Environment International 60 (2013) 242–248

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors

Zhanyun Wang [a], Ian T. Cousins [b], Martin Scheringer [a,*], Konrad Hungerbühler [a]

[a] Institute for Chemical and Bioengineering, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland
[b] Department of Applied Environmental Science (ITM), Stockholm University, SE-10691 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 30 May 2013
Accepted 27 August 2013
Available online 26 October 2013

Keywords:
Perfluorinated alkyl substances
Perfluorinated carboxylic acids
Perfluorinated sulfonic acids
Fluorinated alternatives

ABSTRACT

Since 2000 there has been an on-going industrial transition to replace long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their precursors. To date, information on these replacements including their chemical identities, however, has not been published or made easily accessible to the public, hampering risk assessment and management of these chemicals. Here we review information on fluorinated alternatives in the public domain. We identify over 20 fluorinated substances that are applied in [i] fluoropolymer manufacture, [ii] surface treatment of textile, leather and carpets, [iii] surface treatment of food contact materials, [iv] metal plating, [v] fire-fighting foams, and [vi] other commercial and consumer products. We summarize current knowledge on their environmental releases, persistence, and exposure of biota and humans. Based on the limited information available, it is unclear whether fluorinated alternatives are safe for humans and the environment. We identify three major data gaps that must be filled to perform meaningful risk assessments and recommend generation of the missing data through cooperation among all stakeholders (industry, regulators, academic scientists and the public).

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Since 2000 long-chain perfluoroalkyl carboxylic acids [PFCAs, $C_nF_{2n+1}COOH$, $n \geq 7$], perfluoroalkane sulfonic acids [PFSAs, $C_nF_{2n+1}SO_3H$, $n \geq 6$] and their potential precursors (Buck et al., 2011), have attracted attention as global contaminants. Long-chain PFCAs and PFSAs are problematic because they are highly persistent (Frömel and Knepper, 2010; Parsons et al., 2008), bioaccumulative (Conder et al., 2008) and have been detected ubiquitously in the abiotic environment (Rayne and Forest, 2009), biota (Giesy et al., 2001), food items (Clarke and Smith, 2011) and humans (Vestergren and Cousins, 2009). As a result perfluorooctane sulfonate (PFOS) and related substances based on perfluorooctane sulfonyl fluoride (POSF) were listed under Annex B (restriction of production and use) of the Stockholm Convention in 2009. In 2012 C_{11}–C_{14} PFCAs were identified as vPvB chemicals (very persistent and very bioaccumulative), and were included in the Candidate List of Substances of Very High Concern under the European chemicals regulation, REACH (ECHA, 2013a). In 2013, also perfluorooctanoic acid (PFOA) and ammonium perfluorooctanoate (APFO) were listed in the Candidate List of Substances of Very High Concern ECHA (2013a).

Driven by concerns about their undesired impacts on humans and the environment, there has been a trend among global producers to replace long-chain PFCAs, PFSAs and their potential precursors with their shorter-chain homologues (Ritter, 2010) or other types of (non)fluorinated chemicals (UNEP, 2012) (these replacements are referred to as *alternatives* in the following). These industry initiatives began in 2000 when 3M announced a global phase-out of its products based on C_6, C_8 and C_{10} chemistry and replaced them with products based on C_4 chemistry such as perfluorobutane sulfonic acid (PFBS) (3M, 2000; Ritter, 2010). In 2006, eight major producers of PFCAs, fluoropolymers and fluorotelomer substances joined the US EPA 2010/15 PFOA Stewardship Program (US EPA, 2006) to work towards the elimination of long-chain PFCAs and their potential precursors by 2015.

In this study we address the question: are the fluorinated alternatives to long-chain per- and polyfluoroalkyl products safe for humans and the environment? Recent experience with replacements of other chemicals has shown a "lock-in" problem, i.e. one chemical from a group of structurally similar chemicals was removed from the market and replaced by other chemicals from the same group, but the basic problem was not really solved (Goldstein et al., 2013; Strempel et al., 2012). For example, polychlorinated biphenyls (PCBs) were replaced by short-chain chlorinated paraffins, which are currently being evaluated under the Stockholm Convention.

To answer this question, information regarding alternatives (including chemical structures, physicochemical properties, (bio)degradability,

* Corresponding author. Tel.: +41 44 632 30 62.
E-mail address: martin.scheringer@chem.ethz.ch (M. Scheringer).

0160-4120/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envint.2013.08.021

bioaccumulation potential, (eco)toxicity, production and releases, and environmental and human exposure) is needed. However, due to concerns of business confidentiality, most of the information required to assess the safety of alternatives has not been published or made easily accessible to the public. This lack of data makes it unclear whether alternatives have been fully tested before they are commercialized. It also inhibits scientists and civil society organizations, as an essential supplement to regulators and industry, from proactively minimizing the risks associated with alternatives by conducting monitoring activities and research into the environmental fate and potential adverse effects of alternatives (Goldstein et al., 2013).

Here, we review information on fluorinated alternatives in the public domain in two respects: (i) to identify which chemicals are (possibly) applied in various industry branches or consumer products; and (ii) to summarize current knowledge on their environmental releases, persistence, and exposure of biota and humans. With the information provided, we aim to give an overview of the on-going transitions to fluorinated alternatives and of the potential environmental and human exposure to these chemicals. Due to space limitations, we do not address potential adverse effects of these chemicals. Related information, however, can be found in the following references: Asahi (2006), Borg and Hakansson (2012), ECHA (2013b), EFSA (2010, 2011a, 2011b), Gordon (2011), Hagenaars et al. (2011), Lau et al. (2007), Nørgaard et al. (2010), and Wang et al. (2013a). In addition, it should be noted that several types of nonfluorinated substances are also available as alternatives (e.g., dendrimers, siloxanes and silicone polymers) (Poulsen et al., 2005; UNEP, 2012), but may not perform as well as fluorinated substances, particularly in situations where extremely low surface tension and/or durable oil- and water-repellence is needed (Holt, 2011). For information on nonfluorinated alternatives, we recommend readers to consult other studies that specifically address these substances (e.g., Ulaszewska et al., 2012; Wang et al., 2013b).

2. Production and use of fluorinated alternatives

Here, we summarize the publicly accessible information on the production and use of fluorinated alternatives in different industrial branches (for examples, see Fig. 1). Other fluorinated alternatives might also be on the market; their identities, however, could not be identified.

2.1. Fluoropolymer manufacture

Historically, almost all producers applied ammonium or sodium perfluorooctanoate (APFO and NaPFO) as processing aids in the (emulsion) polymerization of polytetrafluoroethylene (PTFE), perfluorinated ethylene-propylene copolymer (FEP), perfluoroalkoxy polymer (PFA) and certain fluoroelastomers; and applied ammonium perfluorononanoate (APFN) in the emulsion polymerization of polyvinylidene fluoride (PVDF) (Prevedouros et al., 2006). However, during the recent transition, most of the producers have developed their own alternatives. Known commercialized fluorinated alternatives are functionalized perfluoropolyethers (PFPEs), including (i) ADONA from 3M/Dyneon ($CF_3OCF_2CF_2CF_2OCHFCF_2COO^-NH_4^+$, CAS No. 958445-44-8) (Gordon, 2011); (ii) GenX from DuPont ($CF_3CF_2CF_2OCF(CF_3)COO^-NH_4^+$, CAS No. 62037-80-3) (DuPont, 2010); (iii) cyclic or polymeric functionalized PFPEs from Solvay for its PTFE and PVDF manufacture (Marchionni et al., 2010; Pieri et al., 2011; Spada and Kent, 2011) (e.g., a complex process mixture, C_3F_6ClO-$[CF_2CF(CF_3)O]_n$-$[CF(CF_3)O]_m$-CF_2COOH, n = 1–4, m = 0–2, with a molecular weight in the range of 500 to 650 Da has been registered at the European Food Safety Authority (EFSA), CAS No. 329238-24-6 (EFSA, 2010)); (iv) $C_2F_5OC_2F_4OCF_2COO^-NH_4^+$ (CAS No. 908020-52-0) from Asahi (EFSA, 2011a); and (v) another functionalized PFPE from Chenguang in China (its structure and CAS No. remains unrevealed) (Xie et al., 2010, 2011). In Europe, GenX has been registered under REACH with a production volume of 10–100 tonnes per year (ECHA, 2013b).

