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Review

Microbial degradation of polyfluoroalkyl chemicals in the environment: A review

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ABSTRACT

Polyfluoroalkyl chemicals containing perfluoroalkyl moieties have been widely used in numerous industrial and commercial applications. Many polyfluoroalkyl chemicals are potential perfluoroalkyl acid (PFAA) precursors. When they are released to the environment, abiotic and microbial degradation of non-fluorinated functionalities, polyfluoroalkyl and perfluoroalkyl moieties can result in perfluoroalkyl carboxylic (PFCAs) and sulfonic acids (PFSAs), such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). These highly persistent and ubiquitously detected PFAAs are the subjects of many regulations and actions due to their toxic profiles. In order to confidently evaluate the environmental fate and effects of these precursors and their links to PFSAs and PFCAs, we present the review into the environmental biodegradability studies carried out with microbial culture, activated sludge, soil and sediment in the past decade. First, we propose that the knowledge gap caused by the lack of direct detection of precursor chemicals in environmental samples can be bridged by laboratory investigations of important precursors such as fluorotelomer-based compounds and perfluoroalkane sulfonamido derivatives. Then we evaluate the experimental setups and methodologies, sampling and sample preparation methods, and analytical techniques that have been successfully applied. Third, we provide the most updated knowledge on quantitative and qualitative relationships between precursors and PFSAs or PFCAs, microbial degradation pathways, half-lives of precursors, defluorination potential, and novel degradation intermediates and products. In the end, we identify knowledge gaps and suggest research directions with regard to future biodegradation studies, environmental monitoring and ecotoxicological assessment of perfluoroalkyl and polyfluoroalkyl chemicals.

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1. Introduction and objectives

Perfluorooctane sulfonic acid [PFOS, $C_8F_{17}SO_3H$] and perfluorooctanoic acid [PFOA, $C_7F_{15}COOH$] are among the most prominent organic pollutants in the environment, biota and human serum (Ahrens, 2011; Davis et al., 2007; Giesy and Kannan, 2001; Hansen et al., 2001, 2002; Higgins et al., 2005; Houde et al., 2011; Yamashita et al., 2005). The compounds are highly persistent and can undergo long-distance transport (Scheringer, 2009). The bioaccumulation potential and toxicity demonstrated in laboratory animals suggest a cause of great concern for the environment and human health (Conder et al., 2008; Lau et al., 2007). Due to the wide global distribution and hazardous properties of PFOS and PFOA, manufacturing and use of the compounds and related perfluoroalkyl and polyfluoroalkyl substances (PFAS) have been reduced or restricted in recent years. PFOS was phased out of production during 2000–2002 in North America (3M, 2000), banned in European countries (European Parliament, 2006), and was included in the *Stockholm Convention on Persistent Organic Pollutants* as an Annex B substance (United Nations Environment Programme, 2009). Even though the total global PFOS production has fallen compared to the years prior to 2002, PFOS production has increased dramatically in China since 2003 (Carloni, 2009; China MEP, 2008; MEPFECO, 2009). Through a global stewardship program, PFOA and its longer chained homologues and chemical precursors are on track to be phased out by 2015 by major manufacturers (U.S. EPA, 2006). In addition, U.S. Environmental Protection Agency's (U.S. EPA) Provisional Health Advisory for drinking water has been proposed for PFOS (200 ng/L) and PFOA (400 ng/L)(U.S. EPA, 2009), while other regulations are likely to follow in the near future (Ritter, 2010).

As the direct emissions of PFOA and PFOS have been declining in recent years, various PFASs that eventually are converted into PFOS, PFOA and other perfluoroalkyl acids (PFAA) are now key factors for determining the exposure and effect of PFASs. Subsequently, a primary research interest is to what extent the concentrations of perfluoroalkyl carboxylic acids [PFCA, $C_nF_{2n+1}COOH$] and sulfonic acids [PFSA, $C_nF_{2n+1}SO_3H$], in particular PFOS and PFOA, originate from the breakdown of non-fluorinated functionalities, or even polyfluoroalkyl and perfluoroalkyl moieties in the environment. The research in the past decade has particularly disclosed the role of microbial degradation in producing PFAAs. Owing to dozens of studies published in the past decade, we have gained rudimentary understanding of how environmental conditions, chemical structures and properties affect biodegradability of PFAS, degradation kinetics, and yields to PFAAs. This review will focus on these studies that were conducted with mixed and pure microbial culture, activated sludge, soil and sediment, and with direct applicability to natural and engineered treatment systems.

Aside from the generation of PFAAs, here we further present novel biodegradation pathways, mechanisms, and products, all of which have greatly challenged our perception on the stability of fluorochemicals. In the end, knowledge gaps are identified and research directions are suggested with regard to future microbial degradation studies, environmental monitoring and ecotoxicological assessment of PFASs. In this review, the terms *biotransformation* and *biodegradation* are used interchangeably as in most of the cited literature, even though no complete mineralization is expected for PFASs under natural conditions. The findings presented herein are both scientifically intriguing and of high practical values. For example, one area that can immediately benefit is assessing the environmental fate of polyfluoroalkyl surfactants in contaminated soil and groundwater sites (Moody et al., 2003). Historical uses of PFAS-containing aqueous film-forming formulations (AFFFs) for firefighting activities have led to widespread soil and groundwater contamination (Backe et al., 2013; Moody and Field, 1999; Schultz et al., 2004). The knowledge of how those polyfluoroalkyl surfactants have degraded and evolved under various subsurface conditions is urgently needed for guiding site characterization, site management and remediation efforts (Backe et al., 2013; Moody et al., 2003).

1.1. The PFAS chemical family

PFCAs and PFSAs present in the environment originate from a myriad of sources (Ahrens, 2011; Buck et al., 2011). In general, the identified sources include industrial use and release, use and disposal of PFAS-containing consumer products, and abiotic and biotic transformation of polyfluoroalkyl precursor chemicals (Buck et al., 2011; Paul et al., 2009; Prevedouros et al., 2006). These polyfluoroalkyl precursors to PFAAs are the focus of this review. To indicate the role of natural transformation processes in creating PFOS or PFOA, the terms “direct” and “indirect” sources are particularly defined in recent literature (Buck et al., 2011). The “direct” sources refer to emissions of PFAAs as such, throughout their product life cycle no matter if they be purposeful products or unintended product residuals or impurities. The “indirect” sources refer to emissions of polyfluoroalkyl chemicals, whose environmental transformation lead to PFAAs. Inventory studies (Paul et al., 2009; Prevedouros et al., 2006) and mathematical simulations (Armitage et al., 2009) concur that on a global scale direct emissions have been more significant historical sources to PFOS and PFOA in the environment. Yet, the production volumes of polyfluoroalkyl chemicals, most of which are likely precursors, greatly exceeded those of PFOA and PFOS; there are also large uncertainties surrounding the routes and magnitude of indirect sources (Paul et al., 2009; Prevedouros et al., 2006). In addition, Martin et al. (2010) have discovered exposure scenarios that precursors might be significant sources of PFOS to humans and wildlife. Similarly, D'eon and Mabury (2011) demonstrated that precursor exposure could represent

a significant portion of observed PFAAs in humans. This highlights the need to investigate natural transformation processes of precursors and their links to PFOS and PFOA (Armitage et al., 2009; Paul et al., 2009; Prevedouros et al., 2006).

As revealed by an OECD report, there are about one thousand polyfluoroalkyl chemicals commercially produced that could potentially degrade to PFCAs (OECD, 2007). Buck et al. (2011) have detailed 42 families and subfamilies and 268 individual PFASs as likely to be of environmental importance, while only a small fraction of these compounds have been evaluated for their biodegradability. The most studied precursors are fluorotelomer-based compounds, produced through telomerization technology (Buck et al., 2011). Their chemical structures are characterized by the linear, even-numbered perfluoroethyl moiety [$C_nF_{2n+1}CH_2CH_2-$]. Many commercially important surfactants (e.g., fluorotelomer phosphate esters) and side-chain fluorinated polymers (e.g., fluorinated acrylate-, methacrylate- and urethane-based polymers) are synthesized from key intermediates such as fluorotelomer alcohols [(n:2) FTOHs, $C_nF_{2n+1}CH_2CH_2OH$] and fluorotelomer iodides [(n:2) FTIs, $C_nF_{2n+1}CH_2CH_2I$] (Buck et al., 2011). Electrochemical fluorination is another major technology to produce many commercially important surfactants and polymers (Banks et al., 1994). Prior to 2000–2002, perfluorooctane sulfonyl fluoride [POSF, $C_8F_{17}SO_2F$] had been the key raw material used for synthesizing a range of chemicals, such as PFOS, perfluoroalkyl sulfonamides [$C_nF_{2n+1}SO_2NR_1R_2$, where R_1 and R_2 are various hydrocarbon groups], sulfonamide alcohols [$C_nF_{2n+1}SO_2N(C_mH_{2m+1})CH_2CH_2OH$, where m = 1 or 2], and sulfonamide acrylates [$C_nF_{2n+1}SO_2N(C_mH_{2m+1})CH_2CH_2OC(O)CH{=}CH_2$, where m = 1 or 2], and other commercial surfactants and polymers (3M, 1999). Distinctly different from fluorotelomer-based compounds, POSF-based compounds are generally mixtures of linear and branched isomers, and roughly 70–80% is linear in the case of synthesis of PFOS and PFOA (3M, 1999).

