WORKING TOWARDS A GLOBAL EMISSION INVENTORY OF PFASS: FOCUS ON PFCAS - STATUS QUO AND THE WAY FORWARD

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TABLE OF CONTENTS

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FOREWORD

The document was prepared by the OECD/UNEP Global PFC Group, established to respond to the International Conference on Chemicals Management (ICCM 2) 2009 Resolution II/5 regarding PFCs under the framework of the Strategic Approach to International Chemicals Management (SAICM). The report aims to inform discussions on progress with respect to the ICCM Resolution at ICCM 4 in September 2015.

TABLE OF ACRONYMS

AFFF	aqueous film-forming foams
APFO	ammonium perfluorooctanoate
CFCs	chlorofluorocarbons
ECF	through electrochemical fluorination
FEP	fluorinated ethylene propylene
FP	fluoropolymer
FT	fluorotelomer
FTOH	fluorotelomer alcohol
HCFCs	hydrochlorofluorocarbons
HFCs	hydrofluorocarbons
HFEs	hydrofluoroethers
ICCM	International Conference on ChemicalManagement
OECD	Organisation for Economic Cooperation and Development
PACFs	perfluoroalkane carbonyl fluorides
PASFs	perfluoroalkane sulfonyl fluorides
PBSF	perfluorobutane sulfonyl fluoride
PDSF	Perfluorodecane sulfonyl fluoride
PFA	perfluoroalkoxyl polymer
PFAAs	perfluoroalkyl acids
PFAIs	perfluoroalkyl iodides
PFASs	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBE	perfluorobutylethlyene
PFBF	perfluorobutane carbonyl fluoride
PFBS	perfluorobutane sulfonic acid
PFCAs	perfluoroalkyl carboxylic acids
PFCs	per- and polyfluorinated chemicals; perfluorocarbons
PFDS	perfluorodecane sulfonic acid
PFECAs	perfluoroether carboxylic acids
PFESAs	perfluoroether sulfonic acids
PFHxA	perfluorohexanoic acid

PFHxS	perfluorohexane sulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFPAs	perfluoroalkyl phosphonic acids
PFPEs	Perfluoropolyethers
PFPiAs	perfluoroalkyl phosphinic acids
PFSAs	perfluoroalkyl sulfonic acids
PHxSF	perfluorohexane sulfonyl fluoride
POSF	perfluorooctane sulfonyl fluoride
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene fluoride
SAICM	Strategic Approach to International Chemicals Management
SFAs	Semifluorinated alkanes
UNEP	United Nations Environment Programme
US	United States
US EPA	United States Environmental Protection Agency

EXECUTIVE SUMMARY

This paper aims to support a process to establish a global emission inventory for per- and polyfluoroalkyl substances (PFASs). It uses perfluoroalkyl carboxylic acids (PFCAs) as a reference to present an overall picture of global and regional emissions of PFASs and other related fluorinated substances due to the numerous interlinkages between PFCAs and many other fluorinated substances. The analysis provides a comprehensive overview of the current understanding of historical and ongoing global and regional emissions of C_4–C_{14} PFCAs and identifies critical gaps and key uncertainties in terms of data collection and integration to accurately measure global and regional emissions of C_4–C_{14} PFCAs. The paper does not provide direct data on substances other than PFCAs, such as perfluoroalkane sulfonic acids (PFSAs) and perfluoroalkane phosphonic acids (PFPAs); however, information on and/or estimates of the emissions of these substances is an important element of understanding the global emissions of PFCAs and are provided in the background assessment and estimation. Recommendations for improving knowledge on global and regional emissions of PFASs are presented.

After over a decade of research and systematic integration of many individual findings, four important sources of PFCAs are relatively well understood. Among them, commercial perfluorooctanoic acid (PFOA or C_8 PFCA) and perfluorononanoic acid (PFNA or C_9 PFCA) used in the fluoropolymer production are identified as the sources responsible for the majority of C_7–C_9 and C_{11} PFCAs in the global environment. While former major global manufacturers in the US, Western Europe and Japan are stepwise eliminating the production and use of long-chain PFASs (including commercial PFOA, PFNA and perfluorooctane sulfonyl fluoride- and fluorotelomer-based substances) by or shortly after 2015, new manufacturers in emerging economies recently initiated large-scale production and use of certain long-chain PFASs with limited quantitative information publicly available. In general, a trend in the geographical distribution of major industrial sites is that production of long-chain PFCAs, fluoropolymers and other PFAS products has shifted from the US, Western Europe and Japan to the emerging economies in continental Asia (e.g., China and India), suggesting that the proportion of global emissions of PFCAs originating from continental Asia has increased. These new sources may more than offset the reductions obtained by the former major global manufactures. Therefore, there is an urgent need to capture this ongoing geographical shift of industrial sources, as a basis for future actions towards global elimination of long-chain PFASs.

Also, the understanding of (potential) sources of some other PFCA homologues, particularly C_4, C_5, C_{10}, C_{12}–C_{14} PFCAs, is still incomplete. Multiple overlooked sources of PFCAs have been identified, but can currently not be quantified due to a lack of information. Thus, their contribution to the global and regional emissions of PFCAs cannot be quantitatively assessed, although some of the sources may have been significant in the past (e.g., historical use of perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), their derivatives, and perfluorobutane sulfonyl fluoride (PBSF)- and perfluorohexane sulfonyl fluoride (PHxSF) based derivatives), whereas others can be significant in the long-term (e.g., (bio)degradation of various side-chain fluorinated polymers, atmospheric degradation of hydrofluorocarbons and hydrofluoroethers). In addition, releases of PFCAs from some sources are ongoing and likely increasing (e.g., ongoing use of PFBA, PFHxA, their derivatives, and PBSF- and PHxSF-based derivatives as alternatives to their longer-chain homologues). Therefore, studies on the global and/or regional emissions of PFCAs from (at least some of) these overlooked sources are needed in order to understand their potential risk.

Furthermore, efforts to assess and understand the exposure and associated risk to the environment and human health from many fluorinated alternatives to long-chain PFASs, starting from source identification and quantification, are also urgently needed. Given the emerging knowledge on the properties of some of these alternatives, it is essential to understand the global emissions of these alternatives, in order to prevent emissions and exposures from occurring on a large scale. Although information on alternatives has been provided to regulatory agencies to seek approval of specific uses in the context of new chemical regulatory frameworks, limited information is available in the public domain. Hence, considerable efforts to understand the global production, use and releases of these fluorinated alternatives to long-chain PFASs are also needed.

Based on lessons learned and the uncertainty and gap analysis presented in this report, three recommendations for improving knowledge on global and regional emissions of PFASs are presented as follows:

[i] The OECD 2007 list of PFASs needs to be updated. In 2007, OECD published an exhaustive, revised list of PFASs containing over 920 PFASs. However, this list is likely no longer up-to-date. In order to provide all stakeholders with an extensive, consistent and easily accessible list of PFASs for future work, it is recommended that the OECD list be updated with possible new features as outlined in the recommendation section of the report

[ii] A new survey on the global production, use and release of PFASs is necessary in order to properly assess historical and ongoing exposure and to understand global trends. Making such information publicly available is key to establishing the big picture of global and regional emissions of PFASs; thus, a new survey, which encompasses critical information needs and includes all relevant regions, and public consultation, should be considered to collect this information.

[iii] Synergies among stakeholders and links to the existing programs are needed. Another challenge in estimating the global emissions of PFASs is to fill those critical knowledge gaps, where systematic studies and advance of science and knowledge are needed. For this purpose, synergies among stakeholders (intergovernmental organisations, governments, industry, academia and civil society) and links to the existing programs should be used. A broader and more transparent and intense dialogue among stakeholders and relevant actors is needed. The OECD/UNEP Global PFC Group could provide a forum for this dialogue.

1. BACKGROUND, AIMS AND SCOPE

The OECD/UNEP Global PFC[1] Group was established to respond to the International Conference on Chemicals Management (ICCM 2) 2009 Resolution II/5, calling upon intergovernmental organisations, governments and other stakeholders to “consider the development, facilitation and promotion in an open, transparent and inclusive manner of national and international stewardship programmes and regulatory approaches to reduce emissions and the content of relevant perfluorinated chemicals of concern in products and to work toward global elimination, where appropriate and technically feasible”. This work is conducted within the framework of the Group.

This paper provides a detailed and descriptive inventory of global historic and potential future emissions of perfluoroalkyl carboxylic acids (PFCAs) as a basis for future establishment of a comprehensive global emission inventory for per- and polyfluoroalkyl substances (PFASs)[2]. The paper uses perfluoroalkyl carboxylic acids (PFCAs) as a reference to present an overall picture of global and regional emissions of PFASs and other related fluorinated substances. This is because the emissions of PFCAs are directly or indirectly interlinked with emissions those of many other PFASs and related fluorinated substances (these interlinkages are elaborated in Wang et al. (2014a), its *Supporting Material*, and in the section *Terminology* below). As such, although the paper does not present data on the global emissions of PFASs other than PFCAs, such as perfluoroalkane sulfonic acids (PFSAs) and perfluoroalkane phosphonic acids (PFPAs), the emissions of these other substances form a component of the global emissions of PFCAs and are considered in the background assessment and estimation. Thus, the paper aims to provide a comprehensive overview of the current understanding of historical and ongoing global and regional emissions of C_4–C_{14} PFCAs and identify critical gaps and key uncertainties in terms of data collection and integration to accurately measure global and regional emissions of C_4–C_{14} PFCAs. For existing estimates of global emissions of perfluorooctane sulfonic acid (PFOS) and its major precursors, readers are referred to Paul et al. (2009) and Armitage et al. (2009a). Finally, the report concludes with recommendations for further work in order to improve knowledge on global and regional emissions of PFASs. These aims are further elaborated below.

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[1] PFCs refer here to per- and polyfluorinated chemicals, and not to perfluorocarbons.

[2] PFASs refer to per- and polyfluoroalkyl substances. Perfluoroalkyl substances refer to those for which all hydrogen atoms attached to carbon atoms have been substituted with fluorine atoms (except for hydrogen atoms whose replacement would change the properties of the present functional groups). Polyfluoroalkyl substances refer to those for which all hydrogen atoms attached to at least one (but not all) carbon atoms have been replaced by fluorine atoms (Buck *et al*. 2011). See section 2 for further terminology

PFASs have been widely used in various industrial and consumer applications since the 1950s, most usually where extremely low surface energy or surface tension and/or durable water- and oil-repellency is needed, e.g., (non-polymeric PFASs) in the polymerization of PTFE, chromium metal plating, various fire-fighting foams, or (mainly polymeric PFASs) for surface treatment of textiles, carpets and papers (details on their production and use can be found in Armitage et al., 2009a; Buck et al., 2011; Kissa, 2001; OECD, 2013; Prevedouros et al., 2006 and Wang et al., 2014a,b).

For over a decade, long-chain PFSAs and PFCAs, in particular PFOS and perfluorooctanoic acid (PFOA), and their precursors derived from perfluoroalkane sulfonyl fluorides (PASFs) and fluorotelomer raw materials have attracted most attention among PFASs as emerging contaminants of global concern. This is because [i] PFSAs and PFCAs are persistent and distributed ubiquitously in the global environment, biota and humans, even in remote areas (i.e. they have high long-range transport potential); [ii] long-chain PFCAs and PFSAs are bioaccumulative and can cause various adverse effects in wildlife and humans. Scientific evidence on the persistence, bioaccumulation potential, toxicity and long-range transport potential of long-chain PFSAs and PFCAs is reviewed in OECD (2013).

Driven by concerns about the potential adverse impacts of certain PFASs on the environment and humans, various risk reduction actions have been implemented to reduce the environmental and human exposure to long-chain PFSAs and PFCAs (OECD, 2015a). For instance, major global manufacturers in OECD countries have voluntarily discontinued production of long-chain PFAAs, including PFSAs such as PFOS and PFHxS and PFCAs such as PFOA (3M, 2000a,b) or plan to discontinue the production and use of PFOA, its longer-chain homologues and precursors by 2015 (e.g. US EPA 2010/15 PFOA Stewardship Program; US EPA, 2006). In addition, the production and use of several long-chain PFCAs, PFSAs and their precursors have been restricted under national, regional or international regulatory frameworks (OECD, 2015a). PFOS and related substances derived from perfluorooctane sulfonyl fluoride (POSF) were added to Annex B (restricted production and use) of the Stockholm Convention on Persistent Organic Pollutants in 2009. In addition, C_{11}–C_{14} PFCAs (in 2012) as well as PFOA and its ammonium salt (APFO) (in 2013) were included in the Candidate List of Substances of Very High Concern for Authorisation under the European chemicals regulation, REACH (ECHA, 2012, 2013, 2015). According to the Decision COM (2015) 133, the EU Commission will submit, on behalf of the European Union and its Member States, a proposal to the Secretariat of the Stockholm Convention for inclusion of PFOA and related chemicals in Annex

A. Further information on control actions in several individual countries can be found in OECD (2015a).

As a result of these industry and regulatory actions, an industrial transition is taking place to replace long-chain PFSAs, PFCAs, and their precursors with alternative fluorinated and non-fluorinated chemicals (these replacements are referred to as *alternatives* hereafter), mostly in the United States (US), Western Europe and Japan (UNEP, 2012; Wang et al., 2013). To date, a fair amount of information on alternatives has been or is being generated; however, this information is focused on a small selection of alternatives (e.g., short-chain PFCAs, PFSAs and some 6:2 fluorotelomer-based derivatives), and much information was claimed as confidential business information (CBI) under national regulatory frameworks. Thus determining the exposure to, hazards of and risks associated with most alternatives to long-chain PFASs is still not straightforward, which is a cause of concern (Scheringer et al., 2014; UNEP, 2014; Wang et al., 2013). Additionally, recent studies reveal concerning evidence that many fluorinated alternatives, which are still PFASs, are often not only structurally similar to, but can also have similar hazardous properties as their predecessors (Gomis et al., 2015; UNEP, 2014; Wang et al., 2015). Therefore, further studies to understand and assess the risks associated with the environmental and human exposure to fluorinated alternatives to long-chain PFASs are needed.

Furthermore, while major manufacturers in most OECD countries are phasing out production and use of long-chain PFASs in a series of steps, new manufacturers in developing countries and countries with economies in transition (hereafter referred as *developing and transition countries*) have begun to produce a significant amount of long-chain PFSAs and PFCAs (details see Wang et al., 2014a and the references therein, Li et al. 2015 and *Section* 3.3 below). Unless Best Environmental Practices (BEP) during production, use and disposal of these compounds are employed, it can be expected that the environmental and human exposure to long-chain PFASs in these developing and transition countries will continue to rise. Additionally, due to their high persistence and long-range transport potential via mobile environmental media (such as wind and ocean currents) and intensified global trading activities of products/articles containing them (Feng et al., 2015; Herzke et al., 2012; Kotthoff et al., 2015; Vestergren et al., 2015), it can be expected that long-chain PFASs originating from developing and transition countries will result in further continuous contamination of the global environment.

