates. Paint & Coatings Industry 2011;41:17–21. (in Chinese)
Yamashita N, Kannan K, Taniyasu S, Horii Y, Petrick G, Gamo T. A global survey of perfluorinated acids in oceans. Mar Pollut Bull 2005;51:658–68.
Yamashita N, Taniyasu S, Petrick G, Wei S, Gamo T, Lam PKS, Kannan K. Perfluorinated acids

1102 as novel chemical tracers of global circulation of ocean waters. Chemosphere
1103 2008;70:1247–55.
1104 Yarwood G, Kemball-Cook S, Keinath M, Waterland RL, Korzeniowski SH, Buck RC, Russell
1105 MH, Washburn ST. High-resolution atmospheric modeling of fluorotelomer alcohols and
1106 perfluorocarboxylic acids in the North American troposphere. Environ Sci Technol
1107 2007;41:5756–62.
1108 Young CJ, Furdui VI, Franklin J, Koerner RM, Muir DCG, Mabury SA. Perfluorinated acids in
1109 Arctic snow: new evidence for atmospheric formation. Environ Sci Technol
1110 2007;41:3455–61.
1111 Young CJ, Mabury SA. Atmospheric perfluorinated acid precursors: chemistry occurrence
1112 and impacts. Rev Environ Contam Toxicol 2010;208:1–109.
1113 Zhang L, Liu J, Hu J, Liu C, Guo W, Wang Q, Wang H. The inventory of sources environmental
1114 releases and risk assessment for perfluorooctane sulfonate in China. Environ Pollut
1115 2012;165:193–8.
1116 Zhao D, Jin F, Pan D. Research on the applicability of paint-grade PVDF resins that do not
1117 contain PFOA. In 2011 Annual conference on fluoro-silicone coatings, Jinan 2011; pp. 1–
1118 4. (in Chinese) http://www.pvdf-feve.com/kejitiandi/10110921.html
1119 Zhao Z, Xie Z, Möller A, Sturm R, Tang J, Zhang G, Ebinghaus R. Distribution and long-range
1120 transport of polyfluoroalkyl substances in the Arctic Atlantic Ocean and Antarctic coast.
1121 Environ Pollut 2012;170:71–7.