It is essential to understand the biodegradability of the major building blocks, such as (n:2) FTOHs or *N*-ethyl perfluorooctane sulfonamidoethanol [EtFOSE, $C_8F_{17}SO_2NH(C_2H_5)CH_2CH_2OH$], because their degradation is directly linked to PFOA or PFOS generation. A number of laboratory studies have demonstrated their high susceptibility to biotransformation as evidenced by short half-lives (Table 1). Of equal importance is the understanding of the environmental stability of key chemical linkages (ester, ether, urethane, etc.), which functionalize the intermediates into the surfactants or polymers present in commercial products (Kissa, 2001). Stability of these linkages determines the overall stability of PFASs. As illustrated in Fig. 1A, the hydrolytical breakdown of the ester bond in fluorotelomer derivatives precedes the biodegradation of 8:2 FTOH into PFOA. Similar biodegradation schemes are expected for EtFOSE derivatives containing hydrolysable functional groups (Fig. 1B).

Many chemicals discussed in the review have recently been or are being phased out in favor of those with better human and environmental safety profiles (Ritter, 2010). In particular, PFASs with shorter perfluoroalkyl chains, due to their low bioaccumulation potential, have been used to replace their long-chain counterparts. For instance, 8:2 FTOH has been replaced by 6:2 FTOH, and PFOS with perfluorobutane sulfonic acid [PFBS, $C_4F_9SO_3H$] (Ritter, 2010). It is expected that other environmentally benign PFASs will be developed. Therefore, there is clearly a great need to have validated methodologies that can be reliably used for evaluating natural biodegradability of PFASs in order to assess their environmental fate and effects.

1.2. Environmental occurrence of polyfluoroalkyl compounds

Detection of *perfluoroalkyl* acids in the environment, human and wildlife has been widely documented (Ahrens, 2011; Davis et al., 2007; Giesy and Kannan, 2001; Hansen et al., 2001, 2002; Higgins et al., 2005; Houde et al., 2011; Yamashita et al., 2005). *Polyfluoroalkyl* precursors have also been found in various environmental compartments, though less frequently probably because they are less often included in targeted environmental analysis. Many polyfluoroalkyl chemicals are detected in air or associated with airborne particulate matter, such as FTOHs (from 4:2 to 10:2 FTOHs), fluorotelomer phosphate diesters [x:2/y:2 diPAPs, $(C_xF_{2x+1}CH_2CH_2O)(O)P(OH)(OCH_2CH_2C_yF_{2y+1})$, where x = 4, 6, 8 and 10, and y = 4, 6, 8, 10 and 12], EtFOSE, *N*-ethyl perfluorooctane sulfonamide [EtFOSA, $C_8F_{17}SO_2NH(C_2H_5)$], *N*-methyl perfluorooctane sulfonamidoethanol [MeFOSE, $C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$], *N*-methyl perfluorooctane sulfonamide [MeFOSA, $C_8F_{17}SO_2NH(CH_3)$], *N*-methyl perfluorobutane sulfonamide [MeFBSA, $C_4F_9SO_2NH(CH_3)$], and *N*-methyl perfluorobutane sulfonamidoethanol [MeFBSE, $C_4F_9SO_2N(CH_3)CH_2CH_2OH$] (Barber et al., 2007; De Silva et al., 2012; Dreyer et al., 2009b; Haug et al., 2011; Jackson and Mabury, 2012; Martin et al., 2002; Weinberg et al., 2011). FTOHs have been detected in rainwater, river water, wastewater treatment effluents, and soil amended with sludge of industrial origins (Mahmoud et al., 2009; Yoo et al., 2010). Some of the microbial degradation products of FTOHs including fluorotelomer carboxylic acids [(n:2) FTCA, $C_nF_{2n+1}CH_2COOH$] and unsaturated carboxylic acids [(n:2) FTUCA, $C_nF_{2n+1}CH{=}COOH$] have been detected in WWTP sludge and effluents (Sinclair and Kannan, 2006; Zhang et al., 2010). Perfluoroalkyl sulfonamide derivatives are commonly found in aqueous environments, for example, perfluorooctane sulfonamide [FOSA, $C_8F_{17}SO_2NH_2$], *N*-ethyl perfluorooctane sulfonamidoacetic acid [EtFOSAA, $C_8F_{17}SO_2N(C_2H_5)CH_2COOH$], *N*-methyl perfluorooctane sulfonamidoacetic acid [MeFOSAA, $C_8F_{17}SO_2N(CH_3)CH_2COOH$] and MeFBSA. Their presence has been confirmed in ocean water, river and lake, drinking water, wastewater effluent and landfill leachate (Ahrens et al., 2009a, 2010; Ericson et al., 2009; Huset et al., 2011; Kim and Kannan, 2007; Schultz et al., 2006). FOSA, as one of the most often targeted precursors, has been found to be present at levels comparable to those of PFOA in a few studies (Ahrens et al., 2010; Busch et al., 2010; Meesters and Schröder, 2004), but other types of precursors when analyzed side by side were sometimes found to be more dominant, such as EtFOSAA and MeFOSAA (Ahrens et al., 2009c; Benskin et al., 2012b; Higgins et al., 2005; Huset et al., 2011). These two precursors have often been detected in solid environmental matrix, such as activated sludge and biosolids from wastewater treatment plants (WWTPs) and sediment, likely due to their high affinity for solid matrix and organic matter (Ahrens et al., 2009b; Benskin et al., 2012a; Higgins et al., 2005; Sepulvado et al., 2011). In addition, a suite of diPAPs of varying perfluoroalkyl headgroups and EtFOSE-based phosphate diester [SAmPAP diester, $(O)P(OH)(OCH_2CH_2N(C_2H_5)SO_2C_8F_{17})_2$] were detected in WWTP sludge and marine sediment, respectively (Benskin et al., 2012a; D'eon et al., 2009).

Aside from the reported environmental occurrences, a larger number of *polyfluoroalkyl* chemicals are likely to be present in the environment, but elude our direct detection due to the lack of authentic standards and the lack of information on what might be significant species, especially when targeted environmental analyses are mostly used. The prominent example is the frequent detection of higher levels of PFOA and PFOS in WWTP effluents relative to influents (Becker et al., 2008; Loganathan et al., 2007; Murakami et al., 2009b; Schultz et al., 2006; Sinclair and Kannan, 2006). It has been ascribed to the widespread presence of polyfluoroalkyl precursors in incoming waste streams and subsequent microbial degradation throughout treatment processes. For instance, landfill leachates, which have been found to contain elevated levels of polyfluoroalkyl precursors (Benskin et al., 2012b; Huset et al., 2011), are often sent to WWTP for treatment. Similarly, levels of some PFAAs in groundwater were found higher than those in street runoffs, arising from the degradation of precursors when water infiltrates through soil columns (Murakami et al., 2009a, 2009b; Zushi and Masunaga, 2009; Zushi et al., 2008). Houtz and Sedlak (2012) recently demonstrated that the total concentration of C5–C11 PFCAs in urban runoff samples increased by a median of 69% after oxidative conversion, suggesting direct monitoring of perfluoroalkyl

acids could only account for part of the total PFASs present in urban runoff samples, while missing out precursors. Recently, Place and Field (2012) have identified ten classes of polyfluoroalkyl surfactants in AFFF formulations, and eight of the newly identified compounds have been detected in groundwater samples impacted by firefighting activities (Backe et al., 2013). Most of these newly identified PFASs have not been included in most monitoring studies, and their biodegradability remains largely unknown.

It is unpractical and technically very challenging to screen for the large number of polyfluoroalkyl compounds present in the environment; thus, by studying transformation processes of key polyfluoroalkyl precursors and identifying process-specific (natural degradation process-specific, and manufacturing process-specific) marker compounds, more information on PFAS precursors and their potential impact on the environment can be obtained. Such knowledge gap can be bridged by laboratory degradation studies as discussed in this review.