In order to take relevant, adequate measures to reduce the global environmental and human exposure, it is important to understand the levels and trends of long-chain PFASs and fluorinated alternatives in the global environment and biota, starting with source identification and quantification. To date, many efforts have been made to understand the production, use and releases of individual PFASs by intergovernmental organisations and governments. Among others, OECD conducted three international surveys in 2004, 2006 and 2009, respectively (OECD, 2005, 2006, 2011); the 2004 and 2006 surveys requested participating countries to provide information on all PFASs and related products manufactured in or imported into their jurisdictions, whereas the 2009 survey focused on manufacturers of a defined list of PFASs and/or PFAS-containing products in OECD and non-OECD countries. Despite issues related to confidentiality and incomplete response, the surveys provided the public with useful information on the actual market shift of the production and use of PFASs after 3M, then the largest manufacturer worldwide, ceased its global production of C_6-C_{10} chemistry, including PFOS and PFOS-related substances, in 2002. However, the surveys also have some limitations: [i] the results are snapshots of the situation in certain years and do not reflect the entire historical production and use; [ii] the results focused on individual PFASs and do not reflect interlinkages among PFASs (e.g., in FT-based products, also PFCAs can be present, namely as impurities and transformation products); [iii] incomplete responses do not allow to construct a more precise global view.

In the same period, there have been continuous efforts by scientists in estimating global emissions of selected PFSAs, PFCAs and their PASF- and fluorotelomer-based precursors from relevant sources by systematically integrating a wide range of fragmented information through interpolation, extrapolation and consistency checks. In particular, Prevedouros et al. (2006) developed the first global emission inventory of total PFCAs and relevant precursors in 1951–2004 by investigating the fate of PFCAs and their precursors during the life-cycle (production, use and disposal) of commercial PFOA, perfluorononanoic acid (PFNA), and POSF- and fluorotelomer-based substances. Prevedouros et al. (2006) identified the major direct sources of PFOA and PFNA, namely the direct use of them in the production of relevant fluoropolymers. Later on, the application of this methodology was extended to global emissions of PFOS and related chemicals (Paul et al., 2009; Armitage et al., 2009a). Most recently, built on Prevedouros et al. (2006), Wang et al. (2014a,b) further refined the methodologies and parameters and updated the global emission inventory of C_4–C_{14} PFCAs and related precursors from 1951 to 2015 by introducing the following new elements: [i] breakdown of emissions on a homologue basis; [ii] breakdown of emissions on a regional basis to assess the geographical shift of industrial sources over time; [iii] incorporation of the ongoing industrial transition to alternatives in estimating the emissions of PFCAs; [iv] identification of eleven overlooked sources of PFCAs that currently cannot be quantified in addition to the known ones in Prevedouros et al. (2006).

This paper builds on findings from Wang et al. (2014a,b) and aims to work towards a global emission inventory for PFASs. It is noted that a number of relevant articles have been published since Wang et al. (2014a,b) (including Brazil, 2014; Y. Feng et al., 2015; Korucu et al., 2014; Li et al., 2015a,b; Vestergren et al., 2015; Yan et al., 2015). For example, a new study was published after Wang et al. (2014a,b), estimating the industrial and domestic environmental releases of PFOA in China in 2004–2012 (Li et al., 2015a). Hence, results in Wang et al. (2014a,b) were examined against the newly available information. In general, there is no discrepancy found regarding the overall picture and key messages, although some detailed numbers in different studies may differ within a factor of less than five. In brief, the key content of this paper consists of three major parts: [i] a comprehensive overview of the current understanding of historical and ongoing global and regional emissions of C_4–C_{14} PFCAs (*Section* 3), [ii] critical information gaps and key uncertainties in terms of data collection and integration to accurately measure global and regional emissions of C_4–C_{14} PFCAs (*Section* 4), and [iii] recommendations for future work in addressing these critical information gaps and key uncertainties (*Section* 5). Because emissions of PFCAs are interlinked with emissions of most PFASs and some fluorinated substances other than PFASs, as residuals, impurities or degradation products, this paper uses PFCAs as a reference to present an overall picture of global and regional emissions of PFASs and other related fluorinated substances. It focuses primarily on C_4–C_{14} PFCA homologues and related precursors from quantifiable sources, where adequate quantitative information for estimating release is available. For other relevant PFASs including fluorinated alternatives, available qualitative information on their production, use and release is briefly discussed with a highlight of critical data and knowledge gaps. It should be noted that only final results of previous studies are presented here; for detailed methodologies and calculations, the readers need to consult the references cited below.

2. TERMINOLOGY

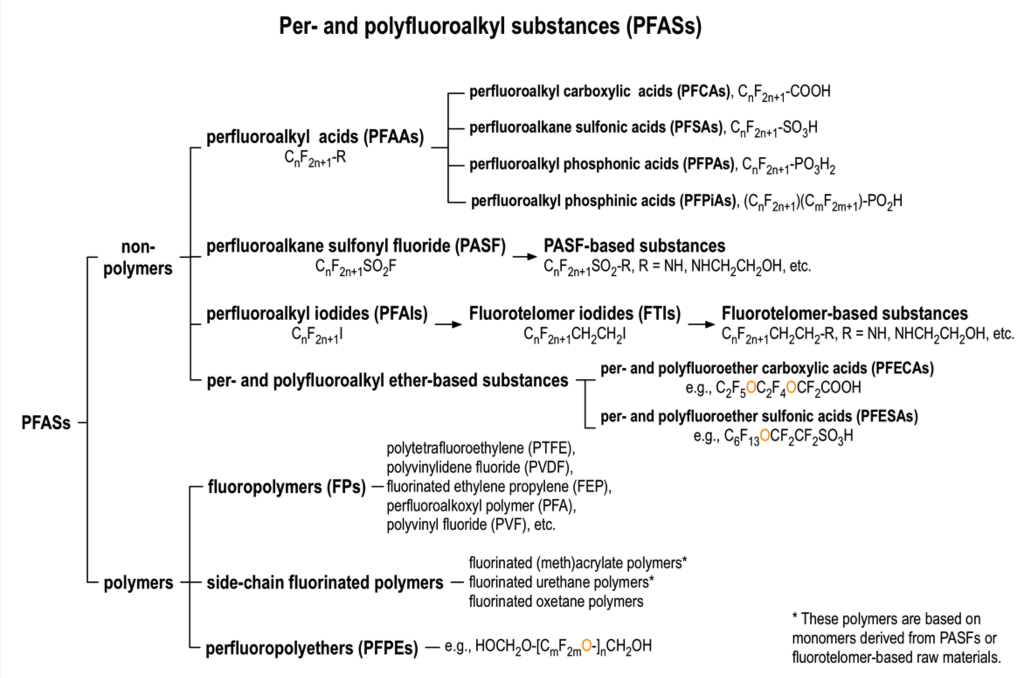
This paper on global emissions of PFASs, focusing on PFCAs, builds on previous findings from peer-reviewed scientific articles, books, theses, monographs, conference abstracts, industrial studies, patents, and databases and technical reports from national and international bodies, in which various terminologies have been used. To avoid confusion and misunderstanding, this section outlines a general overview of the terminology used throughout this paper.

2.1 Terminology regarding chemicals

PFASs are a large family of industrial chemicals containing at least one perfluoroalkyl moiety, $–C_nF_{2n+1}$. In the past, some PFASs have been referred to as “PFCs”; however, “PFCs” is a term coined and widely recognized within the global scientific and regulatory community to describe perfluorocarbons, substances that contain only carbon and fluorine atoms, and have properties and functionalities that are fundamentally different from those of many PFASs. Here we follow a commonly agreed terminology for nomenclature of PFASs (Buck et al. 2011) that was adopted in the Synthesis Paper published by the OECD/UNEP Global PFC-Group (OECD, 2013). In brief, PFASs comprise two subsets, namely non-polymeric and polymeric PFASs (see Figure 1).

Non-polymeric PFASs can be further divided into four groups: [i] perfluoroalkyl acids (PFAAs) including perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs), [ii] compounds derived from perfluoroalkane sulfonyl fluorides (PASFs; hereafter referred to as *PASF-based substances*), [iii] compounds derived from fluorotelomer raw materials (hereafter referred to as *FT-based substances*), and [iv] per- and polyfluoroalkyl ether-based substances. PASF-based substances can partially be transformed into PFCAs and/or PFSAs in the environment and in biota, whereas FT-based substances can partially be transformed into PFCAs in the environment and in biota (for more details, see Buck et al. (2011), Liu and Avendaño (2013), Young and Mabury (2010), and references therein).

Figure 1: General classification of per- and polyfluoroalkyl substances (PFASs) based on the a commonly agreed terminology for nomenclature of PFASs (Buck et al. 2011); this figure is reproduced from OECD (2013) and updated with new information available (in particular, regarding per- and polyfluoroalkyl ether-based substances).



Among polymeric PFASs, different groups of substances can be differentiated as follows.

[i] Fluoropolymers: These consist of carbon-only backbones with fluorine atoms directly attached to this backbone (e.g., polytetrafluoroethylene or PTFE, polyvinylidene fluoride or PVDF; fluorinated ethylene propylene or FEP; perfluoroalkoxyl polymer or PFA). They are not made from non-polymeric PFASs raw materials (except that perfluorobutylethlyene (PFBE) can be used as a co-monomer in some cases); however, the long-chain PFCAs such as PFOA and PFNA have been used extensively as processing aids in the polymerization process of certain types of fluoropolymers.

[ii] Side-chain fluorinated polymers: fluorinated polymers consisting of variable compositions of non-fluorinated carbon backbones with polyfluoroalkyl (and

possibly perfluoroalkyl) side-chains, which often originate from PASF- or FT-based substances.

[iii] Perfluoropolyethers (PFPEs): fluorinated polymers consisting of backbones containing carbon and oxygen with fluorines directly attached to carbon. PFPEs are not made from PFAAs and PASF- and FT-based substances; nor are these non-polymeric PFASs involved in the manufacturing of PFPEs. However, in some cases, PFPEs are longer-chain homologues of non-polymeric per- and polyfluoroalkyl ether-based substances.

The terminology "long-chain" and "short-chain" is used to distinguish different types of PFCAs, PFSAs and their precursors. The term "long-chain PFASs" refers only to the following PFASs (see OECD, 2013):

[i] PFCAs with 7 and more perfluoroalkyl carbons, such as perfluorooctanoic acid (PFOA or C8 PFCA; with 8 carbons) and perfluorononanoic acid (PFNA or C9 PFCA; with 9 carbons);

[ii] PFSAs with 6 and more perfluoroalkyl carbons, such as perfluorohexane sulfonic acid (PFHxS or C6 PFSA; with 6 perfluoroalkyl carbons) and perfluorooctane sulfonic acid (PFOS or C8 PFSA; with 8 perfluoroalkyl carbons); and

[iii] Precursors that have the potential to transform to long-chain PFCAs or PFSAs in the environment or biota, such as PASF- and FT-based substances.

For PFASs other than PFCAs, PFSAs and their precursors, no official distinction between "long-chain" and "short-chain" homologues has been proposed.

2.2 Terminology regarding product life-cycle and emission sources

PFASs can be present in various industrial and consumer products in four forms, namely as main ingredients, as unreacted raw materials (hereafter referred to as *residuals*), as undesired reaction byproducts (hereafter referred to as *impurities*), or as cross contaminants along the production and supply chains. As a simplification, here we group and refer to those relevant products by the PFASs as main ingredients therein. For example, products containing 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 main ingredients are grouped and categorized as commercial PFOA.

The releases of PFASs can occur during the production of PFASs and during the production, use and disposal of products containing PFASs. In addition, some PFASs can transform into other PFASs in the environment and/or biota (e.g., PFCA precursors vs. PFCAs). Thus, here we divide the sources of individual substances into two categories, namely direct and indirect sources. *Direct* sources include emissions from the life-cycle of [i] products that contain the substance as a main ingredient and [ii] other products in which the substances is present as a residual or an impurity. *Indirect* sources refer to formation of the substance from chemical transformation of its precursors in the environment and biota. This terminology is slightly different from that used by (Prevedouros et al. 2006), regarding whether releases of PFCAs as impurities or residuals in products are considered as direct (here) or indirect sources (by Prevedouros et al., 2006).

3. COMPREHENSIVE OVERVIEW OF GLOBAL AND REGIONAL EMISSIONS OF C_4–C_{14} PFCAS

3.1 Overview of identified sources of C_4–C_{14} PFCA homologues.

To date, multiple emission sources have been identified that can potentially contribute to emissions of C_4–C_{14} PFCAs, either directly (PFCAs as main ingredients, residuals or impurities in the products) or indirectly (PFCAs as degradation products from precursors); an overview of these sources is illustrated in Figure 2.

Among identified sources, emissions of C_4–C_{14} PFCAs from four sources can currently be quantified (Figure 2, left column), namely releases of C_4–C_{14} PFCAs from the life-cycle of [i] commercial PFOA used in the production of certain fluoropolymers (i.e., PTFE, FEP, PFA and PVDF), [ii] commercial PFNA used in the production of PVDF, [iii] commercial POSF-based derivatives[3] and [iv] commercial n:2 fluorotelomer-based substances. General information on these four sources including the production and use of relevant commercial products and their relevance to the emissions of PFCAs is sketched in Figure 3, whereas estimated global and regional emissions of C_4–C_{14} PFCAs from these sources are presented in *Sections 3.2, 3.3* and 3.5 below. It should be noted that although the commercial products listed above may contain only a single substance as the major ingredient (e.g., PFOA in commercial PFOA), the commercial products often contain a mixture of homologues with various chain lengths as impurities and/or residuals (e.g., C_4–C_7 and C_9–C_{14} PFCAs may present in certain commercial PFOA as impurities). Details about the production and uses of relevant products and the emission estimation along the life-cycle of relevant products are elaborated in the *Supplementary Data* of Wang et al. (2014a).