In addition, some producers, such as Daikin (Iwai, 2011), may have used ammonium perfluorohexanoate (APFHx) as polymerization processing aids (supported by higher levels of perfluorohexanoic acid (PFHxA) in comparison to other PFCA homologues detected in water samples from a fluoropolymer manufacturing site in France (Dauchy et al., 2012)). Finally, a Chinese producer may use 6:2 fluorotelomer carboxylic acid (6:2 FTCA, $C_6F_{13}CH_2COOH$, CAS No. 53826-12-3) as an alternative processing aid replacing perfluorooctanoic acid (PFOA) (Xu et al., 2011). No information is available on the processing aids currently used by other fluoropolymer manufacturers.

2.2. Surface treatment of textile, leather and carpets

Side-chain fluorinated polymers, which comprise non-fluorinated carbon backbones and side-chains containing a mixture of 6:2–14:2 fluorotelomer moieties ($C_nF_{2n+1}C_2H_4$−, n = 6–14) or moieties derived from POSF, were widely used in surface treatment products to impart water- and oil-resistance to textile, leather and carpets (Buck et al., 2011). A current trend is to use shorter-chain homologues to replace long-chain flurotelomer- or POSF-based derivatives on side-chains (Ritter, 2010). Since 2003, 3M has commercialized a series of surface treatment products such as Scotchguard PM-3622 (CAS No. 949581-65-1), PM-490 (CAS No. 940891-99-6) and PM-930 (CAS No. 923298-12-8) containing C_4 ($C_4F_9SO_2$−) side-chain fluorinated polymers derived from perfluorobutane sulfonyl fluoride (PBSF) (Renner, 2006). Fluorotelomer manufacturers have developed products based on highly purified fluorotelomer raw materials (mostly 6:2, see examples on the OECD Portal on Perfluorinated Chemicals (OECD, 2013)), including copolymers derived from 6:2 fluorotelomers and organosiloxane (Unidyne® TG-5521 developed by Daikin and Dow-Corning (Dow Corning, 2007)). Miteni has commercialized polyfluoroalkyl alcohols (3:1 and 5:1 FTOHs, $C_nF_{2n+1}CH_2OH$, n = 3, 5, CAS No. 375-01-9 and 423-46-1) that can be used as building blocks for side-chain fluorinated polymers (Miteni, 2012) and Solvay has applied PFPEs such as Fluorolink® as alternatives to side-chain fluorinated polymers for textile surface treatment (Solvay, 2011).

Some producers in China and Italy have initiated the production of perfluorohexane sulfonyl fluoride (PHxSF, $C_6F_{13}SO_2F$)-based derivatives as alternatives in surface treatment products (China MEP, 2012; Miteni, 2012), but these can degrade into perfluorohexane sulfonate (PFHxS) in the environment (D'eon et al., 2006; Martin et al., 2006) and are thus considered as long-chain PFSA precursors (Buck et al., 2011). In China, it is estimated that in the next 5–10 years production of surface treatment products containing PHxSF- or PBSF-derivatives will reach more than 1000 tonnes per year (Huang et al., 2010).

2.3. Surface treatment of food contact materials

After 3M ceased its production of POSF-based side-chain fluorinated polymers (e.g., CAS No. 92265-81-1) and phosphate diesters (SAmPAP, e.g., FC 807, CAS No. 30381-98-7) that were used in food contact materials (3M, 2000), there is no evidence that PBSF-based derivatives are used as alternatives. Fluorotelomer manufacturers have developed products based on 6:2 fluorotelomers to replace their earlier products [both side-chain fluorinated polymers and phosphate diesters (diPAPs)] that were based on longer-chain fluorotelomer derivatives (Loi et al., 2013). For example, since 2008, seven 6:2 fluorotelomer-based side-chain fluorinated polymers have been registered in the Inventory of Effective Food Contact Substance (FCS) Notifications of the United States Food and Drug Administration; they are CAS No. 1345817-52-8 by Asahi, CAS No. 1012783-70-8, 1158951-85-9, and 1206450-09-0 by Daikin, and CAS No. 1071022-25-7, 357624-15-8, and 1071022-26-8 by DuPont (US FDA, 2013a). In addition, products based on PFPEs such as Solvera® from Solvay (chemical structures are likely similar to $HO(O)(OH)PO$-$(CH_2CH_2O)_n$-CH_2CF_2-

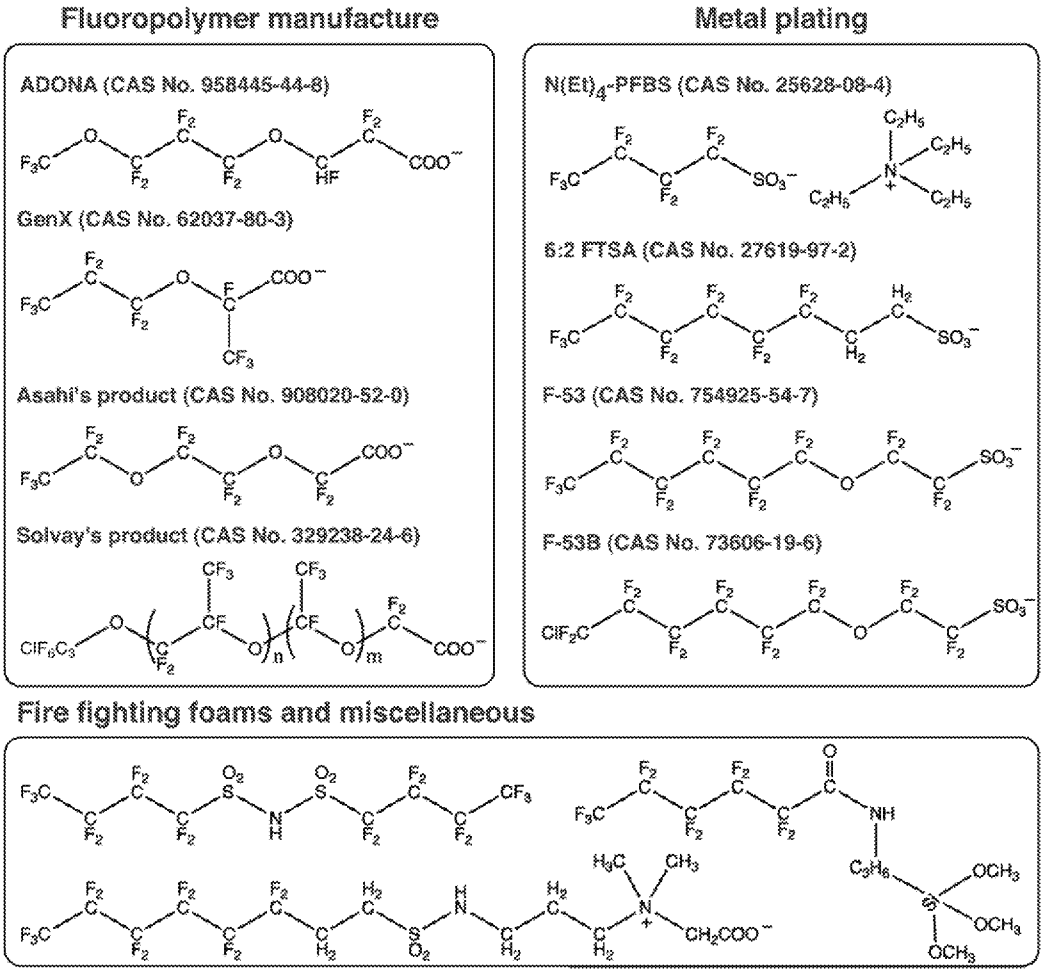

Fig. 1. Examples of fluorinated alternatives identified in different industry branches.