2. Methodology, sample preparation and chemical analysis

2.1. General experimental methodology

Laboratory investigation of microbial degradability of PFASs needs to be preceded with good understanding of physical and chemical properties of compounds of interest. Polyfluoroalkyl chemicals that have been investigated are generally poorly soluble in water and can significantly adsorb onto labware. Volatile loss from test solutions for some PFASs, such as FTOHs, perfluoroalkane sulfonamide alcohols and fluorotelomer methacrylates of high vapor pressures, can be significant (Dreyer et al., 2009a; Krusic et al., 2005; Wang et al., 2005b). Therefore, standardized biodegradability test methods such as those in the *OECD Guidelines for Testing of Chemicals* (OECD, 2006), which are more suitable for non-volatile and non-adsorbing compounds, need to be modified to minimize the mass loss. In the meantime, since PFASs have low oxygen demand and do not undergo complete mineralization, non-specific endpoints such as CO_2, dissolved organic carbon (DOC) and biological oxygen demand (BOD) are largely not applicable. Instead, chemical-specific analyses to identify biodegradation products and measure degradation kinetics are major tasks, which require extensive use of advanced analytical techniques such as mass spectrometry (Section 2.3). In addition, as a number of precursors defluorinate during biodegradation (Liu et al., 2010b; Wang et al., 2005a), monitoring fluoride ion generation could be a quick approach to indicate PFAS biodegradation and to estimate the extent of defluorination.

In any study on PFASs, the uses of fluoropolymers, such as polytetrafluoroethylene [PTFE, $-(CF_2CF_2)_n-$] and polyvinylidene fluoride [PVDF, $-(CH_2CF_2)_n-$] must be minimized during any stage of the work. Fluoropolymers may contain residual PFAAs, or PFASs to be tested may have high affinity for fluoropolymers to result in poor mass balance. For example, Wang et al. (2005b) found that a significant fraction of [3-^{14}C] 8:2 FTOH partitioned into the PTFE septa while degrading in a mixed bacterial culture. Partitioning of 6:2 FTOH into bottle rubber stoppers has also been found significant in *abiotic* soil vessels (Liu et al., 2010b), when about 52% 6:2 FTOH was recovered from vessel stoppers after 180 days. However, such mass loss to labware is less significant and can often be ignored when precursors actively degrade to non-volatile ionizable degradation products (Liu et al., 2010b).

2.2. Microcosms and microbes

Activated sludge from WWTPs has been commonly used as a source of microorganisms to test biodegradability of PFASs, either as the test medium (Rhoads et al., 2008), or used as an inoculum (Dinglasan-Panlilio, 2008; Lee et al., 2010). For the studies that used fluoride ion as an end point, dilution of activated sludge was required to reduce the high fluoride ion background (Liu et al., 2010b; Wang et al., 2005a). Bacterial culture inoculated with activated sludge could also be acclimated with compounds of interest to enhance biodegradation potential (Wang et al., 2005b). The origin of activated sludge was found critical in one study where 6:2 fluorotelomer sulfonic acid [6:2 FTSA, $C_6F_{13}CH_2CH_2SO_3H$] was found non-biodegradable in one activated sludge, but biodegradable in the sludge from a different WWTP (Wang et al., 2011).

Soil microcosms have been tested for fluorotelomer compounds under aerobic conditions (Dasu, 2011; Dasu et al., 2012; Liu et al., 2010b; Russell et al., 2008; Wang et al., 2009; Washington et al., 2009). As expected, biodegradation outcomes vary with the soil type and origin, aside from the chain length of the fluorotelomer-based precursors. Wang et al. (2009) observed that 8:2 FTOH was biodegradable in three aerobic soils tested, but the half-life (2–7 days) and the yield to PFOA (10–40%) varied significantly from soil to soil. The degradability of several polyfluorinated monomers and polymers also showed huge variations from soil to soil owing to different native microbial assemblies in the soils (Dasu, 2011; Royer, 2011; Russell et al., 2008). For instance, toluene-2,4-di-(8:2 FTOH urethane) [FTU, $(CH_3)C_6H_3(NHC(O)OCH_2CH_2C_8F_{17})_2$] did not degrade in an agricultural soil, but showed significant degradation in a forest soil, which presumably had higher fungal biomass (Dasu, 2011). Biodegradation of PFASs has also been demonstrated in sediment microcosms. Zhao et al. (2013) found that 6:2 FTOH was biodegraded in river sediment and Benskin et al. (2009) observed EtFOSE biodegradation in marine sediment. It is noted that the degradation outcomes vary substantially with different incubating matrix for the same compound. For example, when 6:2 FTOH was incubated with mixed bacterial cultures, PFHxA [PFHxA, $C_5F_{11}COOH$] was either observed as the more prominent degradation product or at least with much closer yields to PFPeA [PFPeA, C_4F_9COOH]; while the most prominent product was observed to be PFPeA when incubated with soil or sediment (Liu et al., 2010b; Zhao et al., 2012).

In addition to microbes originated from WWTPs and soil microcosms, a mixed bacterial culture started from contaminated aquifer materials was also found to be able to degrade 8:2 FTOH (Dinglasan et al., 2004). Very importantly, microbial degradation of several fluorotelomers was observed in pure bacterial cultures. Key et al. (1998) first reported that a *Pseudomonas* sp. bacterium desulfonated and defluorinated 6:2 FTSA to produce six fluorinated compounds. Liu et al. (2007) discovered that *Pseudomonas* sp. stains isolated from soils with octanol as the sole carbon source could biotransform 8:2 FTOH without prior acclimation. Kim et al. (2012, 2013) further demonstrated that alkane-oxidizing bacteria strains (*Pseudomonas* sp. and *Mycobacteriaum* sp.) and one fluoroacetate-degrading bacterium (*Pseudomonas* sp.) were capable of defluorinating 4:2, 6:2 and 8:2 FTOHs. No bacterial growth was found when FTOHs were the sole carbon source, indicating that such transformation by pure culture was likely via co-metabolic processes (Kim et al., 2012; Liu et al., 2007).

2.3. Test conditions

In aerobic biodegradation studies, an appropriate setup needs to ensure oxygen availability, while minimizing mass loss through sorption to labware or volatilization. Completely closed test vessels were chosen for minimal volatile loss (Dinglasan et al., 2004; Liu et al., 2010b; Wang et al., 2005a), but the trade-off was limited oxygen availability. Consequently re-aeration might be required especially for the microbial culture that had high oxygen demands or for long-term studies (Frömel and Knepper, 2010b). Rhoads et al. (2008) used pure oxygen to replace the air in headspace of a closed vessel to reduce the need for re-aeration. Semi-closed vessels, with vents attached to porous adsorbents to capture semi-volatile compounds, have been found effective in reaching satisfactory mass balance, while ensuring adequate oxygen (Zhao et al., 2013). Dynamic incubation systems, such as “flow-through” systems or “purge-and-trap” vessels, where air was continuously supplied and porous sorbents at air exits captured volatile compounds, proved to be equally effective (Lee et al., 2010; Liu et al., 2010a). Although it is unclear

Table 1
Summary of biodegradation of polyfluoroalkyl chemicals.