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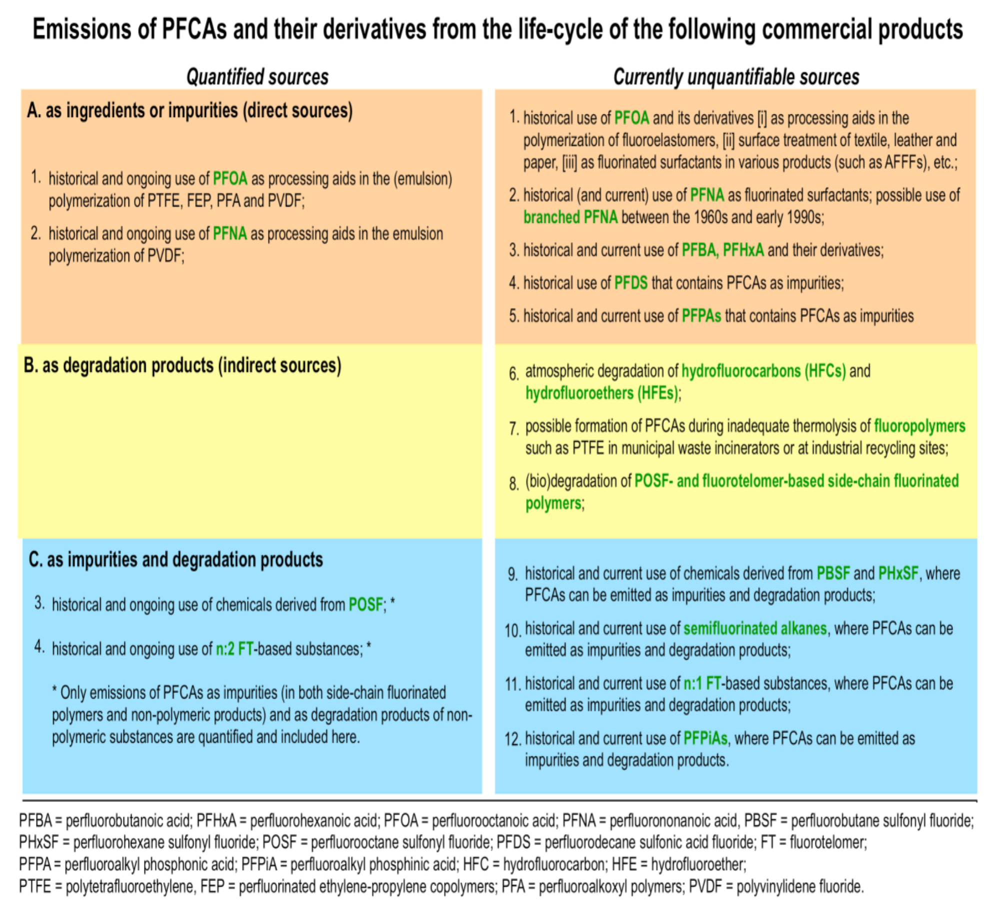
[3] Please note, global historic and ongoing emissions of PFOS from commercial POSF-based derivatives are not included in this study but some estimates exist (Paul *et al.*, 2009; Armitage *et al.*, 2009a).

Figure 2. Overview of (potential) sources of C_4–C_{14} PFCA homologues (quantified vs. currently unquantifiable; direct and/or indirect); this figure is reproduced from Figure 1 in Wang et al. (2014b) and has been updated with new information available (in particular, inclusion of perfluoroalkyl phosphonic and phosphinic acids (PFPAs and PFPiAs) and combination of linear and branched PFNA as a single source).

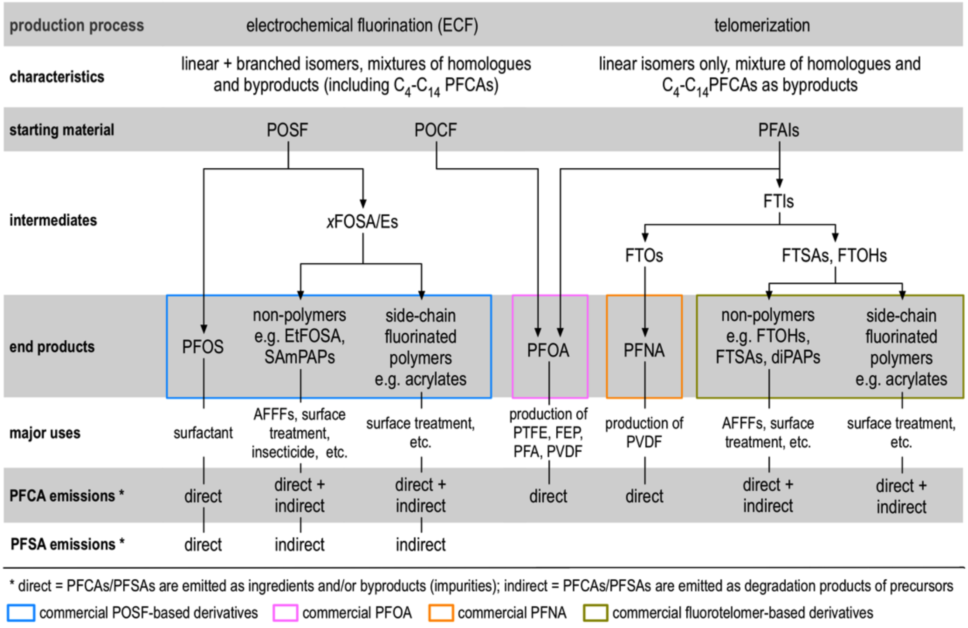


Emissions of PFCAs and their derivatives from the life-cycle of the following commercial products

Quantified sources	*Currently unquantifiable sources*
A. as ingredients or impurities (direct sources) 1. historical and ongoing use of **PFOA** as processing aids in the (emulsion) polymerization of PTFE, FEP, PFA and PVDF; 2. historical and ongoing use of **PFNA** as processing aids in the emulsion polymerization of PVDF;	1. historical use of **PFOA** and its derivatives [i] as processing aids in the polymerization of fluoroelastomers, [ii] surface treatment of textile, leather and paper, [iii] as fluorinated surfactants in various products (such as AFFFs), etc.; 2. historical (and current) use of **PFNA** as fluorinated surfactants; possible use of **branched PFNA** between the 1960s and early 1990s; 3. historical and current use of **PFBA, PFHxA** and their derivatives; 4. historical use of **PFDS** that contains PFCAs as impurities; 5. historical and current use of **PFPAs** that contains PFCAs as impurities
B. as degradation products (indirect sources)	6. atmospheric degradation of **hydrofluorocarbons (HFCs)** and **hydrofluoroethers (HFEs)**; 7. possible formation of PFCAs during inadequate thermolysis of **fluoropolymers** such as PTFE in municipal waste incinerators or at industrial recycling sites; 8. (bio)degradation of **POSF- and fluorotelomer-based side-chain fluorinated polymers**;
C. as impurities and degradation products 3. historical and ongoing use of chemicals derived from **POSF**; * 4. historical and ongoing use of **n:2 FT**-based substances; * * Only emissions of PFCAs as impurities (in both side-chain fluorinated polymers and non-polymeric products) and as degradation products of non-polymeric substances are quantified and included here.	9. historical and current use of chemicals derived from **PBSF** and **PHxSF**, where PFCAs can be emitted as impurities and degradation products; 10. historical and current use of **semifluorinated alkanes**, where PFCAs can be emitted as impurities and degradation products; 11. historical and current use of **n:1 FT**-based substances, where PFCAs can be emitted as impurities and degradation products; 12. historical and current use of **PFPiAs**, where PFCAs can be emitted as impurities and degradation products.

PFBA = perfluorobutanoic acid; PFHxA = perfluorohexanoic acid; PFOA = perfluorooctanoic acid; PFNA = perfluorononanoic acid, PBSF = perfluorobutane sulfonyl fluoride; PHxSF = perfluorohexane sulfonyl fluoride; POSF = perfluorooctane sulfonyl fluoride; PFDS = perfluorodecane sulfonic acid fluoride; FT = fluorotelomer; PFPA = perfluoroalkyl phosphonic acid; PFPiA = perfluoroalkyl phosphinic acid; HFC = hydrofluorocarbon; HFE = hydrofluoroether; PTFE = polytetrafluoroethylene, FEP = perfluorinated ethylene-propylene copolymers; PFA = perfluoroalkoxyl polymers; PVDF = polyvinylidene fluoride.

Figure 3. General information on the production and uses of commercial PFOA, PFNA, and POSF- and fluorotelomer-based derivatives as well as their relevance to the emissions of C_4–C_{14} PFCAs; this figure is reproduced from Figure 1 in Wang et al. (2014a) and updated with new information.



* direct = PFCAs/PFSAs are emitted as ingredients and/or byproducts (impurities); indirect = PFCAs/PFSAs are emitted as degradation products of precursors

PFCA = perfluoroalkyl carboxylic acid; PFSA = perfluoroalkane sulfonic 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 = polytetrafluoroethylene; FEP = perfluorinated ethylene-propylene copolymers; PFA = perfluoroalkoxyl polymers; PVDF = polyvinylidene fluoride

In addition to the four quantified sources in Wang et al. 2014a, there are twelve currently unquantified sources that may emit PFCAs directly and/or indirectly (see Figure 2, right column). Due to a lack of information (such as production volume, usage, and/or degradation half-lives and yields), these additional sources currently cannot be quantified; thus, their contribution to the global emissions of C_4–C_{14} PFCAs cannot be assessed. However, there are some indications that they may not contribute significantly to the global emissions of C_7–C_9 and C_{11} PFCAs, but may contribute significantly to the global emissions of the other PFCA homologues such as C_4–C_6 PFCAs (see section 3.4 below). In addition, some sources may not contribute significantly on the global scale, but may be significant in a local setting. These newly identified sources cover a large range of PFASs, including [i] overlooked use of long-chain PFASs (e.g., sources #1, 2, 4, 9 and 10), [ii] historical and ongoing use of short-chain PFASs (e.g., sources #3 and 9), [iii] historical and ongoing use of fluorinated alternatives other than short-chain PFASs (e.g., sources #5, 11 and 12), [iv] degradation of rather stable polymeric PFASs under certain conditions (e.g., sources #7 and 8), and [v] degradation of fluorinated substances other than PFASs (e.g., source 6). As they may constitute important contributions to historical and/or future emissions of certain PFCA homologues, here we summarize available information on these sources in *Section 3.6 and Annex 3* and highlight critical knowledge/data gaps in Table 3 in *Section 4.2* below, so as to provide an up-to-date overall picture of the sources of PFCAs and to highlight future research needs (e.g., identification of overlooked point sources or human exposure routes).

3.2 Estimated global emissions of sum C_4–C_{14} PFCAs from quantified sources in 1951–2012

In general, Wang et al. (2014a) estimated the global emissions of C_4–C_{14} PFCAs from the four quantifiable sources by combining data on relevant products (such as production processes, production volumes as a function of time and use patterns) with estimated or empirically derived emission factors during each stage in the product life-cycle (production, use and disposal); details on parameters including data treatment and references are provided in the *Section S1* in the *Supplementary Data* of Wang et al. (2014a). The methods in Wang et al. (2014a) rest on many assumptions derived from limited empirical studies, which introduce uncertainties into the estimates. Regarding the remaining uncertainties, a detailed analysis was conducted by Wang et al. (2014a) and is summarized in *Section 4.1* below. In addition, it is noted that Wang et al. (2014a) set an extra so-called “plausible” scenario in the estimation of emissions from the use of commercial PFOA in the production of fluoropolymers. In this “plausible” scenario, one parameter - the usage rate of commercial PFOA in the process - was adjusted to 0.3 wt% of relevant fluoropolymers produced instead of using a wide range collected from the patents. This usage rate of 0.3 wt% is based on a value in 1999 reported by industry (Kälin et al., 2012; Pinchot, 2004; Will et al., 2005); thus, it is likely close to the actual industrial practice and used as a reference value.

Figure 4 and Table 1 display the estimated total global annual and cumulative emissions of C_4–C_{14} PFCAs from the four quantified sources, respectively. In general, the total global annual emissions show a steady increase between 1951 and 2002 (sum: 1790–14220 tonnes) with the highest annual emissions from the mid-1990s to ca. 2001, followed by a sudden and sharp decrease of ca. 40% and then another increase between 2002 and 2012 (sum: 820–7180 tonnes). This recent re-increase is caused by the industrial transition regarding the production and use of long-chain PFASs, in particular of PFOA and PFOS, in opposite directions in the US, Western Europe and Japan (decrease) and the rest of the world (increase), which is elucidated in detail in *Section 3.3* below. Among the four quantified sources, the estimated releases during the life-cycle of commercial PFOA and PFNA contribute 67% to 95%, respectively, to the total emissions of C_4–C_{14} PFCAs before 2015, as far as they could be quantified here. Further illustrations of the emissions of C_4–C_{14} PFCAs from individual source categories and their relative contributions as well as an illustration of the emissions and relative contribution of individual C4–C14 PFCA homologues can be found in Annex 1 and Annex 2 respectively.

3.3 Projected global emissions of sum C_4–C_{14} PFCAs from quantified sources after 2012

After 2012, a further decline of PFCA emissions from industrial sites in the US, Western Europe and Japan is expected, and thus far has been demonstrated based on the companies' commitments to the US EPA 2010/15 PFOA Stewardship Program (US EPA, 2006 and the annual company-specific and/or summary reporting tables therein) and the on-going industrial transition to replacements of long-chain PFCAs and their precursors (for details and examples, see Wang et al., 2013). The results of this commitment are reflected in the lower scenario (Figure 4 left). On the contrary, it is still unclear if and when the production, use and releases of long-chain PFSAs, PFCAs and related precursors in countries other than the US, Western Europe and Japan will be eliminated, although emission reduction actions and substitution of long-chain PFSAs, PFCAs and related precursors in the industrial processes by some manufacturers in China have been reported, but in a rather qualitative manner with no clear timeline given (for details and references, see *Section 3.5* below). Assuming that countries other than the US, Western Europe and Japan keep the same emission level after 2015 until 2030, up to 5510 tonnes of C_4–C_{14} PFCAs could be released in the period of 2015–2030 from the use of commercial PFOA in the production of fluoropolymers. In the period after 2015, the potential contributions from possible continuing production and use of commercial PFOA in fluoropolymer production in countries other than the US, Western Europe and Japan (0–90%) and degradation of fluorotelomer-based substances (10–100%) are estimated to be the dominant emissions.

Figure 4. Estimated total global annual emissions of C_4–C_{14} PFCAs (1951–2030) from quantified sources (lower and higher scenario); this figure is reproduced from Figure 4 in Wang et al. (2014a).

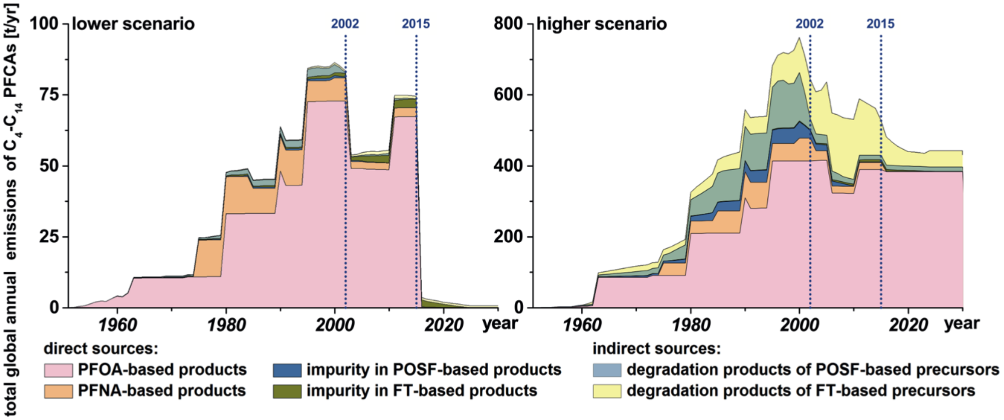


Table 1. Estimated global cumulative emissions of total C_4–C_{14} PFCAs from 1951 to 2030; this table is reproduced from Table 1 in Wang et al. (2014a) with a modification by removing the data comparison to that in Prevedouros et al. (2006). Figures in brackets represent estimates based on a usage rate of 0.3 wt% (of relevant fluoropolymers produced) PFOA-based products in the production of fluoropolymers (i.e., the plausible scenario).