$(OCF_2)_p$-$(OCF_2CF_2)_q$-OCF_2CH_2-$(OCH_2CH_2)_n$-OP(OH)(O)(OH) (Trier et al., 2011)) have been used as alternatives (Solvay, 2011).

2.4. Metal (chromium) plating

Historically, salts of PFOS have been used as wetting agents and mist-suppressing agents in decorative plating and non-decorative hard plating. Recent technology development using chromium-III instead of chromium-VI has made PFOS use in decorative chrome plating obsolete. Chromium-III, however, cannot be used for hard chrome plating (UNEP, 2012). In Europe, salts of 6:2 fluorotelomer sulfonic acid (6:2 FTSA, $C_6F_{13}C_2H_4SO_3H$) are applied as alternatives to PFOS, however, they can only partly be applied in decorative plating due to slightly higher surface tension compared to PFOS (UNEP, 2012). In addition, $N(Et)_4$-PFBS (CAS No. 25628-08-4) is registered for metal plating under REACH with a production volume of 1–10 tonnes per annum (ECHA, 2013b). Also, a German producer reported a production of 20–50 tonnes of PFBS-based $[C_4F_9SO_2N(CH_3)CH_2CH_2O]_2P(O)OH$ (CAS No. 120945-47-3) in 2003, which is used as defoamer in the electroplating industry (OECD, 2005). In China, several producers have used F-53 (salts of $C_6F_{13}OCF_2CF_2SO_3H$, CAS No. 754925-54-7) and F-53B (Cl-$C_6F_{12}OCF_2CF_2SO_3K$, CAS No. 73606-19-6), likely derived from fluorotelomer raw materials, since the late 1970s (Huang et al., 2010; UNEP, 2012). It is estimated that about 20–30 tonnes of F-53 and F-53B were used in 2009 in the metal plating industry (both decorative and hard metal plating) in China (Huang et al., 2010).

2.5. Fire-fighting foams

In the past, various PFCA-, PFSA-, and fluorotelomer-based derivatives were added (i) as film formers in aqueous film forming foams (AFFFs) and film forming fluoroproteins (FFFPs), (ii) as fuel repellents in fluoroprotein foams (FPs), and (iii) as foam stabilizers in FFFPs and alcohol-resistant aqueous film-forming foams (AR-AFFFs) (Backe et al., 2013; Kleiner and Jho, 2009; Place and Field, 2012). In 2002 3M, which was the only producer, ceased its global production of POSF-based AFFFs (Place and Field, 2012); and thereafter has developed a fire suppression agent based on a gaseous fluorinated ketone $[CF_3CF_2C(O)CF(CF_3)_2$, CAS No. 756-13-8] (UNEP, 2012). Also, AFFFs based on pure 6:2 fluorotelomers are under development to replace the early generations that are based on a mixture of predominantly 6:2 and 8:2 fluorotelomers (Klein, 2012; Kleiner and Jho, 2009). For example, DuPont commercialized Forafac® 1157 that is based on 6:2 fluorotelomer sulfonamide alkylbetaine [6:2 FTAB, $C_6F_{13}C_2H_4SO_2$-$NHC_3H_6N^+(CH_3)_2CH_2COO^-$] (Hagenaars et al., 2011; Moe et al., 2012; Pabon and Corpart, 2002) and Forafac® 1183 that is based on 6:2 fluorotelomer sulfonamide aminoxide $[C_6F_{13}C_2H_4SO_2NH$ $C_3H_6N(O)(CH_3)_2$, CAS No. 80475-32-7] (Jensen et al., 2008). In addition, a Chinese institute has developed an AFFF formulation based

on a PFBS derivative [$C_4F_9SO_2NH(CH_2)_3NH(CH_3)_2^+$] (Yang et al., 2009; Zhao, 2012), its commercialization, however, is unclear.

2.6. Miscellaneous

In addition to those mentioned above, we have identified the following fluorinated alternatives and their potential uses: (i) The potassium salt of PFBS (CAS No. 29420-49-3) is marketed as a flame retardant for polycarbonate resins; 30–50 tonnes of it were produced in 2003 in Germany (Hubei Hengxin, 2013; Miteni, 2012; Mitsubishi, 2013; OECD, 2005; Wuhan Chemical, 2013). (ii) The imide salt of PFBS [$(C_4F_9SO_2)_2NH$, CAS No. 39847-39-7] is marketed as a surfactant, acid catalyst, and as a raw material for ionic liquids (Mitsubishi, 2013). (iii) A PFHxA-derivative [$CF_3(CF_2)_4CONH(CH_2)_3Si(OCH_3)_3$, CAS No. 154380-34-4] is marketed as a surface treatment for glasses, natural stones, metals, wood, cellulose, cotton, leather and ceramics (Miteni, 2012). (iv) In Europe, Dow Corning registered a copolymer comprising 6:2 fluorotelomers and siloxane ($C_6F_{13}CH_2CH_2Si(OCH_3)_3$, CAS No. 85857-16-5) under REACH; its intended use is unknown (ECHA, 2013b). (v) Nanofilm spray products based on polysiloxanes with 6:2 fluorotelomers in (some of) the side-chains are marketed for coatings of nonabsorbing floor materials (Nørgaard et al., 2010). (vi) In the US DuPont produced $CF_2{=}CF\text{-}OCF_2CF(CF_3)CF_2CF_2SO_2F$ (CAS No. 16090-14-5) in an amount larger than 11.4 tonnes in 2011 (US EPA, 2012), which is likely used as a monomer for a copolymer used in polymer electrolyte fuel cells (Uematsu et al., 2006). (vii) In the US DuPont produced $CF_3OCF(CF_3)COF$ (CAS No. 2927-83-5) in an amount larger than 11.4 tonnes in 2011 (US EPA, 2012); and its use remains unknown.

3. Environmental and human exposure to fluorinated alternatives

3.1. Environmental releases

Similarly to APFO and APFN, fluorinated alternatives applied as polymerization processing aids may enter the environment at manufacturing sites where they are produced and used to produce fluoropolymers as well as during use and disposal of fluoropolymer resins. For example, ADONA was monitored between June 2008 and November 2009 in the River Alz (Germany) downstream of wastewater effluent discharges from 3M/Dyneon's factory and was detected in all samples (range from 0.32 to 6.2 μg/l (BaLfU, 2010a)). In addition, ADONA is emitted to air through exhaust gases and then deposited to the ground nearby 3M/Dyneon's factory. The average deposition rate of ADONA to surface soil near the plant between December 2009 and May 2010 is estimated at 684 ng/(m^2 d) (BaLfU, 2010b). GenX has also been detected in river water downstream of effluent discharges from the DuPont factory in North Carolina (USA) (Strynar et al., 2012). The discharge of PFHxA from a fluoropolymer manufacturing plant in France to the receiving river is estimated at 10 t/yr (Dauchy et al., 2012).

To date, there is no information on releases during use and disposal of fluoropolymer resins that contain fluorinated alternatives; but residual levels of some fluorinated alternatives in fluoropolymer resins are reported. The residual levels of ADONA in the final sintered fluoropolymer materials and an unsintered fluoropolymer micropowder are <0.02 mg/kg and 3.3 mg/kg, respectively (EFSA, 2011b); and GenX residuals in fluoropolymer resins are below 0.2 mg/kg (DuPont, 2010).