Precursors	Types of microbes or microcosms	Incubation conditions	Incubation duration	Estimated half-live ($t_{1/2}$)	Yields to PFCAs or PFASs[a]	References
Fluorotelomer alcohols						
8:2 FTOH	Activated sludge — diluted	Shaken closed vessels at 25-28 °C, using [3-^{14}C] 8-2 FTOH	28 d	n.a.[b]	PFOA: 2.1%	Wang et al. (2005b)
	Mixed bacterial culture	Shaken closed vessels using [3-^{14}C] 8-2 FTOH	90 d	n.a.	PFOA: 6%; PFHxA: 0.9%	Wang et al. (2005a)
	Bacterial enrichment culture	Shaken closed vessels	81 d	0.2–0.8 d	PFOA: 3%	Dinglasan et al. (2004)
	Aerobic soils	Static closed vessels using at 20-25 °C, using [3-^{14}C] 8-2 FTOH	7 months	<7 d	PFOA: 10 ~ 40%; PFHpA: <1% PFHxA: 1–4%	Wang et al. (2009)
	Aerobic soils	Flow-through system at 20-25 °C, using [3-^{14}C] 8-2 FTOH	28 d	<2 d	PFOA: 20%	Wang et al. (2009)
	Pseudomonas sp. bacteria enriched on octanol	Shaken closed vessels at 23 °C	67 d	n.a.	PFOA: 1%; PFHxA: 0.3%	Liu et al. (2007)
	Alkane-oxidizing Pseudomonas sp. bacteria	Shaken closed vessels	28 d	n.a.	PFHxA: 2.6%; PFBA: 0.62%	Kim et al. (2012)
6:2 FTOH	Mixed bacterial culture	Shaken closed vessels at 20-25 °C	90 d	<2 d	PFHxA: 5%; PFPeA: <0.5%	Liu et al. (2010b)
	Aerobic soils	Static closed vessels at 20–25 °C	180 d	<2 d	PFHxA: 8.1%; PFPeA: 30%; PFBA: 1.8%	Liu et al. (2010b)
	Aerobic soils	Flow-through system using [1,2-^{14}C2] 6:2 FTOH	84 d	<2 d	PFHxA: 4.5%; PFPeA: 4.2%; PFBA: 0.8%	Liu et al. (2010a)
	Aerobic river sediment	Shaken semi-closed vessels	100 d	<2 d	PFHxA: 8.4%; PFPeA: 10.4%; PFBA: 1.5%	Zhao et al. (2013)
	Alkane-oxidizing Pseudomonas sp. bacteria	Shaken closed vessels	28 d	n.a.	PFHxA: 2.8%; PFBA: 0.44%	Kim et al. (2012)
Fluorotelomer sulfonate						
6:2 FTSA	Activated sludge — diluted	Shaken closed vessels	90 d	>90 d	PFBA: 0.14%; PFPeA: 1.5%; PFHxA: 1.1%	Wang et al. (2011)
	Pseudomonas sp. enriched on difluoromethane sulfonate	Shaken closed vessels at 30 °C	5 d	n.a.	n.a.	Key (1996)
Fluorotelomer derivatives						
8:2 FTS	Aerobic soils	Static closed vessels at 22 °C	80–94 d	5–28 d	PFOA: 1.7–4.0%; PFHpA: 0.38–0.9%; PFHxA: 0.16%	Dasu et al. (2012, 2013)
8:2 TBC	Aerobic soils	Static closed vessels 22 °C	7 months	>7 months	n.a.	Dasu et al. (2013)
PAPs	Mixture of raw wastewater and sewage sludge	Purge-and-trap vessels	92 d	Varied widely	n.a.	Lee et al. (2010)
8:2 FTAC	Aerobic soils	Static closed vessels	105 d	3–5 d	PFOA: 8.4% (at 70 days); PFHpA: ~1%	Royer (2011)
	Microbial cultures inoculated with sludge	Shaken closed vessels	52 d	~2 d	n.a.	Dinglasan-Panlilio (2008)
8:2 FTMAC	Aerobic soils	Static closed vessels	105 d	15 d	PFOA: 10%; PFHpA: ~3%	Royer (2011)
	Microbial cultures inoculated with sludge	Shaken closed vessels	42 d	~1 day	n.a.	Dinglasan-Panlilio (2008)
HMU	Aerobic soils	Static closed vessels at 22 °C	180 d	>180 d	PFOA: 0.9%; PFHpA: 0.1% PFHxA: 0.1%	Dasu (2011)
	Microbial cultures inoculated with sludge	Shaken closed vessels	18 d	No degradation	No degradation	Dinglasan-Panlilio (2008)
FTU	Aerobic soils	Static closed vessels 22 °C	117 d	n.a.	PFOA[c]: 0.8%; PFHpA: <0.1% PFHxA: <0.1%	Dasu (2011)
FTEOs	WWTP unfiltered effluent	25 °C	Up to 48 d	~1 day	PFOA: 0.3%; PFHxA: 2.5%	Frömel and Knepper (2010b)
Perfluoroalkane sulfonamido derivatives						
EtFOSE	Activated sludge	Shaken vessels at 28 °C	35 d	≤2 d (low dose), 2-3 d (high dose)	PFOS: 7%; PFOA: 0.6%	Lange (2000)
	Activated sludge	Shaken vessels at 25 °C	4 d	4.2 d	PFOS: 0.6%	Boulanger et al. (2005)
	Activated sludge	Shaken closed vessels at 30 °C	10 d	0.7 d	n.a.	Rhoads et al. (2008)
	Marine sediment	Semi-closed vessels at 25 and 4 °C	120 d	44 d (25 °C) 160 d (4 °C)	PFOS: 12% (25 °C) and 0.44% (4 °C)	Benskin et al. (2013)
SAmPAP	Marine sediment	Semi-closed vessels at 25 and 4 °C	120 d	380 d (25 °C) 3400 d (4 °C)	n.a.	Benskin et al. (2013)
Side-chain fluorinated polymers						
	Aerobic soils		2 years		n.a.	Russell et al. (2008)

Table 1 (*continued*)

Precursors	Types of microbes or microcosms	Incubation conditions	Incubation duration	Estimated half-life ($t_{1/2}$)	Yields to PFCAs or PFASs[a]	References
Polyacrylate polymer		Static closed vessels at 20 °C		1200–1700 years		
Polyurethane polymer	Aerobic soils	Static closed vessels at 20 °C	2 years	24–281 years	PFOA: 0.6–1.7%	Russell et al. (2010)
Other polyfluoroalkyl chemicals						
8:2 oxetane	Microbial culture inoculated with activated sludge	Shaken closed vessels	13 d	No degradation	No degradation	Dinglasan-Panlilio (2008)
DTFA	Microbial culture inoculated with activated sludge	Static closed vessels, and a flowthrough system	49 d	n.a.	PFOA: 0.2%	Arakaki et al. (2010)

[a] Unless otherwise stated, the values reported are molar yields.
[b] Data or information is not available.
[c] The yields include contributions from both the test compound(s) and impurities.

whether limited oxygen can impact PFAS biodegradation pathways, it appeared that degradation kinetics was affected. For example, Dasu (2011) observed that accumulative production of PFOA reached a plateau from breakdown of polyfluoroalkyl urethane monomers after 65 days, and attributed it to the limited oxygen based on the observation of increased PFOA generation after soil re-aeration. Arakaki et al. (2010) observed faster generation of metabolites from 1H,1H,2H,2H,8H,8H-perfluorododecanol [DTFA, $C_3F_7CH_2C_5F_{10}CH_2CH_2OH$] with continuous aeration. It has been recommended that a minimal of 10% oxygen saturation can be a general reference to decide the need for re-aeration (Hurst et al., 1996; King et al., 1997).

Many test compounds have non-negligible impurities. Some impurities, such as FTOHs or fluorotelomer olefins [(n:2) FTOs, $C_nF_{2n+1}CH_2{=}CH_2$] present in fluorotelomer-based surfactants or polymers, could be problematic, because it would be difficult to differentiate the actual yields to PFCAs originated from test compounds as opposed to those generated from impurities (Russell et al., 2008; Washington et al., 2009). Lee et al. (2010) used air purging to remove volatile impurities from test materials when dissolved in aqueous solutions. When the test compounds were difficult to purify, 'molar mass balance' was applied to mathematically correct for the contribution of PFOA by impurities (Russell et al., 2008, 2010).

As there is no agreement of what constitutes an appropriate dosage for testing biodegradability of PFASs, a wide range of dosages have been used. The potential toxicity to microbial activities at high concentrations has not been reported to be an issue for PFASs. Dr. Berti at DuPont (personal communications) did not find any inhibition of microbial respiration exerted by 8:2 FTOH up to 2000 mg per liter in activated sludge. We have also examined the impact of 8:2 FTOH on soil microbial communities by monitoring the changes in microbial community structures, but did not find any observable change relative to soil controls even when 2000 mg 8:2 FTOH per kg-soil was applied (unpublished data).