	Quantified emission source category	**This study**					
		1951–2002 [t]		**2003–2015 [t]**		**2016–2030 [t]** [a]	
		lower	**higher**	**lower**	**higher**	**lower**	**higher**
Direct sources	***commercial PFOA***						
	I. PFOA production	90 (200)	970 (570)	30 (90)	430 (280)	0	630 (440)
	II. fluoropolymer (FP) production with PFOA	1220 (2790)	6560 (3850)	660 (1700)	3870 (2430)	0	4520 (3130)
	III. use & disposal of FP dispersions containing PFO	90 (210)	490 (290)	50 (140)	320 (200)	1 (3)	320 (220)
	commercial PFNA						
	IV. PFNA production	20	180	0	50	0	0
	V. PVDF production with PFNA	270	1270	30	220	0	0
	VI. use & disposal of PVDF dispersions containing PFNA	10	20	0	0	0	0
	commercial POSF-based derivatives, as impurities						
	VII. production phase	1	30	0	0.1	0	0
	VIII. use & disposal phase	12	746	1.5	101	0	20
	commercial fluorotelomer-based substances, as impurities						
	IX. production phase	0	0	0	0	0	0
	X. use & disposal phase	17	34	30	61	10	20
Indirect	***commercial POSF-based derivatives, as degradation products***						
	XI. production, use & disposal	50	2400	6	226	0	180
	commercial FT-based derivatives, as degradation products						
	XII. production, use & disposal	9	1518	13	1902	11	726
	Total direct sources [b]	1730 (3530)	10300 (6990)	800 (1990)	5050 (3340)	10 (10)	5510 (3830)
	Total indirect sources [b]	60	3920	20	2130	10	910
	Total emissions (direct + indirect) [b]	1790 (3590)	14220 (10910)	820 (2010)	7180 (5470)	20 (20)	6420 (4740)

[a] Two scenarios for countries other than the US, Western Europe and Japan 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 figures are rounded to the nearest 10.

3.4 Comparison of estimated global emissions of C_4–C_{14} PFCAs from quantified sources to estimates from previous studies and the "ocean inventory"

Wang et al. (2014a) compared their estimates to that in Prevedouros et al. (2006); both studies used similar methodologies but different input parameters to estimate PFCA releases from the same four sources in 1951–2002 (data not shown here). Estimated emissions of sum C_4–C_{14} PFCAs from commercial PFOA and PFNA used in fluoropolymer production are comparable in both studies, particularly when the "plausible scenario" is used in Wang et al. (2014a). For example, with the "plausible scenario", Wang et al. (2014a) estimated that total 3200–4710 tonnes of C_4–C_{14} PFCAs released from the life-cycle of commercial PFOA used in fluoropolymer production in 1951–2002, whereas Prevedouros et al. (2006) estimated 2600–5000 tonnes of C_4–C_{14} PFCAs released from the same sources. On the contrary, Wang et al. (2014a) estimated considerably higher emissions of C_4–C_{14} PFCAs as impurities in commercial POSF-based substances (ca. 5 times in their higher scenario; source VIII in Table 1) and as degradation products of POSF- and fluorotelomer-based precursors (ca. 12 and 80 times in their higher scenario, respectively; sources XI and XII in Table 1) than that in Prevedouros et al. (2006).

For the former, the discrepancy is caused by that Wang et al. (2014a) considered impurity levels of all C_4–C_{14} PFCA homologues (400–13300 ppm), whereas Prevedouros et al. (2006) considered only the PFOA content in products (200–1600 ppm). It is possible that these estimated levels of PFCA impurities in commercial POSF-based substances in Wang et al. (2014a) are still underestimated because in an early study, a 1% (i.e. 10000 ppm) yield of solely perfluorooctanoyl fluoride impurity (which is the starting material to produce PFOA) formed in the electrochemical fluorination to produce POSF was reported (Gramstad and Haszeldine, 1957). In addition, measurements of PFCAs in a small selection of technical products show that the levels of PFCA impurities vary considerably within a production line and among products (Jackson and Mabury, 2013; Naile et al., 2010; Reagen et al., 2007; Seacat et al., 2003). Hence, further studies on PFCA impurities in commercial POSF-based substances are needed to improve the understanding of this historical source. For the latter discrepancy, two changes made in Wang et al. (2014a) contribute to the higher estimates of PFCA releases as degradation products: [i] in addition to residuals, which were treated as the only source of PFCA precursors in Prevedouros et al. (2006), Wang et al. (2014a) took additional sources into account, namely POSF- and fluorotelomer-based PFCA precursors that are present in products as ingredients. To evaluate their estimates for emissions of

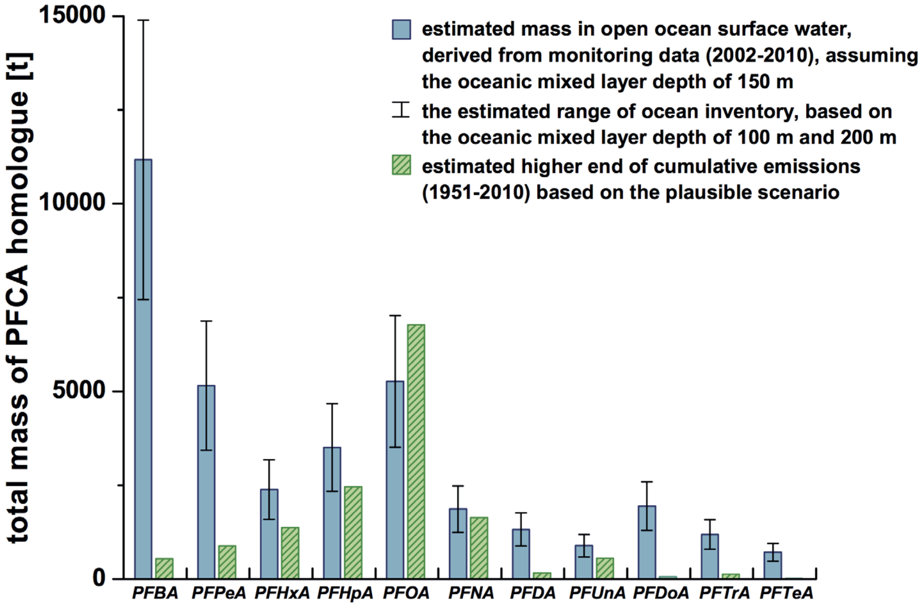
POSF- and fluorotelomer-based PFCA precursors, Wang et al. (2014a) compared estimated emissions of 8:2–14:2 FTOHs and perfluorooctane sulfonamides and sulfonamidoethanols (*x*FOSA/Es, x = CH_3 and C_2H_5) with three studies conducted with different approaches (Buser and Morf, 2009; Müller et al., 2012; Wang et al., 2012; Yarwood et al., 2007); the comparison is illustrated in Figure 7 in Wang et al. (2014a). In brief, estimated emissions of POSF- and fluorotelomer-based PFCA precursors in the four studies agree well with each other, giving confidence to the estimates in Wang et al. (2014a).

Furthermore, since ocean water is the major global reservoir of PFOA, PFNA and likely the other PFCA homologues (Cousins et al., 2011), Wang et al. (2014a) used an inventory of C_4–C_{14} PFCA homologues in open ocean surface water (denoted as the “ocean inventory” below) derived from monitoring studies (Ahrens et al., 2009a, 2010; Benskin et al., 2012a,b; Cai et al., 2012a,b; Wei et al., 2007; Yamashita et al., 2005, 2008; Zhao et al., 2012) for an independent evaluation of their estimated global emissions of C_4–C_{14} PFCA. For details on raw data and data analysis, see *Section S2.5* in the *Supplementary Data* of Wang et al. (2014a). The comparison of the estimated emissions and the ocean inventory is shown in Figure 5.

The higher values of estimated global emissions 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 (150 m); they are within or close to a factor of 1.5. This indicates that the major sources of these PFCA homologues are mostly from the quantified sources. Thus, direct sources (i.e. PFCA releases from the life-cycle of commercial PFOA and PFNA used in fluoropolymer production) contribute significantly to the overall presence of PFOA and PFNA in the oceans on a global scale, as it is also supported by previous studies including Armitage et al., 2006, 2009b,c; Prevedouros et al., 2006; Schenker et al., 2008; Stemmler and Lammel, 2010; Wania, 2007. On the contrary, indirect sources (i.e. degradation of precursors such as POSF- and fluorotelomer-based derivatives) are important origins of PFCAs in remote inland ecosystems (Ellis et al., 2004) such as the Arctic ice caps (Schenker et al., 2008; Young et al., 2007) or alpine lakes (Benskin et al., 2011).

For the other homologues, particularly C_4, C_5, C_{10}, C_{12}–C_{14} PFCAs, the ocean inventory substantially exceeds the estimated global emissions and there thus appear to be missing sources or the ocean inventories of these PFCA homologues have been substantially overestimated due to limited monitoring data available. 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., 2010; Cai et al., 2012a,b), the substantial discrepancy between the ocean inventory and the estimated global emissions could have the following plausible explanations. First, the newly identified but currently unquantifiable sources shown in Figure 2 may have contributed significantly to the presence of some PFCA homologues in the global environment; for further details, see *Section 3.4* below. 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. Third, emissions of long-chain fluorotelomer-based precursors (e.g. 14:2 FTOH) may have been substantially underestimated due to a lack of information on production after 2006. For detailed elaboration on the latter two reasons see the uncertainty analysis summarized in *Section 4.1* below.

Figure 5. Blue: estimated ocean inventories C_4–C_{14} PFCAs derived from monitoring studies (Ahrens et al., 2009a, 2010; Benskin et al., 2012a,b; Cai et al., 2012a,b; Wei et al., 2007; Yamashita et al., 2005, 2008; Zhao et al., 2012) based on the median oceanic mixed-layer depth of 150 m. Green: higher values of the estimated global cumulative emissions of C_4–C_{14} PFCAs until 2010 in Wang et al. (2014a), based on the usage rate of 0.3 wt% PFOA-based products used in the production of fluoropolymers (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. This figure is reproduced from Wang et al. (2014a).



3.5 Historical emissions of C_4–C_{14} PFCA homologues from quantified sources on the regional scale and future perspective

As shown in Table 1, 63% to 89% of historical global PFCAs emissions from quantified sources occurred at industrial sites where related products were produced, used or disposed of (sources #I, II, IV and V in Table 1). Based on available information, Wang et al. (2014a) were able to break down the global emissions of PFCAs from industrial production and use of commercial PFOA on a regional basis quantitatively, whereas the geographical shift of industrial emissions in relation to the other quantified sources was assessed qualitatively. In contrast, for PFCA emissions from domestic releases (i.e., from households and waste treatment facilities), it is currently not possible to break down the global emissions of PFCAs on a country or regional basis, due to a lack of data on the product content and trade among countries.

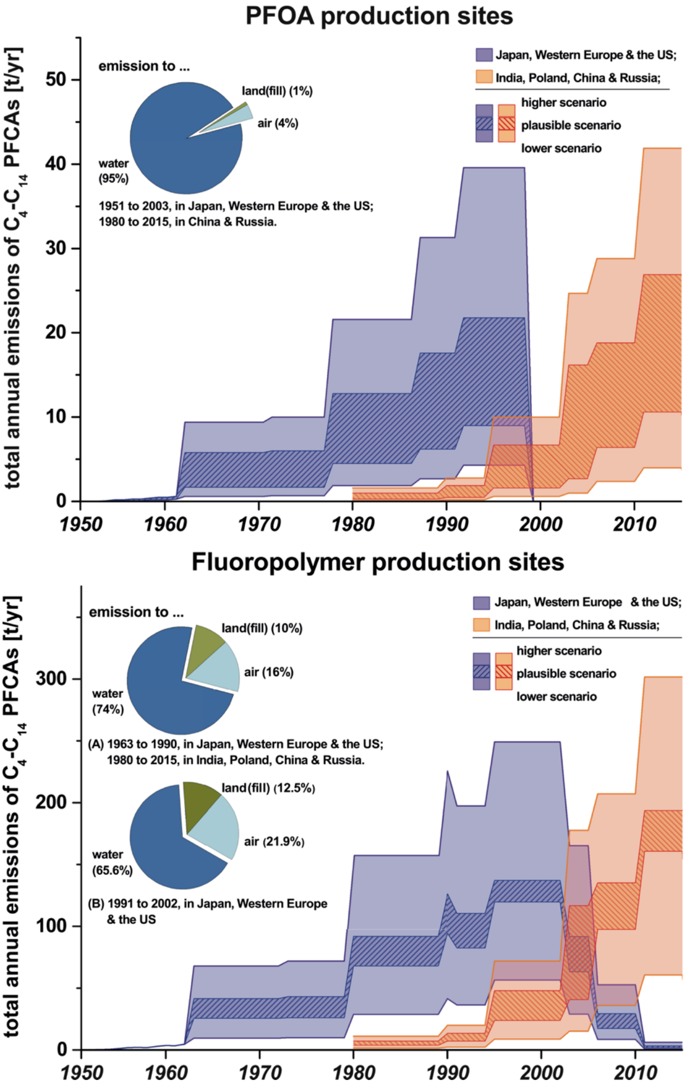
In general, a trend in the geographical distribution of major industrial sites is that production of long-chain PFCAs, fluoropolymers and other PFAS products has shifted from the US, Western Europe and Japan to the emerging economies in continental Asia (e.g., China and India), suggesting that the proportion of global emissions of PFCAs originating from continental Asia has increased. Detailed analyses for the four quantified sources (including references) are provided as follows.

i. commercial PFOA used in fluoropolymer production. There has been a rapid increase in domestic demand and production of PTFE in China since the late 1990s (from 6.6 kt/yr in 1999 to about 64 kt/yr in 2012) (Cai, 2009; Fang, 2004; Kälin et al., 2012; Wang, 2006). Thus, the amounts of PFOA-based products produced in China (initiated in the 1960s in Shanghai; Huang et al., 2010) increased accordingly from a negligible amount before the 1990s to an annual production capacity of about 50–80 tonnes in 2009, with at least five production sites now in China (Mei, 2008) and possibly more (Fluorocouncil, 2014). A recent study estimated that about 480 tonnes of commercial PFOA were produced in 2004–2012 in China, of which ~ 420 tonnes were predominantly used in fluoropolymer production (Li et al., 2015a).