For other fluorinated alternatives, no information regarding releases is available. However, elevated levels of PFBS and/or perfluorobutanoic acid (PFBA, an impurity in PBSF-based derivatives) in water samples from the river Rhine watershed (Lange et al., 2007; Möller et al., 2010), German coast (Ahrens et al., 2010a), Tokyo Bay (Japan) (Ahrens et al., 2010b) and Northwest Pacific Ocean (Cai et al., 2012) indicate an increasing use and release of PBSF-based derivatives and other potential precursors.

3.2. Persistence

Extensive studies have suggested that 6:2 fluorotelomer-based (Lee et al., 2010; Liu et al., 2010a, 2010b; Moe et al., 2012; Wang et al., 2011, 2012; Young and Mabury, 2010; Zhao et al., 2013) and PBSF-based alternatives (Benskin et al., 2012, 2013; D'eon et al., 2006; Martin et al., 2006; Plumlee et al., 2009) can undergo similar degradation processes (reaction with OH radicals, photolysis or biodegradation, etc.) as their higher homologues and be transformed into corresponding short-chain PFCAs and/or PFSAs (such as PFBS, PFBA or PFHxA) in the environment or biota. Similarly to 6:2 fluorotelomers, 3:1 and 5:1 FTOHs can undergo reaction with OH radicals and form short-chain PFCA homologues in air (Hurley et al., 2004; Sulbaek et al., 2006). These short-chain PFCAs and PFSAs are as persistent in the environment as their long-chain homologues.

For PFPE-based alternatives, information on degradability is scarce and often incomplete. Available information shows that ADONA is not readily biodegradable (Gordon, 2011), but starts to decompose thermally at 125 °C with completion at 175 °C, leading to formation of volatile substances (details on degradation products were not provided) (EFSA, 2011b). No hydrolysis and biodegradability of GenX was observed in tests according to the OECD test guidelines 111 (tested at pH = 4, 7, 9 at 50 °C) and 301B (tested for up to 28 days), respectively (ECHA, 2013b). In addition, an atmospheric degradation study of a non-functionalized PFPE-based product, Galden® HT70 (consisting of mainly $CF_3OCF(CF_3)CF_2OCF_2OCF_3$ with smaller amounts of $CF_3OCF(CF_3)CF_2OCF_2OCF_2OCF_3$ and longer-chain analogs) indicates that these PFPEs degrade slowly in air with a lifetime greater than 46 years (through reaction with Cl and OH radicals) and 800 years (through photolysis), respectively (Young et al., 2006).

3.3. Exposure of biota and humans

The bioaccumulation potential, in terms of serum elimination half-life, of PFBA, PFBS, PFHxA, PFHxS, PFOA and PFOS in humans and mammals has been well studied (see Table 1). In general, PFBA, PFBS and PFHxA, which can be used as alternatives to their higher homologues in some cases or occur as undesired byproducts or degradation products of PBSF- or 6:2 fluorotelomer-based alternatives, have shorter half-lives in humans and biota than their longer-chain homologues (Borg and Hakansson, 2012; Iwai, 2011; Wilhelm et al., 2010). In contrast, PFHxS has similar or even longer serum half-lives than PFOS in all tested animals (except female rats) and in humans, which makes PFHxS inappropriate as an alternative to PFOS. For other fluorinated alternatives, only two industry studies of GenX in rats and mice were found (reported to the European Chemicals Agency (ECHA)) (ECHA, 2013b); and the data reported are only sufficient to calculate an approximate range of the serum elimination half-life of GenX in rats and mice, see Table 1.

Regarding the absolute exposure levels, a recent study on the temporal trends of PFCAs and PFSAs in serum from primiparous women in Sweden between 1996 and 2010 observed a marked increase of PFBS and PFHxS over time (Glynn et al., 2012). Similar observations of an increasing PFHxS exposure trend after 2006 in the US have also been reported by Kato et al. (2011). For other fluorinated alternatives, no temporal trend data are available.

4. Major data gaps and future perspective

There is some publicly accessible information on fluorinated alternatives; it is, however, still heterogeneous among industrial branches and not sufficient for conducting realistic risk assessments. There are three major data gaps: (i) the identity of many alternatives remains unknown, particularly in those industry branches or regions that are less strictly regulated, whereas e.g. in Europe (EFSA, 2013) and the US (US FDA, 2013b) food contact material producers are obliged to submit specific safety data; (ii) for alternatives that have

Table 1
Serum elimination half-lives of PFBS, PFHxS, PFOS, PFBA, PFHxA, PFOA, GenX, and ADONA in male (M) and female (F) rats, mice, monkeys and humans. In some cases, half-life is expressed in the form of "arithmetic mean ± standard deviation", while in other cases when the standard deviation is less than 15% of the arithmetic mean only the arithmetic mean is provided. Notes on studies on rats, mice and monkeys provide information on dosing method (single oral dose or single intravenous (IV) dose) and dosage (in ppm: mg substance/kg bw). Notes on studies on humans provide sample numbers (n) of humans involved. "–" means no data available.

PFAAs	Rats				Mice				Monkeys				Humans	
	$t_{1/2}$	Notes	$t_{1/2}$	Notes	$t_{1/2}$	Notes	$t_{1/2}$	Notes	$t_{1/2}$	Notes	$t_{1/2}$	Notes	$t_{1/2}$	Notes
PFBS (F)	4 h	IV[1]	8 h	Oral[1]	–	–	–	–	83 ± 42 h	IV[1]	8 ± 2 h	IV[2]	46 d	n = 1[1,17]
PFBS (M)	5 h	30 ppm	5 h	30 ppm	–	–	–	–	95 ± 27 h	10 ppm	15 ± 9 h	10 ppm	24 ± 7 d	n = 5[1,17]
PFHxS (F)	2 d	IV[3]	–	–	25 d	Oral[3]	27 d	Oral[3]	87 ± 27 d	IV[3]	–	–	12.8 ± 0.6 yr	n = 2[4,17]
PFHxS (M)	29 d	10 ppm	–	–	31 d	1 ppm	28 d	20 ppm	141 ± 30 d	10 ppm	–	–	8.2 ± 5.1 yr	n = 24[4,17]
PFOS (F)	62 d	Oral[5]	71 d	Oral[5]	38 d	Oral[5]	30 d	Oral[5]	110 d	IV[5]	–	–	5.9 ± 1 yr	n = 2[4,17]
PFOS (M)	38 d	2 ppm	41 d	15 ppm	43 d	1 ppm	36 d	20 ppm	132 d	2 ppm	–	–	5.4 ± 3.7 yr	n = 24[4,17]
PFBA (F)	1 h	IV[6]	2 h	Oral[6]	3 h	Oral[6]	3 h	Oral[6]	41 h	IV[6]	–	–	87 ± 31 h	n = 2[6,17]
PFBA (M)	6 h	30 ppm	9 h	30 ppm	13 ± 5 h	10 ppm	16 ± 7 h	30 ppm	40 h	10 ppm	–	–	68 ± 35 h	n = 7[6,17]
PFHxA (F)	0.4 h	IV[2]	1.2 h	IV[7]	<72 h	Gastric[8]	–	–	2.4 h	IV[2]	–	–	–	–
PFHxA (M)	1 h	10 ppm	2.4 h	15 ppm	<72 h	50 ppm	–	–	5.3 h	10 ppm	–	–	<28 d	n = 8[9,17]
PFOA (F)	2 h	IV[7]	–	–	17 d	not reported[10]	–	–	33 ± 7 d	IV[11]	–	–	3.3 yr	n = 2[4,17]
PFOA (M)	6 d	20 ppm	–	–	19 d		–	–	21 ± 10 d	10 ppm	–	–	3.8 ± 1.7 yr	n = 24[4,17]
PFOA (all)	–	–	–	–	–	–	–	–	–	–	–	–	3.26 yr	n = 138[12,18]
PFOA (all)	–	–	–	–	–	–	–	–	–	–	–	–	2.3 yr	n = 200[13,18]
PFOA (all)	–	–	–	–	–	–	–	–	–	–	–	–	2.9 yr	n = 643[14,18]
PFOA (all)	–	–	–	–	–	–	–	–	–	–	–	–	8.5 yr	n = 1029[14,18]
GenX (F)	<12 h	Oral[15]	–	–	>12 h, <7 d	Oral[15]	–	–	–	–	–	–	–	–
GenX (M)	<12 h	30 ppm	–	–	>12 h, <7 d	3 ppm	–	–		–	–	–	–	–
ADONA (M)	44 h	5× oral[16]	–	–	–	–	–	–	–	–	–	–	23 ± 11 d	n = 3[16,17]