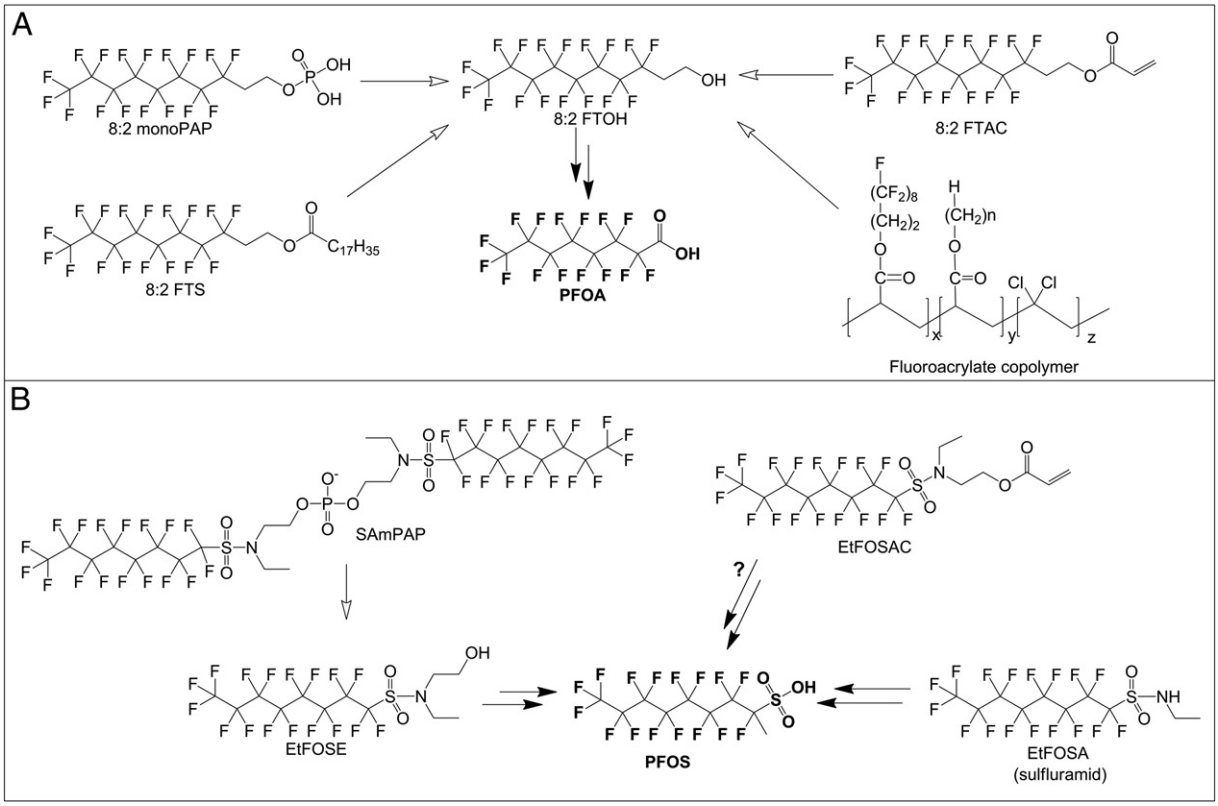

Fig. 1. Illustration of microbial degradation schemes for (A) selected 8:2 fluorotelomer derivatives and (B) selected perfluorooctane sulfonamide derivatives (only linear isomers are illustrated). Except for EtFOSAC and EtFOSA, the microbial degradation for the rest of polyfluoroalkyl precursors has been observed and summarized in Table 1. The biodegradation of EtFOSAC to form PFOS is only a hypothesis, and the biotransformation of EtFOSA in mammalian systems has been observed (Benskin et al., 2009). The initial hydrolysis reactions of ester bonds are shown in hollow arrows. The microbial degradation to form the PFAAs through complex pathways is shown in double solid arrows.

2.4. Sample extraction and processing methods

2.4.1. Headspace samples

For volatile precursors (e.g., FTOHs), their quantitative analysis in headspace of closed vessels is important in reaching satisfactory mass balance. Solid phase microextraction (SPME) coupled with gas chromatography and mass spectrometry (GC/MS) analysis has been tested for quantitation of 8:2 FTOH, 8:2 fluorotelomer acrylate [8:2 FTAC, $C_8F_{17}CH_2CH_2OC(O)CH{=}CH_2$] and 8:2 fluorotelomer methacrylate [8:2 FTMAC, $C_8F_{17}CH_2CH_2OC(O)C(CH_3){=}CH_2$] in the headspace of culture samples (Dinglasan et al., 2004; Dinglasan-Panlilio, 2008). This approach eliminated the use of organic solvents, but required the use of Henry's law constants of targeted compounds to calculate headspace concentrations. Alternatively, volatile compounds could be captured using C18 solid phase extraction (SPE) cartridges (Dasu et al., 2012; Liu et al., 2010a; Rhoads et al., 2008; Wang et al., 2009) or XAD resins (Lee et al., 2010). Both sorbents have been validated to be highly effective for air sampling of volatile and semi-volatile PFASs (Jahnke et al., 2007; Shoeib et al., 2008).

2.4.2. Sludge and bacterial culture samples

For compounds that are weakly sorbed to biomass or suspended solids in activated sludge or bacterial cultures, a liquid–liquid extraction is sufficient for quantitatively isolating the target analytes, such as the use of approximately equal volume of organic solvents (Frömel and Knepper, 2010b; Lee et al., 2010; Liu et al., 2010b; Wang et al., 2011). Solid phase extraction with C18 sorbents and an ion-pairing method have also been used (Boulanger et al., 2005; Lange, 2000; Lee et al., 2010). The ion-pairing method, commonly used for extracting PFCAs and PFSAs from biological matrices (Hansen et al., 2001), was adapted to extract strongly sorbing PFASs from liquid culture samples, such as 10:2 fluorotelomer phosphate monoester [10:2 monoPAP, $(O)P(OH)_2(OCH_2CH_2C_{10}F_{21})$], 6:2 diPAP, and long-chain polyfluorinated carboxylic acids, including C9–C11 PFCAs, 8:2 and 10:2 FTCAs and FTUCAs, 7:3 Acid [$C_7F_{15}(CH_2)_2COOH$] and 9:3 Acid [$C_9F_{19}(CH_2)_2COOH$] (Lee et al., 2010). In addition, lyophilization was used on whole sludge samples to remove liquid, and the resulting solids were then extracted in a similar fashion as soil or sediment samples (Rhoads et al., 2008).

2.4.3. Soil and sediment samples

A range of organic solvents has been tested for extracting test compounds and their biodegradation products from solid matrices, including acetonitrile, methanol, MTBE and ethyl acetate (Dasu et al., 2012; Liu et al., 2010b; Wang et al., 2009; Washington et al., 2008; Yu et al., 2009). Elevated temperatures (e.g. 50 °C) were used in a few studies to enhance recoveries (Liu et al., 2010b; Wang et al., 2009). Alkaline treatment (e.g., NaOH) can assist breaking strong interactions (presumably via covalent bonds) of PFASs with natural organic matter, to enhance recoveries (Liu et al., 2010b; Wang et al., 2009); however, its use should be carefully evaluated for the compounds with hydrolysable function groups (e.g., an ester group) to minimize experimental artifacts. Though such base-catalyzed hydrolysis could affect fluorotelomer stearate monoesters [(n:2) FTS, $FTC_{17}H_{35}C(O)OCH_2CH_2C_nF_{2n+1}$] and citrate triesters [(n:2) TBC, $HOC(C(O)OCH_2CH_2C_nF_{2n+1})(CH_2C(O)OCH_2CH_2C_nF_{2n+1})_2$] (Liu, 2007), it appeared to have little impact on 8:2 monoPAP and diPAP (D'eon and Mabury, 2007b), polyfluorinated amides (Jackson et al., 2013) or polyfluorinated acrylate and urethane polymers of high molecular weights (Russell et al., 2008, 2010). In addition, rare solvent-enhanced hydrolysis has been observed during the extraction of 8:2 FTS from soils, even in the absence of a base (Dasu et al., 2010). Solvents with high dielectric constants (e.g., acetonitrile or methanol) were found to increase hydrolysis by an order of magnitude compared to less polar solvents such as MTBE and ethyl acetate (Dasu et al., 2010). In addition, Washington et al. (2008) developed a multi-step extraction and cleanup method to achieve complete recovery and minimization of matrix effects in LC/MS/MS analysis. Their resulting method involved alkaline pre-treatment, extraction with acetonitrile and water, ion-pairing extraction, evaporation and reconstitution in clean solvents (Washington et al., 2008).

The choice of extraction methods and the number of sequential extractions need to be carefully evaluated prior to and during microbial degradation studies. It is noted that 'spike and recovery' tests using sterilized *abiotic* samples cannot reflect the real recoveries for *biotic* environmental samples, which generally show much lower recoveries because of irreversible sorption, unknown degradation products, or formation of bound residues. Some issues during quantitative LC/MS/MS analysis can confound the results of recoveries; in particular, matrix effects can lead to underestimation or overestimation of the levels of target analytes. When radiolabeled test compounds are available, total extraction efficiency in *biotic* environmental samples can be better evaluated. Liu et al. (2010a) were able to quantitatively compare the soil extraction efficiencies of [1,2-$^{14}C_2$] 6:2 FTOH using two extraction methods. However, such radiolabeled standards are not widely available for most PFASs. In addition, as PFAAs are the critical end points of precursor degradation, their recoveries must be adequately assessed. Most of the PFAAs evaluated showed good recoveries (75%–125%) irrelevant of soil (or sediment) aging (Higgins et al., 2005; Liu et al., 2010b; Russell et al., 2008). For instance, the reported recoveries were 95–113% for C4–C7 PFCAs (Liu et al., 2010b), 80–98% for C8–C11 PFCAs (Higgins et al., 2005), 72–119% for C8–C11 PFCAs (Russell et al., 2008) and 81–87% for PFOS (Higgins et al., 2005). C12–C13 PFCAs were shown to have relatively lower recoveries of 61–80% (Higgins et al., 2005). It should be noted that the extraction methods discussed so far are not correlated with bioavailability, which has not been a focus in those studies.