Similarly, PTFE production increased in India after 2010 (ca. 2.3 kt in 2011 and 7.5 kt in 2012; Kälin et al., 2012), resulting in a likely increase in use of commercial PFOA in the fluoropolymer production. Thus, releases of PFCAs from production sites of commercial PFOA and fluoropolymer production sites in China and India have likely increased (see Figure 6, orange areas; it is noted that these estimates of PFCA releases from commercial PFOA in China, India and Russia might be an overestimation by a factor of ~2, as newly available information shows that manufacturers in China may have used less PFOA in fluoropolymer production than those in the US, Western Europe and Japan (Li et al., 2015a)).

In contrast, after 2000, major PFOA producers in the US, Western Europe and Japan subsequently ceased PFOA production (e.g., 3M in 2002 (3M, 2000a); Dyneon in 2004 and Miteni in 2010 (OECD, 2009); Daikin in 2012 (Daikin, 2014); and DuPont in 2013 (DuPont, 2013)), and the remaining production was/is mostly conducted in closed processes with marginal losses only (DuPont, 2005; OECD, 2009; US EPA, 2006). At the same time, major fluoropolymer producers in these regions implemented technologies to recover and reuse PFOA from wastewater streams (3M, 2009; Chapman, 1998; OECD, 2009) and started to use PFOA-free alternatives in the polymerization processes (Dyneon uses alternatives only from 2009 (Dyneon, 2011), Asahi from 2011 (Asahi, 2009 a,b), Daikin and Solvay from 2013 (Daikin, 2014; Solvay, 2013), and DuPont from mid-2013 (DuPont, 2013)). These actions have led to a 95% decrease in PFCA releases from production sites in Japan, Western Europe and the US after 2000 (US EPA, 2006 and the summary tables from annual reporting there) (see Figure 6, purple areas). The increase in PFCA emissions at the manufacturing sites of PFOA and fluoropolymers made with PFOA in countries such as China, India and Russia (Figure 6, orange areas) may likely more than offset the decline at such sites in the US, Western Europe and Japan (Figure 6, purple areas) in the period 2002–2012, causing a re-increase of global annual PFCA emissions as illustrated in Figure 4. It should be noted that several major Chinese fluoropolymer producers have also developed technologies to recycle PFOA from waste streams (Feng and Su, 2007; Tang et al., 2009) or industrialized production with alternative substances replacing PFOA-based products (Wang et al., 2010; Xie et al., 2011; Xu et al., 2011); however, due to a lack of quantitative data, the corresponding reduction of PFCA 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 is not currently available.

Figure 6. Estimated annual releases of PFCAs from PFOA production sites (top) and fluoropolymer production sites (bottom) in the United States (US), Western Europe and Japan (purple) and 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 PFOA usage rates from patents; the areas shaded in dark represent the estimated ranges of annual releases based on the PFOA usage rate of 0.3wt% of relevant fluoropolymers produced (plausible scenario). This figure is reproduced from Wang et al. (2014a).



ii. commercial PFNA used in the production of PVDF. Reports from the only known producer and the major industrial users (i.e., PVDF producers) in the US, Western Europe and Japan show that emissions related to PFNA-based products from their production sites were likely 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), producers there have likely used 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 and will cease after 2015 based on the companies' commitments to the US EPA 2010/15 PFOA Stewardship Program (US EPA, 2006).

iii. commercial POSF-based derivatives. 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 long-chain POSF-based products in 2002, there were still a few producers in Japan and the Western Europe: about 50–160 tonnes of POSF and certain derivatives were produced in 2003 in Belgium, Germany, Italy and Japan (OECD, 2005); and 73–162 tonnes in 2005 (OECD, 2006). Wang et al. (2014a) 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 in emissions of PFCA impurities and POSF-based PFCA precursors from these industrial sites in the US, Western Europe and Japan after 2002. In contrast, large-scale production began in China in 2003, with extensive use of polymeric commercial POSF-based substances 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 of POSF and certain derivatives in China before 2004 was less than 50 t/yr, expanded to about 250 t/yr by 2006, declined to 100 t/yr in 2008, and then varied between 100 and 150 t/yr (China MEP, 2008; Huang et al., 2010, 2013; Lim et al., 2011; Zhang et al., 2012;). Recent estimates show that on average 150 t/yr of POSF and certain derivatives were produced between 2004 and 2012 in China (Li et al., 2015a). Besides a small fraction for exportation (e.g., Brazil imported on average 30 t/yr POSF to produce sulfluramid as insecticide in 2004–2006 (Brazil 2007); this use is ongoing (Brazil, 2014)), the remaining uses in China are mainly in metal plating, aqueous film-forming foams (AFFF) synthesis and sulfluramid formulation (Zhang et al., 2012). Recently, Chinese manufacturers 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 time plan is not yet available.

iv. commercial fluorotelomer-based substances. It is currently unclear how the geographical distribution of PFCAs and precursor 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 commercial fluorotelomer-based substances was only located in the US, Western Europe and Japan (Banks et al., 1994; Prevedouros et al., 2006). The emissions of PFCAs and precursors from these primary production sites have been significantly reduced (95% less than the baseline emissions in 2000–2002) and are expected to be further decreased based on companies' commitment to the US EPA 2010/15 PFOA Stewardship Program (US EPA, 2006 and the annual company-specific and/or summary reporting tables therein). Recently, manufacturers in China also started the production of fluorotelomer-based substances at a minimum of two sites (Fuxin, 2015; 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.

3.6 Overview of currently unquantifiable sources of C_4–C_{14} PFCA homologues

This subsection provides an overview analysis of the relevance of newly identified, but currently unquantifiable sources to the global and regional emissions of C_4–C_{14} PFCAs in terms of where primary emissions occur, time frame, and possible scales (see Table 2 and the text below). For each individual source, detailed information on the production, use, relevance to PFCA emissions in terms of PFCA homologues is presented in Annex 3, whereas details such as degradation mechanisms and kinetics can be found in Wang et al. (2014b) and other references cited in the text. In addition, a checklist regarding what is known and what is unknown is compiled in Table 3 in *Section 4.2* below.

Despite a lack of monitoring data, emissions of PFCAs from the overlooked sources listed here have likely occurred, except for the thermolysis of fluoropolymers. Currently there have been only laboratory studies showing the theoretical possibility of formation of PFCAs from inadequate thermolysis of fluoropolymers. However, whether it may occur in real world, where the situation is more complicated in terms of operation temperature and co-reagents, is still unclear and needs further field studies.

In general, the primary emissions of PFCAs from most of the overlooked sources occurred, are occurring or would occur at the local scale, where relevant substances are produced, used and disposed of, whereas the primary emissions of PFCAs from atmospheric degradation of hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) and (bio)degradation of side-chain fluorinated polymers may occur on the global scale. This is likely because [i] HFCs, HFEs and side-chain fluorinated polymers are likely well distributed all over the world due to their persistence, long emission history and possibly high long-range transport potential, and [ii] the degradation half-lives of these substances are long, ranging from years to decades, maybe even longer. Depending on the substances and their life-cycle, the primary emissions can occur at industry sites (including manufacturing sites, downstream industrial users sites, and waste treatment facilities such as landfills and wastewater treatment plants), in households (e.g., from use of consumer products), or in the environment (e.g., from use of pesticide formulations or aqueous fire-fighting foams).

Among all overlooked sources, some might have been significant in the past (e.g., historical use of short-chain PFCAs, their derivatives, PFPAs and PFPiAs, and PBSF- and PHxSF-based derivatives) and some are still ongoing (e.g., short-chain PFCAs, their derivatives, PBSF- and PHxSF-based derivatives, and n:1 FT-based derivatives are used as replacements of long-chain PFASs in various applications). Most of these sources may emit PFCAs as ingredients, impurities and/or residuals immediately when relevant commercial products are produced, used and disposed of (except that landfills may often act as a rather long-term reservoir) or may emit PFCAs as degradation products shortly (days, weeks to months) after relevant precursor substances (e.g., non-polymeric PBSF- and PHxSF-based PFCA precursors) released; however, HFCs, HFEs and side-chain fluorinated polymers may act as long-term sources due to the long degradation half-lives (years to decades, or even longer).

Table 2. An overview of the relevance of newly identified, but currently unquantifiable sources to the global and regional emissions of C_4–C_{14} PFCAs in terms of primary emission sites, time frame, and possible scales. “industry” includes manufacturing sites, downstream industrial user sites, and industrial/municipal waste treatment facilities.

ID	Emission source	Primary emission sites		Time frame		Possible scales
		global/ local	**industry/ household/ environment**	**historical/ ongoing**	**immediate/ short-term/ long-term**	
#1	historical and ongoing use of **PFOA** other than in the production of fluoropolymers	local	industry/ household/ environment	historical, maybe still ongoing	immediate/ short-term	6 t/yr of 3M’s products sold between the late 1990s and early 2000s
#2	historical and possibly ongoing use of **PFNA** other than in the production of PVDF	local	industry	historical	immediate	unknown
#3	historical and ongoing use of **short-chain PFCAs**	local	industry/ household	historical & ongoing	immediate/ short-term	Some were produced / imported in amounts of 4.54–227 t/yr in the US between 1986 and 1998, others even higher.
#4	historical use of **PFDS**	local	industry/ household	historical	immediate	Production / importation of 4.54–227 t/yr in the US were reported in 1990 and 1994.
#5	historical and ongoing use of **PFPAs**	local	industry/ household/ environment	historical & ongoing	immediate	Production / importation of 4.54–227 t/yr in the US were reported in 1998 and 2002.
#6	atmospheric degradation of relevant **HFCs** and **HFEs**	global	environment	historical & ongoing	long-term	HFEs were reported to be produced/imported in the US, ranging from 4.54–227 t/yr to 454–4540 t/yr in 1998, 2002 and 2006.
#7	inadequate thermolysis of **fluoropolymers**	local	industry	unknown	immediate	unknown
#8	biodegradation of **side-chain fluorinated polymers**	global	environment	historical & ongoing	long-term	80% of fluorotelomer-based substances produced in 2002 were fluorinated polymers.
#9	historical and ongoing use of **PBSF- and PHxSF-based derivatives ***	local	industry/ household	historical & ongoing	immediate / short-term	Some were produced / imported in amounts of 4.54–227 t/yr in the US between 1986 and 1998, others even higher.
#10	historical and ongoing use of **SFAs**	local	industry/ environment	historical & ongoing	immediate / short-term	unknown
#11	historical and ongoing use of **n:1 FT-based derivatives ***	local	industry/ household	historical & ongoing	immediate/ short-term	unknown
#12	historical and ongoing use of **PFPiAs**	local	industry/ household/ environment	historical/ongoing	immediate / short-term	Production / importation of 4.54–227 t/yr in the US were reported in 1998 and 2002.

* Some of these substances may also be side-chain fluorinated polymers; emissions of PFCAs from (bio)degradation of side-chain fluorinated polymers are included in source #8.

4. UNCERTAINTIES AND INFORMATION GAPS IN ESTIMATING GLOBAL AND REGIONAL EMISSIONS OF C_4–C_{14} PFCAS

As shown in *Section 3*, a considerable amount of information and knowledge regarding the global and regional emissions of C_4–C_{14} PFCAs has been generated and systematically assessed and integrated. Built on these previous efforts, in spite of remaining uncertainties associated with the four quantifiable sources, a reasonable estimation of PFCA releases from these four sources on a global scale is possible, as supported by the comparison of global emissions of C_4–C_{14} PFCAs and related precursors to that from previous studies including Armitage et al. (2006, 2009b,c), Prevedouros et al. (2006) and Wang et al. (2012) as well as to the “ocean inventory” derived from measurements in *Section 3* above.

However, currently a lack of information prohibits a better quantification of PFCAs emissions from other identified sources. This section takes a look at the major uncertainties in estimating emissions of PFCAs from quantified sources (see *Section 4.1*) and at critical data and knowledge gaps in relation to currently unquantifiable sources (see *Section 4.2*). This forms the basis for recommendations of options to improve knowledge about global and regional emissions of PFASs in the next section.

4.1 Major uncertainties in estimating emissions of C4–C14 PFCAs from quantified sources

The methods employed by Wang et al. (2014a) rest on many assumptions derived from limited empirical studies, which introduces 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, the authors performed a bounding analysis by setting lower and higher scenarios to represent the likely range of values for those parameters (such as emission factors or levels of PFCA impurities in products) where adequate information is available, as suggested by Morgan (2001) and Refsgaard et al. (2007). Some other uncertainties introduced by using default values cannot be reliably quantified due to a lack of data; for example, an adjustment factor for extrapolating data from laboratory studies to field conditions is currently not available. To quantify such uncertainties caused by knowledge gaps, future in-depth research is needed.

To clearly indicate the uncertainty levels of individual parameters in their study as a basis and guide for future research, Wang et al. (2014a) introduced a scoring system: 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; detailed scores are provided in Tables S66 to S68 in the *Supplementary Data* in Wang et al. (2014a). In general, the uncertainty levels increase in the order: [i] PFOA-based products ≤ PFNA-based products < POSF-based products < fluorotelomer-based products; [ii] production phase < use and disposal phase; [iii] emissions from 1951 to 2015 < emissions from 2016 to 2030; and [iv] global emissions < regional emissions.

As described above, among the four quantified sources, information on the production and use of commercial PFOA and POSF-based substances, releases of PFOA at the primary manufacturing sites and fluoropolymer manufacturing sites, and releases of POSF-based substances at the primary manufacturing sites has the highest certainty, based on the extensive studies that were conducted by a major producer of these products (3M) and the major fluoropolymer producers and reported to the US EPA.

For commercial PFOA, the estimated amounts used in fluoropolymer production have the largest uncertainty range, due to: [i] the usage rates of commercial PFOA are reported with wide ranges in patents; and [ii] the ongoing transition to non-PFCA alternatives after 2002 in all relevant countries has only been roughly reported. To address the first uncertainty, Wang et al. (2014a) proposed a “plausible scenario” that is likely to be close to actual industrial practice for manufacturers in the US, Western Europe and Japan, but not necessarily for manufacturers from outside of these countries. Regarding the second uncertainty, the authors may overestimate the amounts of PFOA used in recent years, which can only be corrected when new information is available. For commercial PFNA, the composition of PFCA homologues in products is the most uncertain parameter, since only one measurement is currently available.