[1]Olsen et al. (2009), [2]Chengelis et al. (2009), [3]Sundström et al. (2012), [4]Olsen et al. (2007), [5]Chang et al. (2012), [6]Chang et al. (2008), [7]Ohmori et al. (2003), [8]Iwai (2011), [9]Nilsson et al. (2010), [10]Lau et al. (2007), [11]Noker and Gorman (2003), [12]Brede et al. (2010), [13]Bartell et al. (2010), [14]Seals et al. (2011), [15]ECHA (2013b), [16]EFSA (2011b). [17]These studies focus on samples from people who were occupationally exposed to these substances and the levels in serum were high. [18]These studies focus on samples from people who were exposed to PFOA mainly through highly contaminated drinking water.

been identified, information on their potential impacts on humans and the environment is insufficient (e.g., knowledge on degradability, bioaccumulation potential and (eco)toxicity of PFPEs is largely missing.); (iii) for all fluorinated alternatives, the actual volumes that are produced, used and emitted remain unknown.

Furthermore, even those fluorinated alternatives that are considered safe because of low acute toxicity and bioaccumulation according to current regulations may still pose risks in the future. For example, short-chain PFCA and PFSA homologues such as PFHxA and PFBS are as persistent in the environment as the long-chain homologues. Thus, the current increasing global production and use of these chemicals and their potential precursors will lead to increasing widespread environmental and human exposure that will last for the foreseeable future. If, in the future, risks associated with short-chain homologues are discovered and regulatory action needed, it is important to be aware that it will take decades for global environmental levels of these short-chain homologues to respond to any emission reductions.

In order to prevent a "lock-in" problem in the field of fluorinated alternatives, much effort is needed. Above all, communication among stakeholders (manufacturers of fluorinated materials, industrial users of these materials, regulators, scientists and the public) needs to be improved and intensified. A transparent knowledge exchange among stakeholders would enable: (i) developing accurate analytical techniques for alternatives that can be used for further laboratory testing and field monitoring of these chemicals (e.g. PFPEs (Di Lorenzo, 2012)); (ii) developing more sophisticated study designs and data analysis for environmental fate, toxicity and bioaccumulation studies to facilitate up-to-date regulatory decisions; and (iii) developing a new industrial ecology where the latest scientific findings can be readily implemented in the product design phase to develop materials with similar function, but with negligible hazardous properties.

Acknowledgment

Funding by the Swiss Federal Office for the Environment (FOEN) is gratefully acknowledged.

References

3M. Letter to US EPA, re: phase-out plan for POSF-based products (226-0600). US EPA Administrative Record 226; 20001–11.

Ahrens L, Gerwinski W, Theobald N, Ebinghaus R. Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: evidence from their spatial distribution in surface water. Mar Pollut Bull 2010a;60(2):255–60. http://dx.doi.org/10.1016/j.marpolbul.2009.09.013.

Ahrens L, Taniyasu S, Yeung LWY, Yamashita N, Lam PKS, Ebinghaus R. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 2010b;79(3):266–72. http://dx.doi.org/10.1016/j.chemosphere.2010.01.045.

Asahi, Asahi Glass Co., Ltd., Non-ECA PFOA information forum, EPA-HQ-OPPT-2003-0012-1094.4; 2006.

Backe WJ, Day TC, Field JA. Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from U.S. military bases by nonaqueous large-volume injection HPLC–MS/MS. Environ Sci Technol 2013;47:5226–34. http://dx.doi.org/10.1021/es3034999.

BaLfU, Bayerisches Landesamt für Umwelt. PFOA und ADONA measurements at the sample site Alz/Hohenwarth (in German),1 p. http://www.lfu.bayern.de/analytik_stoffe/analytik_org_stoffe_perfluorierte_chemikalien/doc/pfoa_adona_alz.pdf, 2010.

BaLfU, Bayerisches Landesamt für Umwelt. Average deposition rate of PFOA and ADONA (in German), 1 p. http://www.lfu.bayern.de/analytik_stoffe/analytik_org_stoffe_perfluorierte_chemikalien/doc/pfoa_adona_mittelwerte_deposition.pdf, 2010.

Bartell SM, Calafat AM, Lyu C, Kato K, Ryan PB, Steenland K. Rate of decline in serum PFOA concentrations after granular activated carbon filtration at two public water systems in Ohio and West Virginia. Environ Health Perspect 2010;118(2):222–8. http://dx.doi.org/10.1289/ehp.0901252.

Benskin JP, Ikonomou MG, Gobas FAPC, Woudneh MB, Cosgrove JR. Observation of a novel PFOS-precursor, the perfluorooctane sulfonamido ethanol-based phosphate (SAmPAP) diester, in marine sediments. Environ Sci Tech 2012;46(12):6505–14. http://dx.doi.org/10.1021/es300823m.

Benskin JP, Ikonomou MG, Gobas FAPC, Begley TH, Woudneh MB, Cosgrove JR. Biodegradation of N-ethyl perfluorooctane sulfonamido ethanol (EtFOSE) and EtFOSE-based

phosphate diester (SAmPAP diester) in marine sediments. Environ Sci Tech 2013;47(3):1381–9. http://dx.doi.org/10.1021/es304336r.

Borg D, Hakansson H. Environmental and health risk assessment of perfluoroalkylated and polyfluoroalkylated substances (PFASs) in Sweden, report 6513. The Swedish Environmental Protection Agency; 2012.

Brede E, Wilhelm M, Göen T, Müller J, Rauchfuss K, Kraft M, et al. Two-year follow-up biomonitoring pilot study of residents "and controls" PFC plasma levels after PFOA reduction in public water system in Arnsberg, Germany. Int J Hyg Environ Health 2010;213(3):217–23. http://dx.doi.org/10.1016/j.ijheh.2010.03.007.

Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, De Voogt P, et al. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integr Environ Assess Manag 2011;7(4):513–41. http://dx.doi.org/10.1002/ieam.258.

Cai M, Zhao Z, Yin Z, Ahrens L, Huang P, Cai M, et al. Occurrence of perfluoroalkyl compounds in surface waters from the North Pacific to the Arctic Ocean. Environ Sci Tech 2012;46(2):661–8. http://dx.doi.org/10.1021/es2026278.

Chang S-C, Das K, Ehresman DJ, Ellefson ME, Gorman GS, Hart JA, et al. Comparative pharmacokinetics of perfluorobutyrate in rats, mice, monkeys, and humans and relevance to human exposure via drinking water. Toxicol Sci 2008;104(1):40–53. http://dx.doi.org/10.1093/toxsci/kfn057.

Chang S-C, Noker PE, Gorman GS, Gibson SJ, Hart JA, Ehresman DJ, et al. Comparative pharmacokinetics of perfluorooctanesulfonate (PFOS) in rats, mice, and monkeys. Reprod Toxicol 2012;33(4):428–40. http://dx.doi.org/10.1016/j.reprotox.2011.07.002.