2.5. Analytical methods

Mass spectrometry (MS) is the most essential tool for quantitative and qualitative analysis of PFASs, especially preceded by liquid chromatography (LC) separation, as discussed by Berger et al. (2004), Voogt and Sáez (2006) and Frömel and Knepper (2008, 2010a). This section highlights a few selected analytical methods for analysis of precursors and some degradation products.

2.5.1. Quantitative analysis

As the most studied precursors, FTOHs can be analyzed using either GC/MS or high performance liquid chromatography coupled with tandem mass spectrometry (LC/MS/MS). During GC/MS analysis, FTOHs could be detected under electron impact (EI) or chemical ionization (CI) (Dinglasan et al., 2004; Martin et al., 2002). The advantages of using LC/MS/MS for FTOHs include good compatibility with aqueous samples and polar organic solvents, and the possibility of analyzing all the analytes (FTOHs and their ionic degradation products) in a single run, in which FTOHs are detected as FTOH-acetate adducts (Szostek et al., 2006). An alternative LC/MS/MS method used an ethanolamine-modified mobile phase to minimize FTOH-acetate adduct formation to enhance FTOH ionization efficiency (Liu et al., 2007). Some of the neutral derivatives of FTOHs can be detected with GC/MS, such as 8:2 FTS, 8:2 FTAC and 8:2 FTMAC under EI or positive CI (Dasu, 2011; Royer, 2011). LC/MS/MS has also been demonstrated for quantitation of 8:2 TBC, 8:2 FTU and hexamethylene-1,6-di(8:2 fluorotelomer urethane) [HMU, $C_8F_{17}CH_2CH_2OC(O)NH(CH_2)_6NHC(O)OCH_2CH_2C_8F_{17}$] (Dasu, 2011) under positive atmospheric pressure chemical ionization mode, and fluorotelomer phosphate esters (PAPs) under negative electrospray ionization (Lee et al., 2010).

2.5.2. Identification of degradation products

Elucidation of degradation products with high resolution mass spectrometry, the use of LC/ARC (accurate radioactivity counting) technique and the availability of in-house synthesized transformation products have contributed to establishing the novel pathways described in Section 3 (Lee et al., 2010; Liu et al., 2010b; Wang et al., 2009; Wang

et al., 2012). Although triple quadruple MS under unit resolution can be used for tentative structural elucidation of degradation products (Martin et al., 2009), the increasing availability of high-resolution MS provides higher confidence in determining the empirical molecular formula of degradation products (Lee et al., 2010; Liu et al., 2010b; Wang et al., 2009, 2012). Another new technique that has proven to be useful is LC/ARC when radiolabeled test compounds are used (Liu et al., 2010a). The technique can accurately detect and quantitate low-level radioactivity without sample pre-concentration. When used in parallel to high-resolution MS, LC-ARC has been demonstrated to successfully reveal the previously unknown degradation products even present in low levels (Liu et al., 2010a; Wang et al., 2009).

2.5.3. Reduction of matrix effect

The potential matrix effects during LC/MS/MS analysis of PFASs in complex environmental matrices, particularly with electrospray ionization, can be greatly mitigated through effective sample cleanup such as the use of dispersed black carbon (e.g. ENVI-Carb^{TM}) as recommended by Powley et al. (2005). The efficacy has been further validated with solvent extracts of soil, sediment and biosolid samples (Sepulvado et al., 2011; Wang et al., 2009; Yu et al., 2009). The ion exchange sites on the black carbon should be blocked to prevent mass loss of the ionic analytes (Powley et al., 2005). In addition, as discussed in Section 2.4, a multiple-step extraction and cleanup method developed by Washington et al. (2008) was found effective, though quite laborious, for reducing matrix effects. Furthermore, isotope enriched internal standards are indispensable for further correcting for matrix effects, and selecting appropriate internal standards should be an integral part of analytical method development (Higgins et al., 2005; Washington et al., 2007).

3. Biotransformation pathways and mechanisms

There is a sizable body of literature on the biological and chemical cleavage of carbon–fluorine (C–F) bond in the environment prior to the burgeoning research on PFASs. Most of the past work concerns organic chemicals with one fluorine atom and fluorine-containing aromatic compounds (Key et al., 1997; Natarajan et al., 2005; Neilson and Allard, 2002). Parsons et al. (2008) and Frömel and Knepper (2010a) have provided comprehensive reviews on earlier studies on biodegradation of PFASs, and the thermodynamics of microbial defluorination has especially been discussed by Parsons et al. (2008). The current review reveals some intriguing and previously unknown mechanisms of C–F cleavage based on a number of newly published studies, and provides a comprehensive summary of qualitative and quantitative relationships between degradation of precursors and generation of PFAAs.

3.1. Biodegradation of fluorotelomer-based precursors

3.1.1. Aerobic microbial degradation of fluorotelomer alcohols

The aerobic biodegradation of FTOHs, especially those of 8:2 and 6:2 FTOHs, have been well studied (Dinglasan et al., 2004; Liu et al., 2010b; Wang et al., 2005a, 2009, 2012). The comprehensive pathways for 8:2 FTOH biodegradation in aerobic soil are illustrated in Fig. 2. The previously unknown pathways were evidenced by the generation novel degradation products such as 7:2 fluorotelomer secondary alcohol (7:2 sFTOH, $C_7F_{15}CH(OH)CH_3$) and 7:3 Acid. Defluorination occurred in multiple reaction steps, mostly due to microbial actions. It was noted that defluorination of 8:2 FTCA to form 8:2 FTUCA, could occur not only biotically, but also abiotically during sample extraction or storage (in the presence of a base and also affected by the basicity of storage glassware) (Wellington Laboratories, 2012). In addition to PFOA, perfluoroheptanoic acid [PFHpA, $C_6F_{13}COOH$] and PFHxA were produced from removal of one and two perfluorocarbons, respectively, suggesting that the perfluoroalkyl carbon chain can be partially mineralized (Wang et al., 2009).

Though β-oxidation is known for hydrocarbon fatty acid metabolism, the mechanism does not seem to be able to explain the aerobic microbial degradation of 8:2 FTOH (Fig. 2). Instead, the conversion of 8:2 FTCA or 8:2 FTUCA to PFOA demonstrated novel "one-carbon removal pathways", where 8:2 FTUCA was first converted to 7:2 sFTOH, and to eventually produce PFOA and CO_2 (Wang et al., 2005a, 2009). The proton deficiency on the α-carbon of 8:2 FTUCA suggests that it cannot be utilized as a substrate for β-oxidation. In the meantime, α-oxidation, which has been commonly observed in animal-based biotransformation

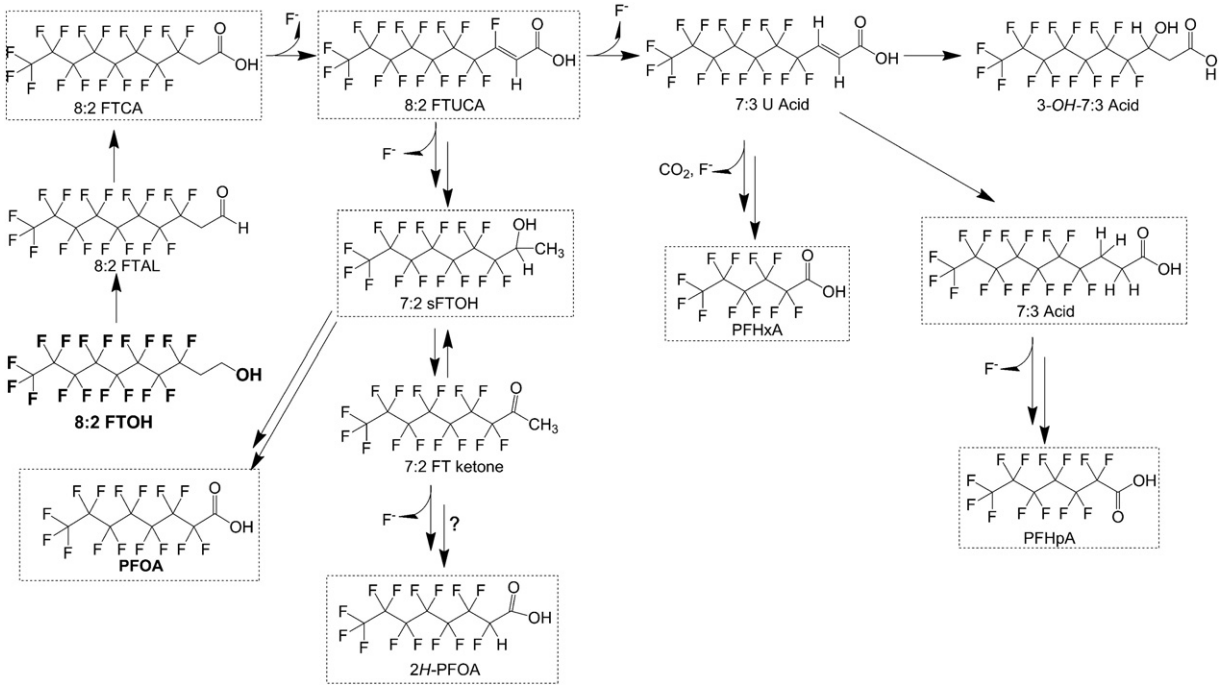

Fig. 2. Aerobic biodegradation pathways of 8:2 FTOH in soil. The double arrows indicate multiple transformation steps. Defluorination reactions are indicated by release of fluoride ions (F^-). Stable and semi-stable compounds are shown inside dashed boxes. *2H*-PFOA has been proposed, but it has not been successfully validated as a PFOA degradation product. Modified from Wang et al. (2009).