For commercial POSF- and fluorotelomer-based substances, only limited information is available for the use and disposal phases on the global scale, due to the large diversity of products involved, leading to wide ranges of emissions estimated and difficulties to break down the global emissions on a country/regional basis in this study. To address such uncertainties and difficulties, more thorough mass flow analyses are needed to close the mass balance of relevant PFASs in the life-cycle of relevant commercial products, in particular during the use (such as textile and paper industry) and disposal (such as wastewater treatment facilities and landfills) phases; for the latter, future efforts can and should be built on existing work, including Ahrens et al. (2009b, 2011), Benskin et al. (2012c), Busch et al. (2010), Hong et al. (2015), Li et al. (2015b), Schultz et al. (2006), Shivakoti et al. (2010), Sun et al. (2012), and Vierke et al. (2011). In addition, the estimated production volume of commercial fluorotelomer-based substances is highly uncertain, as Wang et al. (2014a) assumed that the production volumes stayed on the same level after 2006, which needs to be updated when new information is available. Moreover, Wang et al. (2014a) estimated negligible PFCA emissions from primary industrial sites where commercial fluorotelomer-based substances were produced, due to a lack of information on emission factors. This might be a considerable underestimation, as indicated by two monitoring studies conducted close to manufacturing sites of commercial fluorotelomer-based substances (Dauchy et al., 2012; Ruan et al., 2010).

Furthermore, the projections of PFCA emissions (2016–2030) have much higher uncertainties in comparison to the emission estimates for the period before 2016, due to the large uncertainty associated with the elimination of production and use of long-chain PFASs in countries other than the US, Western Europe and Japan. These ongoing emissions in regions with emerging economies are estimated to be the major contributors to the present and potential future releases of long-chain PFCAs in the global environment. There is evidence that action is being taken in these regions to replace long-chain PFASs with alternatives substances (for references, see *Section 3.5* and Wang et al., 2013); therefore, the production, use and emissions of long-chain PFASs are likely being reduced in these regions. However, a quantitative emission reduction strategy has not currently been reported for these regions.

4.2 Critical data and knowledge gaps that prevent quantification of overlooked sources

This subsection focuses on information gaps that are critical for understanding the releases of PFCAs from individual overlooked sources, which can be used as a map to guide and prioritize future research when an individual source is studied. It should be noted that this subsection does not provide a basis to prioritize which overlooked sources should be studied; such prioritization of overlooked sources could be determined based on the global and/or regional relevance of environmental and human exposure to individual sources, which is elaborated in *Section 3.6* above. An overview of the availability of information along the life-cycle of relevant chemicals (production, use and disposal) that is needed to quantify those newly identified sources is provided in Table 3 below. In general, information gaps can be divided into two categories, for which different strategies are needed to fill in missing information:

[i] critical data gaps where information is not publicly available, but may have been or can be generated by individual relevant manufacturers from their own production and sales data, e.g., information on the production volumes, compositions, use pattern, amounts used in products and trade of relevant chemicals;

[ii] critical knowledge gaps where information is not publicly available and (new) scientific studies are needed to generate such information, e.g., estimating emission factors along the life-cycle based on monitoring studies and measuring degradation kinetics and yields based on laboratory experiments.

Among parameters in relation to critical data gaps, use patterns of relevant chemicals are often best known, whereas production volumes, compositions, usage in products and trade are often treated as confidential business information and thus sealed from the public. Among parameters in relation to critical knowledge gaps, measuring emissions factors along the life-cycle of relevant chemicals, measuring degradation kinetics and yields in the laboratory and extrapolation of results from laboratory studies to field conditions can often be challenging, particularly where adequate analytical methods and/or laboratory settings (e.g., in the case of measuring degradation kinetics of side-chain fluorinated polymers) are not yet established.

Table 3. Overview of availability of information that is needed to quantify newly identified sources of PFCAs. "X" = unknown; irrelevant fields are covered with grey.

ID	Emission source	information on production and use					Emission factors along its life-cycle	Degradability		
		production volumes	compositions (incl. byproducts and residuals)	use pattern	amounts used in products	trade		mechanisms	kinetics and yields	adjustment factor (laboratory → field)
#1	historical and ongoing use of **PFOA** other than in the production of fluoropolymers	X	likely similar to known PFOA-based products	known	X	X	X			
#2	historical and possibly ongoing use of **PFNA** other than in the production of PVDF	X	likely similar to known PFNA-based products	evidence from patents and measurements	X	X	X			
#3	historical and ongoing use of **short-chain PFCAs**	known (in the US in some years)	X	limited information available	X	X	X			
#4	historical use of **PFDS**	known (in the US in some years)	likely similar to known PFOS-based products	known as ingredients in floor polishes	X	X	X			
#5	historical and ongoing use of **PFPAs**	X	X	as defoamers in pesticides and as surfactants	limited information available	X	likely 100%			
#6	atmospheric degradation of relevant **HFCs** and **HFEs**	known (in the US in some years)	X	limited information available	X	X	X	likely mechanism known	limitied information available	X
#7	inadequate thermolysis of **fluoropolymers**	known	X	known	X	X	X	likely mechanism known	X	X
#8	biodegradation of **side-chain fluorinated polymers**	known with high uncertainty	homologue distribution known for 2002	surface protectors and surfactants	X	X	X	likely mechanism known	limited is known and under debate	X
#9	historical and ongoing use of **PBSF- and PHxSF-based derivatives**	known (in the US in some years)	X	surface protectors and surfactants	X	X	X	similarly to POSF-based substances	limitied information available	X
#10	historical and ongoing use of **SFAs**	X	evidence of PFCAs as impurities	used in ski wax and medical applications	X	X	X	likely mechanism known	X	X
#11	historical and ongoing use of **n:1 FT-based derivatives**	X	X	surface protectors and surfactants	X	X	X	likely mechanism known	X	X
#12	historical and ongoing use of **PFPiAs**	X	X	as defoamers in pesticides and as surfactants	limited information available	X	likely 100%	known	X	X

5. RECOMMENDATIONS FOR IMPROVING KNOWLEDGE ON GLOBAL AND REGIONAL EMISSIONS OF PFASS

The issues related to emissions of PFASs are highly complex, as hundreds of chemicals in unaccountable amounts of commercial and consumer products are involved and emissions of many PFASs can occur at any stage of the product life-cycle and are interrelated. This report focuses on the global emissions of PFCAs with many other PFASs and related fluorinate substances considered in the background assessment and estimation, but not on other groups of PFASs and does not provide direct information on other groups of PFASs, e.g. global emissions of PFSAs.

After over a decade of research and systematic integration of many individual findings, four important sources of PFCAs are relatively well understood; these include releases of PFCAs from the life-cycle of commercial PFOA, PFNA, and POSF- and fluorotelomer-based substances in industrial and urban areas, including households and waste treatment facilities. Among them, commercial PFOA (C_8 PFCA) and PFNA (C_9 PFCA) used in the fluoropolymer production are identified as the sources responsible for the majority of C_7–C_9 and C_{11} PFCAs in the global environment. While former major global manufacturers in the US, Western Europe and Japan are stepwise eliminating the production and use of long-chain PFASs (including commercial PFOA, PFNA and POSF- and fluorotelomer-based substances) by or shortly after 2015, new manufacturers in emerging economies recently initiated large-scale production and use of certain long-chain PFASs with limited quantitative information publicly available. Therefore, there is an urgent need to follow up and capture this ongoing geographical shift of industrial sources, as a basis for future actions towards global elimination of long-chain PFASs.

However, the understanding of (potential) sources of some other PFCA homologues, particularly C_4, C_5, C_{10}, C_{12}–C_{14} PFCAs, is still incomplete. Multiple overlooked sources of PFCAs have been identified, but can currently not be quantified due to a lack of quantitative information. Thus, their contribution to the global and regional emissions of PFCAs cannot be quantitatively assessed, although some of the sources may have been significant in the past (e.g., historical use of PFBA, PFHxA, their derivatives, and PBSF- and PHxSF-based derivatives), whereas others can be significant in the long-term (e.g., (bio)degradation of various side-chain fluorinated polymers, atmospheric degradation of HFCs and HFEs). In addition, releases of PFCAs from some sources are ongoing and likely increasing (e.g., ongoing use of PFBA, PFHxA, their derivatives, and PBSF- and PHxSF-based derivatives as alternatives to long-chain PFASs). Therefore, studies on the global and/or regional emissions of PFCAs from (at least some of) these overlooked sources are urgently needed.

Furthermore, efforts to understand and assess the risks associated with the environmental and human exposure to many fluorinated alternatives to long-chain PFASs, starting from source identification and quantification, are also urgently needed. Many fluorinated alternatives, more specifically perfluoroether carboxylic and sulfonic acids (PFECAs and PFESAs), do not contribute to the emissions of PFCAs (see references in Wang et al., 2013, 2015). However, recent studies systematically evaluated available evidence and found that:

[i] these alternatives still possess high environmental stability and mobility, similar to those of their predecessors (long-chain PFASs), which implies that they have a high global contamination potential once released and;

[ii] some PFECAs and PFESAs are shown to possess medium to high toxicity and thus can pose global risks to humans and the environment (detailed analysis see Wang et al. 2015 and the references therein).

Thus, it is essential to understand the global emissions of these alternatives, in order to prevent emissions and exposures from occurring on a large scale. However, in the same way as for many other PFASs discussed above, only the use of such chemicals is known and no information regarding the actual volumes that have been produced, used and released is available (see Wang et al., 2013). Hence, considerable efforts to understand the global production, use and releases of these fluorinated alternatives to long-chain PFASs are also needed.

Based on lessons learned and the uncertainty and gap analysis presented in *Section 4*, three recommendations for improving knowledge on global and regional emissions of PFASs are presented as follows:

[i] The OECD 2007 list of PFASs needs to be updated. In 2007, OECD published an exhaustive, revised list of PFASs containing over 920 PFASs (OECD 2007). However, this list is likely no longer up-to-date. In order to provide all stakeholders with an extensive, consistent and easily accessible list of PFASs for future work, it is recommended that the OECD list be updated with possible new features as follows: [i] inclusion of newly identified legacy PFASs and other fluorinated substances (which are relevant for emissions of PFASs, e.g., relevant HFCs and HFEs); [ii] inclusion of new fluorinated alternatives to long-chain PFASs; [iii] adoption of the commonly accepted terminology and detailed categorization of PFASs as proposed by Buck et al. (2011); [iv] inclusion of additional information such as chemical structures and trade names of commercial products/mixtures, if possible.

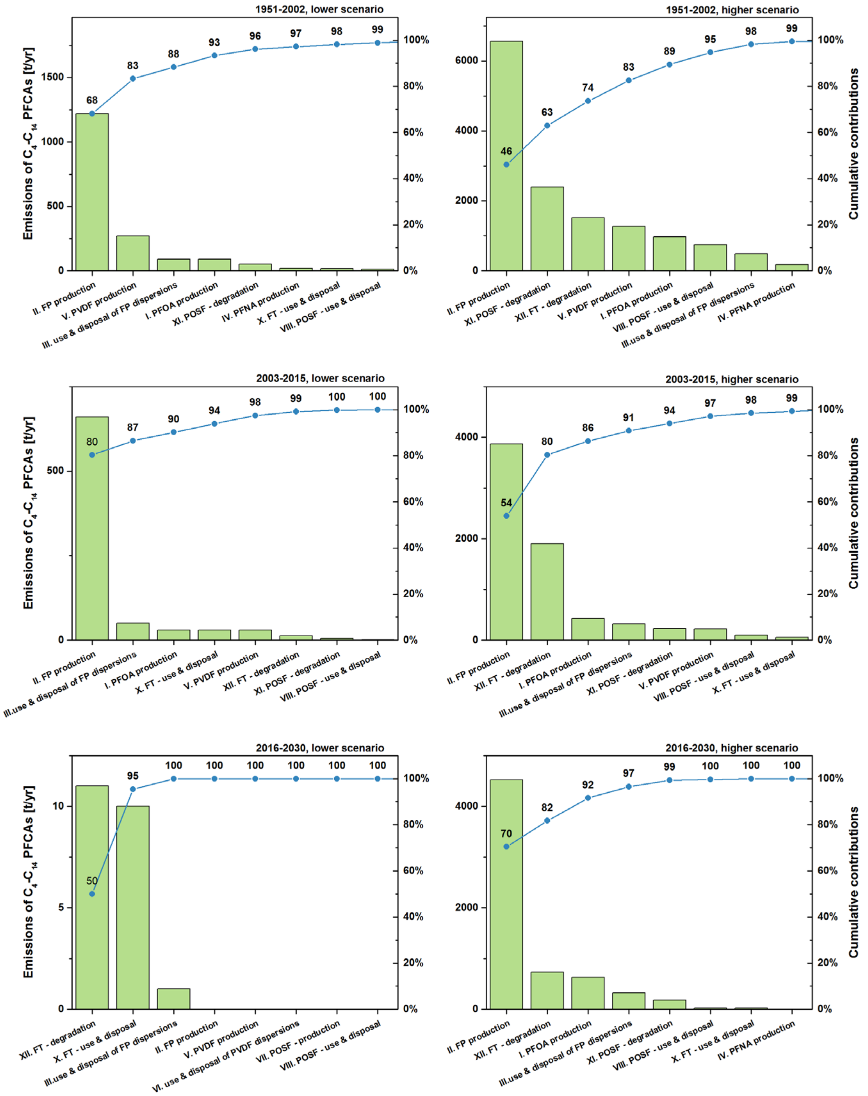
[ii] A new survey on the global production, use and release of PFASs is necessary in order to properly assess historical and ongoing exposure and to understand global trends. It is recognized that a large amount of missing information can be or may have been generated by individual manufacturers from their own production and sales data, e.g., information on the production volumes, compositions, use pattern, amounts used in products and trade of relevant chemicals. In some cases, some manufacturers or regulatory bodies may have also generated information on PFASs emissions at industrial sites. Making such information publicly available is key to establishing the big picture of global and regional emissions of PFASs; thus, a new survey, which encompasses critical information needs and includes all relevant regions, and public consultation, should be considered to collect this information. To ensure a successful survey, several factors need to be considered, namely:

- [i] active participation of industry sectors that produce and/or use various PFASs;
- [ii] an effective system enabling the manufacturers and users to provide information without concern of losing confidentiality, but still making the collected information accessible and useful to other stakeholders;
- [iii] active involvement and participation of stakeholders (including civil society, industry, academia and regulatory bodies) from both OECD member and OECD partner countries (in particular, since much of the production and use of long-chain PFASs has shifted to countries other than Western Europe, Japan and the United States, initiation of a new survey should be contingent upon adequate participation from these countries); and
- [iv] prioritization of information collection for certain PFAS groups depending on existing hazard or risk profiles in order to efficiently direct resources.