Chengelis CP, Kirkpatrick JB, Myers NR, Shinohara M, Stetson PL, Sved DW. Comparison of the toxicokinetic behavior of perfluorohexanoic acid (PFHxA) and nonafluorobutane-1-sulfonic acid (PFBS) in cynomolgus monkeys and rats. Reprod Toxicol 2009;27(3–4):400–6. http://dx.doi.org/10.1016/j.reprotox.2009.01.013.

China MEP. Information on alternatives to the use of perfluorooctane sulfonic acid (PFOS) in open application to the POPs Review Committee from China, POPRC7 follow-up. Secretariate of the Stockholm Convention; 2012.

Clarke BO, Smith SR. Review of "emerging" organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. Environ Int 2011;37(1):226–47. http://dx.doi.org/10.1016/j.envint.2010.06.004.

Conder JM, Hoke RA, De Wolf W, Russell MH, Buck RC. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. Environ Sci Tech 2008;42(4):995–1003. http://dx.doi.org/10.1021/es070895g.

DowCorning. DAIKIN and Dow Corning introduce Unidyne™ TG-5521 for fabric repellency and softness. http://www.dowcorning.com/content/news/dowcorning_daikin.asp, 2007. [accessed April 29, 2013].

Dauchy X, Boiteux V, Rosin C, Munoz J-F. Relationship between industrial discharges and contamination of raw water resources by perfluorinated compounds. Part I: case study of a fluoropolymer manufacturing plant. Bull Environ Contam Toxicol 2012;89(3):525–30. http://dx.doi.org/10.1007/s00128-012-0704-x.

D'eon JC, Hurley MD, Wallington TJ, Mabury SA. Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, $C_4F_9SO_2N(CH_3)CH_2CH_2OH$: kinetics and mechanism of reaction with OH. Environ Sci Tech 2006;40(6):1862–8. http://dx.doi.org/10.1021/es0520767.

di Lorenzo RA. Master thesis: Perfluoropolyethers, analytical method development for a new class of compounds with the potential to be long-lived environmental contaminants. University of Toronto, 2012 <https://tspace.library.utoronto.ca/handle/1807/33398>.

DuPont. DuPontTM GenX processing aid for making fluoropolymer resins. http://www2.dupont.com/Industrial_Bakery_Solutions/en_GB/assets/downloads/DuPont_GenX_Brochure_Final_07July2010.pdf, 2010.

ECHA, European Chemical Agency. Candidate list of substances of very high concern for authorisation. http://echa.europa.eu/web/guest/candidate-list-table, 2013a. [accessed September 14, 2013].

ECHA, European Chemicals Agency. Registered substances. http://echa.europa.eu/information-on-chemicals/registered-substances, 2013b. [accessed April 3, 2013].

EFSA, EFSA Panel on food contact materials. Scientific opinion on the safety evaluation of the substance perfluoro acetic acid, α-substituted with the copolymer of perfluoro-1,2propylene glycol and perfluoro-1,1-ethylene glycol, terminated with chlorohexafluoropropyloxy groups, CAS No. 329238-24-6 for use in food contact materials. EFSA J 2010;8(2):1519. http://dx.doi.org/10.2903/j.efsa.2010.1519.

EFSA, EFSA Panel on food contact materials. Scientific opinion on the safety evaluation of the substance, perfluoro[(2-ethyloxy-ethoxy)acetic acid], ammonium salt, CAS No. 908020-52-0,for use in food contact materials. EFSA J 2011a;9(6):2183. http://dx.doi.org/10.2903/j.efsa.2011.2183.

EFSA, EFSA Panel on food contact materials. Scientific opinion on the safety evaluation of the substance,3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid], ammonium salt, CAS No. 958445-44-8, for use in food contact materials. EFSA J 2011b;9(6):1–11. http://dx.doi.org/10.2903/j.efsa.2011.2182.

EFSA,EuropeanFoodSafetyAuthority. Food contact materials applications. http://www.efsa.europa.eu/en/applicationshelpdesk/foodcontactmaterials.htm, 2013. [accessed April 29, 2013].

Frömel T, Knepper TP. Biodegradation of fluorinated alkyl substances. Rev Environ Contam Toxicol 2010;208:161–77. http://dx.doi.org/10.1007/978-1-4419-6880-7_3.

Giesy JP, Kannan K. Global distribution of perfluorooctane sulfonate in wildlife. Environ Sci Technol 2001;35:1339–42. http://dx.doi.org/10.1021/es001834k.

Glynn A, Berger U, Bignert A, Ullah S, Aune M, Lignell S, et al. Perfluorinated alkyl acids in blood serum from primiparous women in Sweden: serial sampling during pregnancy and nursing, and temporal trends 1996–2010. Environ Sci Tech 2012;46(16):9071–9. http://dx.doi.org/10.1021/es301168c.

Goldstein B, Banda S, Cairncross E, Jiang G, Massey R, Miglioranza K, Samseth J, Scheringer M, Smith J. Chapter "minimizing chemical risks" from UNEP year book 2013: emerging issues in our global environment; 2013 [37–51 pp.].

Gordon SC. Toxicological evaluation of ammonium 4,8-dioxa-3H-perfluorononanoate, a new emulsifier to replace ammonium perfluorooctanoate in fluoropolymer manufacturing. Regul Toxicol Pharmacol 2011;59(1):64–80. http://dx.doi.org/10.1016/j.yrtph.2010.09.008.

Hagenaars A, Meyer IJ, Herzke D, Pardo BG, Martinez P, Pabon M, et al. The search for alternative aqueous film forming foams (AFFF) with a low environmental impact: physiological and transcriptomic effects of two Forafac(®) fluorosurfactants in turbot. Aquat Toxicol 2011;104(3–4):168–76. http://dx.doi.org/10.1016/j.aquatox.2011.04.012.

Holt R. Alternatives to long-chain PFCs, in OECD Webinar on alternatives to long chain PFCs. http://www.oecd.org/env/ehs/risk-management/47651662.pdf, 2011.

Huang C, Li X, Jin G. Electro fluorination and its fine-fluorine production branches. Chem Prod Technol 2010;17(4):1–7. http://dx.doi.org/10.3969/j.issn.1006-6829.2010.04.0001. [in Chinese].

Hubei Hengxin, Hubei Hengxin Chemical Co., Ltd. Products: potassium perfluorobutanesulfonate. http://www.fluoride-cn.com/cgi/search-en.cgi?f=product_en_1_+company_en_1_&id=64418&t=product_en_1_, 2013. [accessed April 4, 2013].

Hurley M, Wallington T, Andersen M, Ellis D, Martin J, Mabury S. Atmospheric chemistry of fluorinated alcohols: reaction with Cl atoms and OH radicals and atmospheric lifetimes. J Phys Chem A 2004;108:1973–9. http://dx.doi.org/10.1021/jp0373088.

Iwai H. Toxicokinetics of ammonium perfluorohexanoate. Drug Chem Toxicol 2011;34(4):341–6. http://dx.doi.org/10.3109/01480545.2011.585162.

Jensen AA, Poulsen PB, Bossi R. Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. Series of survey of chemical substances in consumer products, no. 99. published by Danish Ministry of The Environment and Danish Environmental Protection Agency; 2008.

Kato K, Wong L-Y, Jia LT, Kuklenyik Z, Calafat AM. Trends in exposure to polyfluoroalkyl chemicals in the U.S. Population: 1999–2008. Environ Sci Tech 2011;45(19):8037–45. http://dx.doi.org/10.1021/es1043613.

Klein RA. Comments on the draft technical paper on the identification and assessment on alternatives to the use of perfluorooctane sulfonic (PFOS) acid in open applications. POPRC7 Follow-up. published by the Stockholm Convention Secretariat; 2012.