studies for the generation of perfluorononanoic acid [PFNA, $C_8F_{17}COOH$] (Butt et al., 2010a, 2010b; Fasano et al., 2006, 2009; Henderson and Smith, 2007; Kudo et al., 2005; Martin et al., 2005; Nabb et al., 2007), has not been confirmed in aerobic soil, activated sludge or bacterial culture (Dinglasan et al., 2004; Liu et al., 2007; Wang et al., 2005a, 2005b, 2009). Martin et al. (2005) suggested that the rapid HF elimination to form 8:2 FTUCA in microbial culture was likely to supersede 8:2 FTCA α-hydroxylation, which is necessary for α-oxidation.

Despite of high number of fluorine atoms, the observed half-lives of 8:2 FTOH ranged from <2 days to 30 days in laboratory studies (Dinglasan et al., 2004; Liu et al., 2007; Wang et al., 2005a, 2005b, 2009) (Table 1). The generation of PFOA proceeds much slower, likely caused by the rate limiting step of 7:2 sFTOH biodegradation (Wang et al., 2009). The molar yield of PFOA (Table 1) ranged from 0.5% in a pure bacterial culture (Liu et al., 2007) to 40% in one aerobic soil (Wang et al., 2009), suggesting that 8:2 FTOH could be a very significant PFOA precursor in some environmental compartments.

The novelty of aerobic biodegradation of FTOHs was further demonstrated by 6:2 FTOH. The biodegradation pathways of 6:2 FTOH (Fig. 3) were similar to those of 8:2 FTOH, but differed in the types and yields of terminal products. 6:2 FTOH showed greater defluorination potential than 8:2 FTOH in aerobic soil (Liu et al., 2010b). As illustrated in Figs. 2 and 3, 7:2 sFTOH (a major degradation intermediate from 8:2 FTOH) degraded to PFOA after the loss of one carbon (Wang et al., 2009), while the analogous 5:2 fluorotelomer secondary alcohol [5:2 sFTOH, $C_5F_{11}CH(OH)CH_3$], a degradation intermediate from 6:2 FTOH, degraded to PFHxA and PFPeA after the loss of one and two carbons, respectively. The yields of PFPeA (Table 1) ranged from <0.5% in mixed bacterial culture (Liu et al., 2010b), to 10.4% (Zhao et al., 2012) in aerobic river sediment and to 30% in aerobic soil (Liu et al., 2010b). The higher biodegradability of 5:2 sFTOH relative to 7:2 sFTOH, or 6:2 FTOH relative to 8:2 FTOH was attributed to the smaller size and higher water solubility of a shorter fluorinated carbon chain to result in higher bioavailability.

The higher degradation or defluorination potential of 6:2 FTOH was also demonstrated by the further degradation of one of its major degradation products, 5:3 Acid [$C_5F_{11}(CH_2)_2COOH$] (Wang et al., 2012). 5:3 Acid was found to extensively biodegrade in activated sludge via the "one-carbon removal pathways" (Fig. 3) to form shorter-chain carboxylic acids as 4:3 Acid [$C_4F_9(CH_2)_2COOH$], 3:3 Acid [$C_3F_7(CH_2)_2COOH$], PFPeA and Perfluorobutanoic acid [PFBA, C_3F_7COOH] as illustrated in Fig. 3 (Wang et al., 2012). However, 5:3 Acid was observed to be persistent in aerobic soil biodegradation experiments (Liu et al., 2010a, 2010b). In contrast, 7:3 Acid has been shown to be very persistent both in activated sludge and aerobic soil, partly due to its stronger binding to organic matter, which results in its low bioavailability and biodegradability (Wang et al., 2009, 2012). Very recently, Kim et al. (2013) revealed that multiple factors including bacterial types, reducing energy sources, and enzyme inducer affected the pathways and extent of 6:2 FTOH biodegradation into shorter-chained PFCAs in pure bacterial strains.

Based on the differences in 6:2 and 8:2 FTOH biodegradation, increasing defluorination with the decrease of a molecular size is expected for other FTOHs. Kim et al. (2012) demonstrated the higher defluorination potential in 4:2 FTOH when compared to 6:2 and 8:2 FTOHs based on fluoride ion generation, but no information is yet available on the types of new degradation products produced.

3.1.2. Anaerobic microbial degradation of fluorotelomer alcohols

Anaerobic biodegradability of 6:2 and 8:2 FTOHs has only been recently reported in one peer-review study (Zhang et al., 2013). In WWTP digester sludge under methanogenic conditions, FTOHs were degraded to mainly polyfluoroalkyl acids, such as FTCAs, FTUCAs and x:3 Acids at much slower rates compared to aerobic conditions. The generation of PFAAs was shown to be inefficient, and only ≤0.4% of 6:2 FTOH and 0.3% of 8:2 FTOH were degraded to PFHxA and PFOA, respectively, suggesting that FTOHs are likely insignificant sources to PFAAs anaerobically. A newly identified degradation intermediate, 3-fluoro 5:3 acid [$F(CF_2)_5CFHCH_2COOH$] was also reported. More studies are needed to understand the anaerobic biodegradability of FTOHs and related compounds.

3.1.3. Fluorotelomer sulfonate

6:2 FTSA, which has been observed in contaminated groundwater impacted by firefighting activities (Schultz et al., 2004), has been demonstrated to biodegrade under aerobic conditions in activated sludge (Wang et al., 2011). The degradation started with de-sulfonation of 6:2 FTSA to form 6:2 flurotelomer aldehyde [6:2 FTAL, $C_6F_{13}CH_2CHO$] while releasing a sulfonate (HSO_3^-), bypassing the formation of 6:2 FTOH. The biodegradation pathways from 6:2 FTAL then followed the major pathways observed in 6:2 FTOH (Wang et al., 2011). However, the reactions proceeded much slower with a long half-life (>90 days compared to <2 days for 6:2 FTOH) and a lower yield of total terminal products (2.5% compared to 55% for 6:2 FTOH), suggesting that 6:2 FTSA is much more persistent in the environment. The aerobic biodegradability of 6:2 FTSA has also been demonstrated under a sulfur-limiting condition by a *Pseudomonas* sp. bacterium (Key et al., 1998).

3.1.4. Fluorotelomer stearate and citrate esters

The biodegradability of FTOH-derived surfactants and polymers largely depends on microbial or chemical stability of the chemical linkages. The size of a molecule also affects the biodegradability or biodegradation kinetics as detailed in this section. The initial degradation step of the most fluorotelomer-based compounds is expected to be microbially-mediated or chemical hydrolysis of the hydrolysable functionalities (ester, urethane, etc.) to release FTOHs, and such has been demonstrated by most fluorotelomer derivatives (Fig. 1 and Table 1).

Used in water and oil-repellent textiles (Oharu, 2000; Wu, 1994), 8:2 FTS with one ester bond (Fig. 1A) and 8:2 TBC with three ester bonds were tested for biodegradability, and were found to undergo microbially-mediated hydrolysis in aerobic soils. The resulting 8:2 FTOH then followed typical biodegradation pathways to form a range of polyfluoroalkyl and perfluoroalkyl acids (Fig. 2) (Dasu, 2011; Dasu et al., 2012; Liu, 2007; Royer, 2011). The observed soil half-life of 8:2 FTS during the early stage of incubation varied between 5 to 28 days (Dasu et al., 2012). In comparison, 8:2 TBC with a 'bulky' structure was much more persistent with a half-life of more than 7 months, suggesting a higher molecular weight, or a bulky structure, stabilized hydrolysable functionalities, and subsequently increased the stability of the whole PFAS molecule.