[iii] Synergies among stakeholders and links to the existing programs are needed. Another challenge in estimating the global emissions of PFASs is to fill those critical knowledge gaps, where systematic studies and advance of science and knowledge are needed. For this purpose, synergies among stakeholders (intergovernmental organisations, governments, industry, academia and civil society) and links to the existing programs should be used. For example, the extent of use and release of PFASs in the supply chain is largely unknown; thus, in many cases, importers or downstream industrial users do not have adequate information for them to assess and manage the releases of PFASs from their products (Korucu et al., 2014). This situation can be improved by cooperative actions with the existing programs such as the Pollutant Release and Transfer Register (PRTR) led by OECD (OECD, 2015b) and Chemicals in Products Programme led by the United Nations Environmental Programme (UNEP) under the Strategic Approach to International Chemicals Management (SAICM) (UNEP, 2015). Moreover, information exchange between different stakeholders will also be beneficial. For instance, manufacturers have information regarding the composition and physicochemical properties of various side-chain fluorinated polymers, which can help academic scientists to develop effective and representative laboratory experiments to measure the degradation half-life of these polymers. To increase synergies among stakeholders and links to the existing programs, a broader and more transparent and intense dialogue among stakeholders and relevant actors is needed. The OECD/UNEP Global PFC Group could provide a forum for this dialogue.

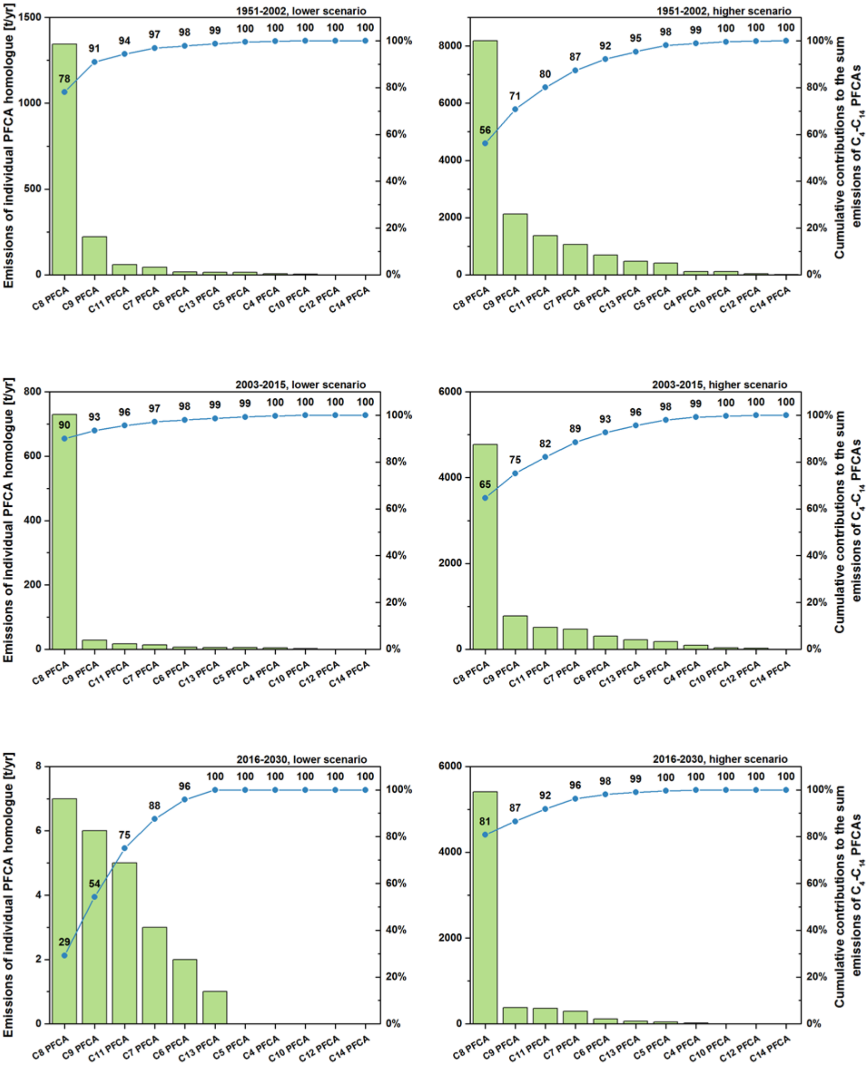
ANNEX 1:

Emissions of C4–C14 PFCAs from individual source categories (only top 8 are shown here) and relative contribution of these source categories between 1951 and 2002, 2003 and 2015, and 2016 and 2030, respectively



ANNEX 2:

Emissions of individual C_4–C_{14} PFCA homologues and relative contribution of individual PFCA homologues to the sum emissions of C_4–C_{14} PFCAs between 1951 and 2002, 2003 and 2015, and 2016 and 2030, respectively.



ANNEX 3:

Overview of currently unquantifiable sources of C_4–C_{14} PFCA homologues

Sources where PFCAs are emitted as ingredients or impurities (direct sources)

Historical use of PFOA other than in the production of fluoropolymers.

Production: There is a lack of information on the production history of PFOA-based products in non-fluoropolymer-related uses, except that 3M's global sales of PFOA and derivatives for such uses were about 6 tonnes per year (t/yr) between the late 1990s and early 2000s (FMG, 2002).

Use: PFOA-based products were or have been used in the following non-fluoropolymer-related industrial and consumer applications. **[i]** PFOA were or have been used in the production of fluoroelastomers including base-resistant elastomers (CAS Nos. 54675-89-7 and 27029-05-6) and CTFE elastomers (CAS No. 9010-75-7) (Millet, 2005; Willis, 2007). In addition, PFOA may also have been used in the production of other fluoroelastomers (CAS Nos. 9011-17-0, 25190-89-0 and 26425-79-6) manufactured by Daikin (Dai-el®), DuPont (Viton®) and Solvay (formerly Ausimont; Tecnoflon®) (Duncan, 2003; Kirk-Othmer, 2000; Yamashita et al., 2004). Among others, 3M/Dyneon had stopped its use of PFOA in the production of CAS Nos. 54675-89-7 and 9010-75-7 as well as its import and sale of CAS No. 27029-05-6 by 2004, whereas Asahi had ceased its use of PFOA in the production of CAS No. 27029-05-6 by 2006 (Millet, 2005; Willis, 2007). **[ii]** Before POSF-based replacements were largely commercialized in the 1960s, PFOA-based chromium complexes were used as oil- and water-repellent finishes for paper (e.g. FC-805, CAS No. 55801-89-3) and stain-repellent finishes for leather (e.g. FC-146, CAS No. 37317-76-3) (Bryce, 1964; Philips et al., 1957; Scherer, 1970; Segal et al., 1958). **[iii]** PFOA derivatives (CAS Nos. 335-90-0, 5158-52-1 and 802270-49-1) were used as intentional ingredients in the early generation(s) of AFFFs (Francen, 1972; Turve and Jablonski, 1966). **[iv]** Small amounts of PFOA were also directly used as an antistatic additive in some medical film applications (3M, 2003), and as a surfactant in various products (e.g. cleaning formulations) (OECD, 2009; Scherer, 1970). **[v]** PFOA was used as a starting material to produce an odd carbon-numbered fluorotelomer alcohol (n:1 FTOH, $C_nF_{2n+1}CH_2OH$), which will be discussed in detail below.

Emissions: C_4–C_{14} PFCAs, mainly PFOA, linear and branched isomers

Historical (and ongoing) use of PFNA other than in the production of PVDF.

Production: Most of the historical PFNA-based products were manufactured as linear isomers. However, several manufacturers, notably Pennwalt and Daikin, developed techniques based on perfluoroisopropyl iodide and thus may have manufactured branched PFNA-based products between the 1960s and early 1990s (Banks et al., 1994; Fielding, 1979). This intentional production of isopropyl PFNA is supported by detection of only the isopropyl PFNA but no other branched isomers in ringed seals from Resolute Bay and a single polar bear from the Canadian Arctic (De Silva et al., 2009).

Use: In addition to their use in the production of PVDF, PFNA-based products were or have been marketed and used as fluorinated surfactants in some industrial applications (Buck et al., 2011), as indicated by monitoring data obtained from sampling and analyzing effluents from a metal plating factory (US EPA, 2009) and a textile factory (Clara et al., 2008); no information is available about whether such industrial practice has been discontinued.

Emissions: C_4–C_{14} PFCAs, mainly PFNA, PFUnA and PFTrA, linear or isopropyl isomers

Historical and ongoing use of short-chain PFCAs and derivatives.

Production: C_4–C_7 perfluoroalkane carbonyl fluorides (PACFs, $C_nF_{2n+1}COF$, n = 3–6), the raw materials used for production of the corresponding short-chain PFCAs or their derivatives, were already produced or imported in the United States (US) in the 1980s or even earlier in amounts exceeding 4.54 t/yr (US EPA, 2013; data on production/import volumes in the US are listed in Table 2 in Wang et al., 2014b), principally through electrochemical fluorination (ECF).

Use: Among C_4–C_7 PFCAs, some limited information on the historical and current use is available only for perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA) and their derivatives. PFBA was previously produced by 3M for use in photographic films, which ceased in 1998 due to decreasing customer demand (3M, 2008). After 2000, production of perfluorobutane carbonyl fluoride (PFBF) was revived by the same company (US EPA, 2013); however, it is unknown whether PFBF has been used, as previously, to produce PFBA and its derivatives. In addition, Miteni has commercialized PFBA and its methyl ester (CAS No. 356-24-1) for unknown use (Miteni, 2013). The historical uses of PFHxA and its derivatives remain unidentified. Some fluoropolymer or fluoroelastomer producers, however, may have started to use PFHxA-derivatives to replace PFOA and PFNA as processing aids in the polymerization process (Iwai, 2011; Matsuoka and Watanabe, 2010), as recently observed at one production site in France (Dauchy et al., 2012). In addition, Miteni has marketed PFHxA, its ammonium salt (APFHx), its methyl ester (CAS No. 424-18-0) and $C_5F_{11}CONH(CH_2)_3Si(OCH_3)_3$ (CAS No. 154380-34-4, used in surface treatment of glasses, natural stones, metals, wood, cellulose, cotton, leather and ceramics) (Miteni, 2013). The current production of PFHxA and its derivatives may involve producers using oxidation of fluorotelomer raw materials (Kishikawa et al., 2009) and ECF (Miteni, 2013).

Emissions: C_4–C_7 PFCAs, linear and branched isomers

Historical use of PFDS.

Production: Perfluorodecane sulfonyl fluoride (PDSF) was also produced/imported by 3M in the US in the 1980s or even earlier (US EPA, 2013). In 2002, 3M ceased its global production of PDSF-based chemistry (3M, 2000a).

Use: PDSF has likely only been used as an intermediate to produce the ammonium salt of perfluorodecane sulfonic acid (NH_4-PFDS), which was used as a wetting and leveling agent in consumer products such as floor polishes (3M, 2000b).

Relevance to PFCA emissions: During ECF of decanesulfonyl fluoride to PDSF, some perfluoroalkyl chains are likely unintentionally reacted to PACFs through the electrochemical oxidation and are subsequently hydrolyzed to PFCAs by moist air or in the subsequent reactions, as occurred during the ECF of octanesulfonyl fluoride to POSF (Gramstad and Haszeldine, 1957). Thus, PFCAs and derivatives were likely present as impurities in NH_4-PFDS-containing consumer products and may have been released into the environment during the product life-cycle.

Emissions: PFSAs, mainly PFDS, C_4–C_{14} PFCAs, linear and branched isomers

Historical and ongoing use of PFPAs.

Production and use: Back in 1972, Hoechst (later Clariant, then Archroma) patented a method to produce perfluoroalkyl phosphonic and phosphinic acids (PFPAs and PFPiAs) from perfluoroalkyl iodides (PFAIs) (Heinz and Dieter, 1974). Since then, blends of PFPAs and PFPiAs with six and more perfluoroalkyl carbons have been marketed as surfactants as possible wetting and leveling agents in coatings and floor finishes (Mason, 2011). In addition, to prevent the formation of foam in the spray tank, several major pesticide manufacturers have tested and patented (or applied for patents for) the use of PFPAs and PFPiAs as anti-foaming agents in solutions (Heid, 1975). Blends of PFPAs and PFPiAs with six and more perfluoroalkyl carbons, with CAS Nos. 68412-68-0 and 68412-69-1, respectively, have been reported to have had annual production volumes in the US in the range of tonnes to hundreds of tonnes in 1998 and 2002 (Howard and Muir, 2010).

Relevance to PFCA emissions: Since PFPAs are derived from PFAIs (Buck et al., 2011), PFCAs occurring in PFPAs can (partly) be impurities from the production of the parent compounds (PFAIs) (Larsen et al., 2006; Telomer Research Program, 2003).

Emissions: PFPAs, PFCAs, linear isomers

Sources where PFCAs are emitted as degradation products (indirect sources)

Atmospheric degradation of HFCs and HFEs.

Production: In the early 1990s, due to near-zero ozone depletion potential, hydrofluorocarbons (HFCs) started to be manufactured as replacements of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which contribute to the depletion of stratospheric ozone (Tsai, 2005a). However, due to their significant global warming potential, several HFCs are considered to be target greenhouse gases under the United Nations Framework Convention on Climate Change (UNFCCC, 2013). Hence, hydrofluoroethers (HFEs) have been developed to replace HFCs since the middle 1990s (Tsai, 2005b, 2009). A list of HFCs and HFEs that can degrade into PFCAs via atmospheric reactions, commercial name, if available, CAS numbers, and structure is compiled in Table 3 in Wang et al. (2014b). The amounts of these HFCs produced and emitted remain unknown, except that $CF_3(CF_2)_5CH_2CH_3$ has been registered under REACH with annual production volumes of between one and ten tonnes (ECHA, 2014). Among HFEs, HFE-7100, 7200/8200 and 7500 have been manufactured/imported in the US for more than a decade (US EPA, 2013; data on production/import volumes in the US are listed in Table 4 in Wang et al., 2014b). Recently, HFE-7500 has also been registered under REACH with annual production volumes of more than ten tonnes (ECHA, 2014).

Use: To date, some of the HFCs mentioned above that may transform to PFCAs in the atmosphere have been commercialized as heat-transfer fluids, cleaning agents or solvents by (at least) Asahi in Japan and Fuxin Hengtong in China (Asahi, 2014; Fuxin, 2014). HFE-7100, 7200/8200 and 7500 are marketed by 3M as heat transfer fluids and solvents for cleaning and coating (ECHA, 2014; Newsted et al., 2002; Sekiya et al., 2006; Tsai, 2005b;Wolf, 2011). In addition, HFE-7100 has been notified as a solvent for the manufacture of cosmetic products, including personal care products (skin, hair and bath care), fragrances and room scents in Australia and as CF-61 for cosmetic applications in the EU (NICNAS, 2006).