Kleiner E, Jho C. Recent developments in 6:2 fluorotelomer surfactants and foam stabilizers. 4th Reebok Foam Seminar, 6–7 July 2009, Bolton, UK; 2009.

Lange FT, Wenz M, Schmidt CK, Brauch HJ. Occurrence of perfluoroalkyl sulfonates and carboxylates in German drinking water sources compared to other countries. Water Sci Technol 2007;56(11):151–8. http://dx.doi.org/10.2166/wst.2007.803.

Lau C, Anitole K, Hodes C, Lai D, Pfahles-Hutchens A, Seed J. Perfluoroalkyl acids: a review of monitoring and toxicological findings. Toxicol Sci 2007;99(2):366–94. http://dx.doi.org/10.1093/toxsci/kfm128.

Lee H, D'eon J, Mabury SA. Biodegradation of polyfluoroalkyl phosphates as a source of perfluorinated acids to the environment. Environ Sci Tech 2010;44(9):3305–10. http://dx.doi.org/10.1021/es9028183.

Liu J, Wang N, Buck RC, Wolstenholme BW, Folsom PW, Sulecki LM, et al. Aerobic biodegradation of [14C] 6:2 fluorotelomer alcohol in a flow-through soil incubation system. Chemosphere 2010a;80(7):716–23. http://dx.doi.org/10.1016/j.chemosphere.2010.05.027.

Liu J, Wang N, Szostek B, Buck RC, Folsom PW, Sulecki LM, et al. 6-2 Fluorotelomer alcohol aerobic biodegradation in soil and mixed bacterial culture. Chemosphere 2010b;78(4):437–44. http://dx.doi.org/10.1016/j.chemosphere.2009.10.044.

Loi EIH, Yeung LW-Y, Mabury SA, Lam PKS. Detections of commercial fluorosurfactants in Hong Kong marine environment and human blood: a pilot study. Environ Sci Tech 2013;47(9):4677–85. http://dx.doi.org/10.1021/es303805k.

Marchionni G, Tortelli V, Wlassics I, Kapeliouchko V. Patent: method for manufacturing fluoropolymers in the presence of cyclic fluorosurfactants with low bioaccumulation/biopersistence. WO 2010003929, 2010.

Martin JW, Ellis DA, Mabury SA, Hurley MD, Wallington TJ. Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. Environ Sci Tech 2006;40(3):864–72. http://dx.doi.org/10.1021/es051362f.

Misubishi, Mitsubishi Materials Electronic Chemicals Co., Ltd., Perfluoroalkyl sulfonyl compounds. http://www.mmc-ec.co.jp/eng/product/perflu.html, 2013. [accessed April 4, 2013].

Miteni. Products catalogue: perfluorinated derivatives. http://www.miteni.com/risultati/perfluorinated.html, 2012. [accessed October 19, 2012].

Moe MK, Huber S, Svenson J, Hagenaars A, Pabon M, Trümper M, et al. The structure of the fire fighting foam surfactant Forafac®1157 and its biological and photolytic transformation products. Chemosphere 2012;89(7):869–75. http://dx.doi.org/10.1016/j.chemosphere.2012.05.012.

Möller A, Ahrens L, Surm R, Westerveld J, van der Wielen F, Ebinghaus R, et al. Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. Environ Pollut 2010;158(10):3243–50. http://dx.doi.org/10.1016/j.envpol.2010.07.019.

Nilsson H, Kärrman A, Westberg H, Rotander A, van Bavel B, Lindström G. A time trend study of significantly elevated perfluorocarboxylate levels in humans after using fluorinated ski wax. Environ Sci Tech 2010;44(6):2150–5. http://dx.doi.org/10.1021/es9034733.

Noker PE, Gorman GS. Final report on a pharmacokinetic study of potassium perfluorooctanoate in the cynomologus monkey (226–1228). US EPA Administrative Record, 226; 20031–60.

Nørgaard AW, Larsen ST, Hammer M, Poulsen SS, Jensen KA, Nielsen GD, et al. Lung damage in mice after inhalation of nanofilm spray products: the role of perfluorination and free hydroxyl groups. Toxicol Sci 2010;116:216–24. http://dx.doi.org/10.1093/toxsci/kfq094.

OECD. Results of survey on production and use of PFOS, PFAS and PFOA, related substances and products/mixtures containing these substances. Document No. ENV/JM/MONO(2005) 1http://search.oecd.org/officialdocuments/displaydocumentpdf/?doclanguage=en&cote=env/jm/mono%282005%291, 2005.

OECD, OECD portal on perfluorinated chemicals. Information on short-chain PFCs and other alternatives. http://www.oecd.org/ehs/pfc/informationonshortchainpfcsandotheralternatives.htm, 2013. [accessed April 29, 2013].

Ohmori K, Kudo N, Katayama K, Kawashima Y. Comparison of the toxicokinetics between perfluorocarboxylic acids with different carbon chain length. Toxicology 2003;184(2–3):135–40. http://dx.doi.org/10.1016/S0300-483X(02)00573-5.
Olsen GW, Burris JM, Ehresman DJ, Froehlich JW, Seacat AM, Butenhoff JL, et al. Half-life of serum elimination of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in retired fluorochemical production workers. Environ Health Perspect 2007;115(9):1298–305. http://dx.doi.org/10.1289/ehp.10009.
Olsen GW, Chang S-C, Noker PE, Gorman GS, Ehresman DJ, Lieder PH, et al. A comparison of the pharmacokinetics of perfluorobutanesulfonate (PFBS) in rats, monkeys, and humans. Toxicology 2009;256(1–2):65–74. http://dx.doi.org/10.1016/j.tox.2008.11.008.
Pabon M, Corpart JM. Fluorinated surfactants: synthesis, properties, effluent treatment. J Fluor Chem 2002;114(2):149–56. http://dx.doi.org/10.1016/S0022-1139(02)00038-6.
Parsons JR, Sáez M, Dolfing J, de Voogt P. Biodegradation of perfluorinated compounds. Rev Environ Contam Toxicol 2008;196:53–71. http://dx.doi.org/10.1007/978-0-387-78444-1_2.
Pieri R, Kapeliouchko V, Chenysheva L. Patent: Method for manufacturing fluoropolymers by polymerization using fluorinated surfactants, WO 2011073337, 2011.
Place BJ, Field JA. Identification of novel fluorochemicals in aqueous film-forming foams used by the US military. Environ Sci Technol 2012;46:7120–7. http://dx.doi.org/10.1021/es301465n.
Plumlee MH, McNeill K, Reinhard M. Indirect photolysis of perfluorochemicals: hydroxyl radical-initiated oxidation of N-ethyl perfluorooctane sulfonamido acetate (N-EtFOSAA) and other perfluoroalkanesulfonamides. Environ Sci Tech 2009;43(10):3662–8. http://dx.doi.org/10.1021/es803411w.
Poulsen PB, Jensen AA, Wallström E. More environmentally friendly alternatives to PFOS-compounds and PFOA. Environmental Project No. 1013, Danish Ministry of the Environment. Environmental Protection Agency; 2005.
Prevedouros K, Cousins IT, Buck RC, Korzeniowski SH. Sources, fate and transport of perfluorocarboxylates. Environ Sci Tech 2006;40(1):32–44. http://dx.doi.org/10.1021/es0512475.
Rayne S, Forest K. Perfluoroalkyl sulfonic and carboxylic acids: a critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. J Environ Sci Health A Toxicol 2009;44(12):1145–99. http://dx.doi.org/10.1080/10934520903139811.
Renner R. The long and the short of perfluorinated replacements. Environ Sci Technol 2006;40(1):12–3. http://dx.doi.org/10.1021/es062612a.
Ritter SK. Fluorochemicals go short. Chem Eng News 2010;88(5):12–7. http://dx.doi.org/10.1021/cen-v088n005.p012.
Seals R, Bartell SM, Steenland K. Accumulation and clearance of perfluorooctanoic acid (PFOA) in current and former residents of an exposed community. Environ Health Perspect 2011;119(1):119–24. http://dx.doi.org/10.1289/ehp.1002346.
Solvay, Solvay Solexis S.p.A., Solvay Solexis expands perfluoropolyethers (PFPE) production capacity in Spinetta Marengo (Italy). http://www.solvay.com/EN/NewsPress/20070222_PFPE_Spinetta.aspx, 2011. [accessed April 3, 2013].
Spada F, Kent BL. Patent: Process for manufacturing a dispersion of a vinylidene fluoride polymer. WO 2011073254, 2011.
Strempel S, Scheringer M, Ng C, Hungerbühler K. Screening for PBT chemicals among the "existing" and "new" chemicals of the EU. Environ Sci Tech 2012;46(11):5680–7. http://dx.doi.org/10.1021/es3002713.
Strynar MJ, Dagnino S, Lindstrom A, Andersen E, McMillan L, Thurman M, et al. Identification of novel polyfluorinated compounds in natural waters using accurate mass TOFMS. 33rd SETAC North America Annual Meeting, 11–15 November, 2012, Long Beach, USA; 2012.
Sulbaek Andersen MP, Toft A, Nielsen OJ, Hurley MD, Wallington TJ, Chishima H, et al. Atmospheric chemistry of perfluorinated aldehyde hydrates (n-C(x)F(2x + 1) CH(OH)2, x = 1, 3, 4): hydration, dehydration, and kinetics and mechanism of Cl atom and OH radical initiated oxidation. J Phys Chem A 2006;110:9854–60. http://dx.doi.org/10.1021/jp060404z.
Sundström M, Chang S-C, Noker PE, Gorman GS, Hart JA, Ehresman DJ, et al. Comparative pharmacokinetics of perfluorohexanesulfonate (PFHxS) in rats, mice, and monkeys. Reprod Toxicol 2012;33(4):441–51. http://dx.doi.org/10.1016/j.reprotox.2011.07.004.
Trier X, Granby K, Christensen JH. Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging. Environ Sci Pollut Res 2011;18(7):1108–20. http://dx.doi.org/10.1007/s11356-010-0439-3.
Uematsu N, Hoshi N, Koga T, Ikeda M. Synthesis of novel perfluorosulfonamide monomers and their application. J Fluor Chem 2006;127(8):1087–95. http://dx.doi.org/10.1016/j.jfluchem.2006.05.015.
Ulaszewska MM, Hernando MD, Uclés A, Rosal R, Rodrguez A, Garcia-Calvo E, et al. Chapter 6: chemical and ecotoxicological assessment of dendrimers in the aquatic environment. Comprehensive analytical chemistry, vol. 59. Elsevier B.V.; 2012. p. 197–233. http://dx.doi.org/10.1016/B978-0-444-56328-6.00006-2.
UNEP. Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid in open applications. UNEP/POPS/POPRC.8/INF/17; 2012.
US EPA, United States Environmental Protection Agency. 2010/15 PFOA Stewardship program. http://www.epa.gov/oppt/pfoa/pubs/stewardship/, 2006.
US EPA, United States Environmental Protection Agency. Chemical data reporting (CDR) database (former Inventory Update Reporting (IUR) database). http://www.epa.gov/oppt/cdr/index.html, 2012. [accessed September 19, 2012].
US FDA, United States Food and Drug Administration. Inventory of effective Food Contact Substance (FCS) notifications. http://www.accessdata.fda.gov/scripts/fcn/fcnnavigation.cfm?rpt=fcslisting, 2013. [accessed April 3, 2013].
US FDA, United States Food and Drug Administration. Packaging & food contact substances (FCS). http://www.fda.gov/Food/IngredientsPackagingLabeling/PackagingFCS/default.htm, 2013. [accessed April 29, 2013].
Vestergren R, Cousins IT. Tracking the pathways of human exposure to perfluorocarboxylates. Environ Sci Tech 2009;43(15):5565–75. http://dx.doi.org/10.1021/es900228k.
Wang N, Liu J, Buck RC, Korzeniowski SH, Wolstenholme BW, Folsom PW, et al. 6:2 Fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants. Chemosphere 2011;82(6):853–8. http://dx.doi.org/10.1016/j.chemosphere.2010.11.003.
Wang S, Huang J, Yang Y, Hui Y, Ge Y, Larssen T, et al. First report of a chinese PFOS alternative overlooked for 30 years: its toxicity, persistence, and presence in the environment. Environ Sci Technol 2013a;47(18):10163–70. http://dx.doi.org/10.1021/es401525n.
Wang D-G, Norwood W, Alaee M, Byer JD, Brimble S. Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment. Chemosphere 2013b. http://dx.doi.org/10.1016/j.chemosphere.2012.10.041. [in press].
Wang N, Buck RC, Szostek B, Sulecki LM, Wolstenholme BW. 5:3 Polyfluorinated acid aerobic biotransformation in activated sludge via novel "one-carbon removal pathways". Chemosphere 2012;87(5):527–34. http://dx.doi.org/10.1016/j.chemosphere.2011.12.056.
Wilhelm M, Bergmann S, Dieter HH. Occurrence of perfluorinated compounds (PFCs) in drinking water of North Rhine-Westphalia, Germany and new approach to assess drinking water contamination by shorter-chained C4-C7 PFCs. Int J Hyg Environ Health 2010;213(3):224–32. http://dx.doi.org/10.1016/j.ijheh.2010.05.004.
Wuhan Chemical, Wuhan Chemical Industry Reserach Institute Co., Ltd. Products. in Chinesehttp://www.whchinst.com/newEbiz1/EbizPortalFG/portal/html/CategoryList.html?ProductPicker_action=Searchcategory&CategoryID=c373e905150fe1158ffa5f16eaf2337c&time=1365080394822#, . [accessed April 4, 2013].
Xie X, Bo R, Li J, Chen B. Favoring PFOA alternative technology, taking enterprise's environmental protection responsibility (in Chinese). 7th Chinese National Workshop on market development and applications of functional fluorine and silicone materials; 2010.
Xie X, Qu J, Bai R, Zhang J, Yang X. Patent: Peroxidic fluoropolyether and its use in emulsion polymerization of fluorin-containing monomer. US 2011/0207880 A1: US Patent Office, 2011.
Xu Y, Zhao M, Li H, Lu W, Su X, Han Z. A novel fluorocarbon surfactant: synthesis and application in emulsion polymerization of perfluoroalkyl methacrylates. Paint Coat Ind 2011;41:17–21. [in Chinese].
Yang B, Chen K, Xing H, Xiao J. Perfluorobutyl-based fluorinated surfactant with high surface activity. Acta Phys Chim Sin 2009;25(12):2409–12. [in Chinese].
Young CJ, Mabury SA. Atmospheric perfluorinated acid precursors: chemistry, occurrence, and impacts. Rev Environ Contam Toxicol 2010;208:1–109. http://dx.doi.org/10.1007/978-1-4419-6880-7_1.
Young CJ, Hurley MD, Wallington TJ, Mabury SA. Atmospheric lifetime and global warming potential of a perfluoropolyether. Environ Sci Tech 2006;40(7):2242–6. http://dx.doi.org/10.1021/es052077z.
Zhao X. Application and development status of foam extinguishing agent. J Hebei Acad Sci 2012;29(3):65–8. [in Chinese, ISSN:1001-9383].
Zhao L, Folsom PW, Wolstenholme BW, Sun H, Wang N, Buck RC. 6:2 Fluorotelomer alcohol biotransformation in an aerobic river sediment system. Chemosphere 2013;90(2):203–9. http://dx.doi.org/10.1016/j.chemosphere.2012.06.035.