Relevance to PFCA emissions: Recent empirical and theoretical studies show that those HFCs that are with the $–CHF_2$, $–CH_2F$, $–CH_3$ or $–C_2H_5$ moiety at the end of a perfluoroalkyl chain and HFE-7100, 7200/8200 and 7500 may undergo a series of atmospheric reactions and partially form C_4–C_{11} PFCAs (mechanisms of atmospheric formation of PFCAs from HFCs and HFEs were reviewed by Young and Mabury (2010) and Wang et al. (2014b); measured rate constants for reaction with OH radicals at 298 K, if available, are compiled in Table 3 in Wang et al. (2014b)). Three reasons prevent estimating the releases of PFCAs from the atmospheric degradation: [i] Most of the studies on the OH radical-mediated transformation of the HFCs and HFEs mentioned above were made for homologues with short perfluoroalkyl chains and PFCA yields were not determined in these studies; it is unknown how changes in the perfluoroalkyl chain length influence the reaction kinetics and PFCA yields. [ii] All studies regarding HFCs and HFEs discussed above and in Wang et al. (2014b) were conducted in the laboratory with zero or low levels of NOx. In reality, when NOx species are abundant, they may compete with those reactions that lead to formation of PFCAs, and thus lower the actual yields of PFCA in the environment. However, the adjustment factor remains unknown. [iii] There has been only limited information on the historical and current global production and emissions of relevant HFCs and HFEs.

Emissions: HFCs, HFEs, C_4–C_{11} PFCAs, linear and branched isomers

Inadequate thermolysis of fluoropolymers such as PTFE.

Relevance to PFCA emissions: Another poorly-studied indirect source of PFCAs is the thermolysis of fluoropolymers such as PTFE. At appropriate temperatures (250–600 °C), fluoropolymers such as PTFE are capable of degrading predominantly to various monomers (C_2F_4, C_3F_6, C_4F_8, etc.) (Ellis et al., 2001; Lewis and Naylor, 1947; Simon and Kaminsky, 1998; Sölch, 2012), which can react with air and partially form PFCAs of different chain lengths (Ellis et al., 2001; Sölch, 2012). Significant releases of PFCAs during cooking with PTFE-coated pans are unlikely at normal cooking temperatures (<230 °C; Coenders, 1992) (Imbalzano, 1991). In addition, the generation of C1–C18 PFCAs was observed in the thermolysis of Nafion N117 (a membrane consisting of a PTFE backbone with perfluoroalkyl ether pendant chains terminating in sulfonic acid groups) below 600 °C (M. Feng et al., 2015). It is unknown, however, to what extent these thermally induced transformations of fluoropolymers may occur in municipal waste incinerators, where (i) flue gases reach higher temperatures (>850 °C, according to the EU Directive 2000/76/EC) and may result in different degradation products (García et al., 2007); (ii) other substances coexist and may interfere with the thermolysis of fluoropolymers (e.g., thermolysis of PTFE is inhibited by a hydrogen or chlorine atmosphere in contrast to steam, oxygen or sulfur dioxide, which accelerate decomposition; Simon and Kaminsky, 1998); and (iii) technologies such as activated carbon injection (ACI) coupled with baghouse filtration (BF) may be installed to remove dioxin or mercury and may also trap PFCAs (EU Commission, 2006). In 2005, the US EPA and four major fluoropolymer and fluoroelastomer producers (Asahi, Daikin, Dyneon and DuPont) reached an enforceable consent agreement (ECA) for a laboratory-scale incineration testing on fluoropolymers (US EPA, 2005). Results from an industry-sponsored study suggested that waste incineration of fluoropolymers does not emit detectable levels of PFOA under conditions representative of typical municipal waste combustor operations in the US (~1000 °C; Taylor, 2009). To date, the final report of the ECA has not yet been published by the US EPA. In particular, it is unclear if and to what extent such emissions of PFCAs from inadequate thermolysis of fluoropolymers may occur in developing and transition countries, where wastes are often not properly incinerated to such high temperatures due to a lack of adequate waste incineration facilities. Furthermore, it is unclear to what extent PFCAs are formed and released at industrial recycling sites where fluoropolymer wastes are thermally decomposed to recycle monomers such as C_2F_4 and C_3F_6 (e.g., in mid-2012, Dyneon started construction of a pilot plant for the thermolysis of PTFE wastes (500 t/yr) at its Gendorf site in Germany; Dyneon, 2013).

Emissions: PFCAs, linear isomers

Biodegradation of side-chain fluorinated polymers.

Relevance to PFCA emissions: The thermolysis of one type of side-chain fluorinated polymer, i.e., fluorotelomer-based acrylate polymer, has been studied and no formation of PFOA at temperatures between 600 and 1000

°C was observed (Yamada et al., 2005). Although thermolysis of side-chain fluorinated polymers is possibly an unimportant source of PFCAs, it has been reported that some side-chain fluorinated polymers (such as fluorotelomer-based acrylate polymer and urethane polymer) might degrade biotically to corresponding PFCA precursors (such as FTOHs) in aerobic soils (Russell et al., 2008, 2010a; Washington et al., 2009). A reliable estimation of the amount of PFCAs from (bio)degradation of side-chain fluorinated polymers is not yet possible, mainly because there is high uncertainty in the degradation half-lives (ranging from decades up to millennia) (Russell et al., 2010b; Washington et al., 2010), which is mostly due to the significant challenges associated with measuring such low degradation rate constants. It is also unknown to what extent laboratory conditions represent the real environment (in terms of temperature, bioavailability of polymers, microbial community, co-existence of other substances, etc.). In addition, many other types of side-chain fluorinated polymers than the ones tested are produced (Buck et al., 2011). It is unknown how their different physical and physicochemical properties would influence the bioavailability and thus the biodegradability.

Emissions: non-polymeric POSF- and FT-based derivatives, PFCAs, PFSAs, linear and branched isomers

Sources where PFCAs are emitted as impurities/residuals and degradation products (direct and indirect sources)

Historical and ongoing use of PBSF- and PHxSF-based substances.

Production and use: The shorter-chain homologues of POSF and their derivatives were produced/imported by 3M in the US in the 1980s or even earlier (US EPA, 2013; data on production/import volumes in the US are listed in Table 2 in Wang et al., 2014b). Among these chemicals, information is available only on perfluorobutane sulfonyl fluoride (PBSF)- and perfluorohexane sulfonyl fluoride (PHxSF)-based derivatives. The historical use of PBSF-based derivatives remains unknown. Since 2002, they have been developed as replacements of their C_8 homologues in various industrial branches and are now produced in the US, Germany, Italy and China (Buck et al., 2011; Huang et al., 2010; Miteni, 2013; Möller et al., 2010; Wang et al., 2013). Information on production and use of many PBSF-based derivatives (including perfluorobutane sulfonic acid (PFBS), its salts and various PBSF-based side-chain fluorinated polymers) is provided in Wang et al. (2013). Recently, a new tetrabutyl phosphonium salt of

PFBS ($(C_4H_9)_4$P-PFBS, CAS No. 220689-12-3) has been identified, which is used as an anti-static additive in plastics (ECHA, 2014; US EPA, 2012). In the US it has been produced by DuPont under the trade name Zonyl® FASP-1 (formerly FC-1) with a production volume of between 11.3 and 227 tonnes in 2005 (DuPont, 2007; US EPA, 2013), whereas in the EU it has been registered by Miteni under REACH with annual production volumes of more than 1 tonne per year (ECHA, 2014).

The production of PHxSF-based derivatives started in the 1960s, mainly for use in aqueous film-forming foams (AFFFs) that are used for fire-fighting purposes and in specific postmarket carpet treatment products (Olsen et al., 2003; Place and Field, 2012; Sundström et al., 2012; US EPA, 2013). In 2000–2002, 3M ceased its global production of PHxSF-based products parallel to the phase-out of POSF-based products (3M, 2000a). However, some manufacturers in China and Italy have recently initiated the production of PHxSF-based products for use in, for example, textile finishing agents (Huang et al., 2010; Miteni, 2013), in unknown amounts.

Relevance to PFCA emissions: Because the production processes for PBSF/PHxSF (through ECF) are similar to those of POSF-based products (Gramstad and Haszeldine, 1957), it is expected that PFCAs are formed as impurities during the production of PBSF/PFHxSF; part of the PFCA impurities can react with the reactants added in the subsequent reactions of PBSF/PHxSF and form derivatives such as perfluoroalkane carboxamides ($C_nF_{2n+1}CONH(R)$, R=CH_3 or C_2H_5) (Jackson and Mabury, 2013). Similar to their C_8 homologues, these PFCA impurities can be released during the life-cycle of PBSF/PHxSF-based products. In addition, PFCA derivatives (Jackson et al., 2013; Seacat, 2004) and PBSF/PHxSF-based substances (Martin et al., 2010) can degrade into PFCAs in the environment and biota. Therefore, PBSF/PHxSF-based products act as direct and indirect sources of PFCAs to the environment.

Emissions: PBSF- and PHxSF-based derivatives, PFSAs, short-chain PFCAs, linear and branched isomers

Historical and ongoing use of SFAs.

Production and use: Semifluorinated alkanes [SFAs, $F(CF_2)_n(CH_2)_mH$, often denoted as F_nH_m] act as an additional source of PFCAs. The short-chain SFAs (with chain lengths up to 14 carbons) are used in various medical applications (as components of artificial blood, in drug delivery and in ophthalmology as so-called endotamponades in complicated vitreoretinal surgery; Broniatowski and Dynarowicz-Łątka, 2008), whereas the long-chain SFAs (≥22 carbons) have been applied in ski waxes since the 1990s (Buck et al., 2011; Freberg et al., 2010; Plassmann and Berger, 2010; Plassmann et al., 2011). Various short-chain SFAs (e.g., F_6H_6, CAS No. 69125-80-0; F_6H_8, CAS No. 133331-77-8; F_8H_8, CAS No. 6145-05-7) have been produced by (at least) Fluoron in Germany and Fuxin Hengtong in China (Fluoron, 2014; Fuxin, 2014), whereas there is no information on production of long-chain homologues.

Relevance to PFCA emissions: Recently, PFCAs were detected in SFA-containing ski waxes (Plassmann and Berger, 2010). Since SFAs are derived from perfluoroalkyl iodides (PFAIs) (Buck et al., 2011; Krafft and Riess, 2009), PFCAs occurring in SFAs can (partly) be impurities from the production of the parent compounds (PFAIs) (Larsen et al., 2006; Telomer Research Program, 2003). In addition, SFAs might degrade into PFCAs under certain conditions based on empirical and theoretical studies (Nielsen et al., 1994; Hurley et al., 2006). In general, however, formation of PFCAs from SFAs still needs to be proven by further research. It is currently not possible to estimate PFCA emissions from SFAs, because there is no information on the historical production of SFAs, in addition to their uncertain degradation. It is expected, however, that PFCA emissions resulting from the life-cycle of SFA-containing ski waxes are of minor global importance because, due to their high cost, these ski waxes are sold in relatively low amounts.

Emissions: SFAs, PFCAs, linear isomers

Historical and ongoing use of n:1 FT-based substances.

Production and use: 3M produced 7:1 FTOH ($C_7F_{15}CH_2OH$, CAS No. 307-30-2), which was used to produce (at least) two acrylate and methacrylate monomers (L-9186, $C_7F_{15}CH_2OC(O)CH=CH_2$, CAS No. 307-98-2; L-9187, $C_7F_{15}CH_2OC(O)C(CH_3)=CH_2$, CAS No. 3934-23-4), as indicated in Chapter 27 of Banks et al. (1994). The polymers based on these acrylic ester monomers were likely used as oil- and water-repellent finishes for textiles (Bryce, 1964; Holzapfel, 1966; Scherer, 1970) and as coatings in electronic applications to provide a humidity barrier on printed circuit boards and to secure silicone oil on precision bearings (3M, 2000c, 2003). In 2000–2002, 3M ceased its global production of 7:1 FTOH along with its phase-out of other long-chain PFASs (3M, 2000a, 2003). Recently, Miteni started to produce the shorter-chain homologues, 3:1 and 5:1 FTOHs, $C_nF_{2n+1}CH_2OH$, n = 3, 5, CAS Nos. 375-01-9 and 423-46-1, which may have been used as building blocks for side-chain fluorinated polymers in unknown amounts (Miteni, 2013). These n:1 FTOHs are likely produced through catalytic hydrogenation of the corresponding PFCAs (e.g., $C_5F_{13}COOH$ ❾ $C_5F_{13}CH_2OH$) (Husted and Albrecht, 1954).

Relevance to PFCA emissions: Due to likely incomplete reactions from PFCAs to n:1 FTOHs, some PFCAs may remain as unreacted residuals in these n:1 FTOHs. In addition, studies have shown that n:1 FTOHs can undergo OH-radical-mediated oxidation and form the corresponding aldehydes (Hurley et al., 2004), $C_nF_{2n+1}CHO$, which can be further oxidized and form PFCAs (Hurley et al., 2006). The rate constant for the reaction of 3:1 FTOH with OH radicals has been measured in laboratory experiments; it has been suggested that this rate constant is largely independent of the perfluoroalkyl chain length and, therefore, is also valid for other n:1 FTOHs (Bravo et al., 2010; Hurley et al., 2004). Note that the starting materials of n:1 FTOHs, which are likely to be PFCAs, are produced by electrochemical fluorination; therefore, n:1 FTOHs and PFCA residuals therein consist of both linear and branched isomers (Missio and Bertola, 2010).

Emissions: n:1 FT-based derivatives, n:1 FTOHs, PFCAs, linear and branched isomers

Historical and ongoing use of PFPiAs.

Production and use: Historical use of blends of PFPiAs with six and more perfluoroalkyl carbons is the same as the historical use of PFPA mixtures mentioned above; therefore, it is not repeated here. In addition, a manufacturer has recently developed technologies based on ECF to produce C_4/C_4 PFPiA and derivatives as replacements of PFOA and PFOS (Welz-Biermann et al., 2007). However, it is unknown to what extent this replacement has been used in the actual practice.

Relevance to PFCA emissions: Similarly to PFPAs, PFPiAs with six and more perfluoroalkyl carbons are derived from perfluoroalkyl iodides (PFAIs) (Buck et al., 2011), PFCAs occurring in such PFPiAs can (partly) be impurities from the production of the parent compounds (PFAIs) (Larsen et al., 2006; Telomer Research Program, 2003). In addition, PFPiAs can undergo hydrolysis under certain conditions and form PFPAs and $C_nF_{2n+1}H$, which can partially further transform and form relevant PFCAs (Mahmood and Shreeve, 1986); this is likely in line with the observation of biodegradation of PFPiAs to PFPAs in rainbow trouts by Lee et al. (2012).

Emissions: PFPAs, PFCAs, linear isomers

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This document has been prepared by the OECD/UNEP Global PFC Group with the aim of raising awareness of perfluorinated chemicals in governments, the private sector and civil society. This report works towards establishing a global emission inventory for per- and polyfluoroalkyl substances (PFASs) and uses perfluoroalkyl carboxylic acids (PFCAs) as a reference to present an overall picture of global and regional emissions of PFASs and other related fluorinated substances. This work supports efforts in the framework of the Strategic Approach to International Chemicals Management (SAICM) to improve information sharing at a global level on these chemistries.

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