3.1.5. Fluorotelomer phosphate esters

PAPs have been used for grease-proofing food packaging (Begley et al., 2005; D'eon and Mabury, 2007a; Trier et al., 2011; United States Food and Drug Administration, 2003). Aerobic biodegradation of 4:2, 6:2, 8:2 and 10:2 mono-substituted PAPs [n:2 monoPAP, $(O)P(OH)_2OCH_2CH_2C_nF_{2n+1}$, n = 4, 6, 8 and 10] and 6:2 diPAPwere evaluated in WWTP mixed liquor (Lee et al., 2010). The initial degradation step was observed to be the microbially-mediated hydrolysis of the phosphate ester bonds to release FTOHs, which were further broken down to their characteristic degradation products. Complex dynamics in the test systems involving multiple degradation steps and sorption to matrix solids confounded interpretation of the observed degradation kinetics of 6:2 diPAP and 6:2 monoPAP (Lee et al., 2010). The fact that more 6:2 FTOH was detected as a result of 6:2 diPAP degradation did not rule out the possibility that that 6:2 diPAP was hydrolyzed at higher rates in the study. In fact, faster hydrolysis for phosphate diesters than the monoesters was observed by Wolfenden et al. (1998), and speculated to be caused by differences in activation energies of esters for enzymatic degradation. For the monoPAPs with different perfluoroethyl moieties, the rate of ester bond hydrolysis showed a clear decreasing trend with

the increasing chain length of the perfluoroethyl moiety (Lee et al., 2010). For example, the generation of 4:2 FTOH from 4:2 monoPAP was almost completed in one day, but the generation of 10:2 FTOH from 10:2 monoPAP was not completed by the end of 92-day incubation (Lee et al., 2010).

3.1.6. Fluorotelomer acrylate and methacrylate

Flurotelomer acrylate and methacrylate monomers are used to synthesize polymers of high molecular weights that are widely used as stain resistant coatings (Russell et al., 2008). The stability of 8:2 FTAC and 8:2 FTMAC monomers were evaluated in aerobic soils and activated sludge (Dinglasan-Panlilio, 2008; Royer, 2011). Similar to the above discussed compounds, 8:2 FTAC and 8:2 FTMAC underwent initial microbial hydrolysis to release 8:2 FTOH (Dinglasan-Panlilio, 2008; Royer, 2011). The observed half-life in aerobic soils was 3–5 days for 8:2 FTAC and 15 days for 8:2 FTMAC (Royer, 2011). It appeared that the addition of a methyl group to the acrylate moiety added sufficient bulk to cause some steric hindrances or elicit electronic differences

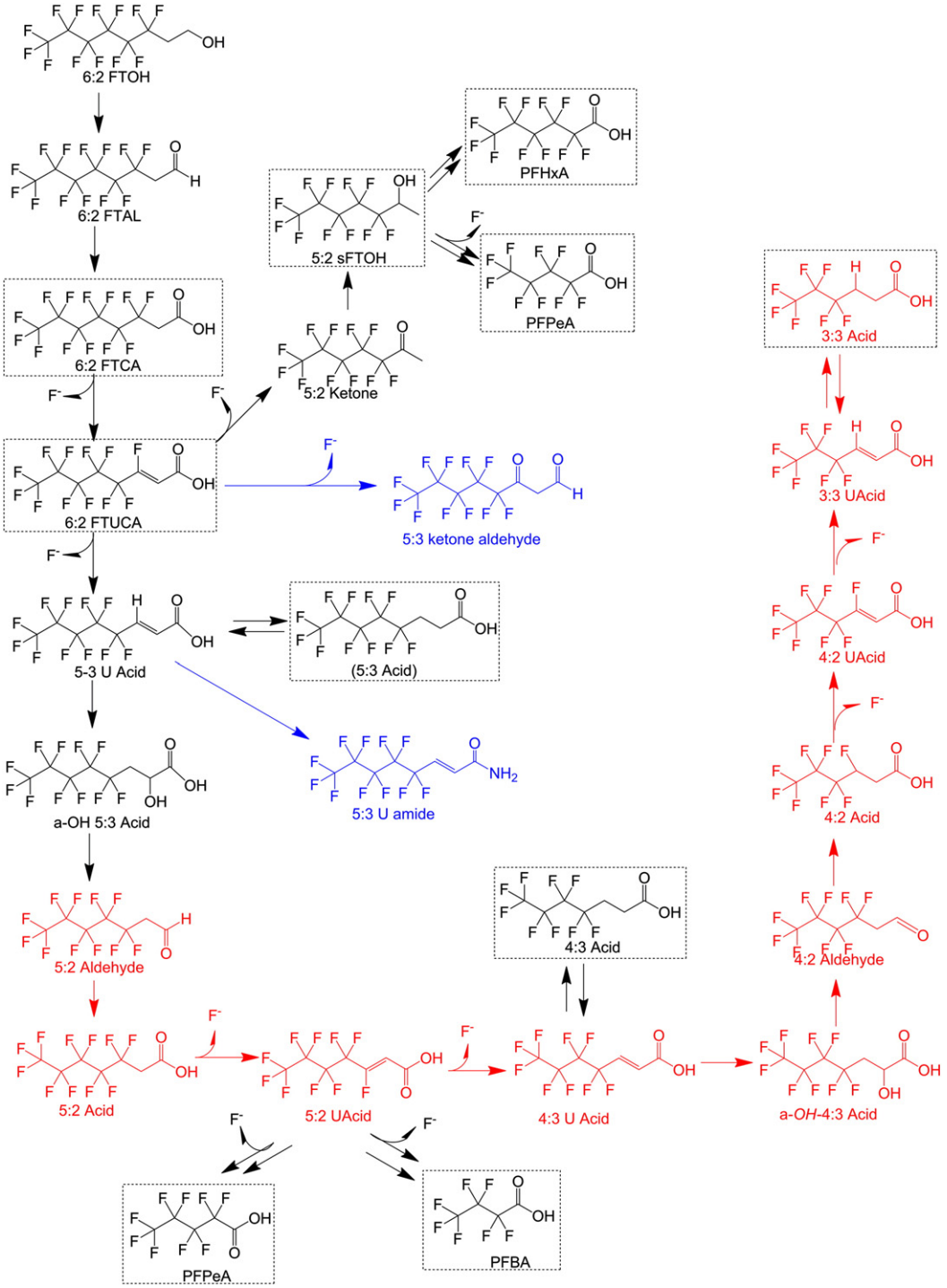

Fig. 3. Aerobic biodegradation pathways of 6:2 FTOH in activated sludge and aerobic soils. The double arrows indicate multiple transformation steps. Defluorination reactions are indicated by release of fluoride ions (F^-). Blue pathways have been observed only in soil (Liu et al., 2010b), while red pathways have been observed only in sludge (Wang et al., 2012). Stable and semi-stable compounds are shown inside dashed boxes.
Modified from Wang et al. (2012) and Liu et al. (2010b).

that could have led to the slower microbially-mediated ester cleavage in 8:2 FTMAC (Royer, 2011). The yields to PFOA in soil appeared significant, about 7.8 mol% at 34 days from 8:2 FTAC, and 10 mol% at 105 day for 8:2 FTMAC (Royer, 2011). The fast degradation of both compounds was also observed in microbial cultures inoculated with activated sludge with half-lives less than 2 days (Dinglasan-Panlilio, 2008).

3.1.7. Fluorotelomer urethanes

Urethane bond is another type of linkage commonly used for creating fluorotelomer-based urethane polymers that are commercially used as stain and soil repellent in textiles (Russell et al., 2010). Though microbial hydrolysis of the urethane linkage (– NH – (C═O) –) would be similar to other ester-containing PFASs, greater stability of the urethane bond was reported (Dasu, 2011; Dinglasan-Panlilio, 2008). Dasu (2011) compared the biological stability of urethane linkages between an aromatic diurethane (8:2 FTU) and an aliphatic diurethane ester (8:2 HMU) in aerobic soils. Both compounds underwent biodegradation to some extent in a forest soil, but 8:2 FTU with the urethane linkages connected to an aromatic ring showed higher resistance to hydrolysis. The generation of PFOA from both compounds did not exceed to 1.0% of the initial mass at the end of 117-d incubation. In addition, the biodegradability of a HMU mixture including 6:2 and 8:2 perfluoroethyl moieties was evaluated with a mixed culture inoculated by activated sludge (Dinglasan-Panlilio, 2008), but no degradation of HMU was confirmed, likely due to lower microbial activities as compared to the aerobic soils discussed above.

3.1.8. Fluorotelomer ethoxylates

Fluorotelomer ethoxylates are another important class of non-ionic fluorinated surfactants. Aerobic biodegradation of a mixture of fluorotelomer ethoxylates (FTEO, $F(CF_2CF_2)_x(CH_2CH_2O)_yH$, x = 4, 6, …, 12; y = 0–18) in WWTP unfiltered effluent was reported by Frömel and Knepper (2010b). Because of the complex composition, only the FTEOs with perfluoroalkyl chain length of 6 and 8 and a degree of ethoxylation between 0 and 13 were monitored in the study. These FTEOs underwent rapid biotransformation with half-life of about 1 day, and the high biodegradability was attributed to the biodegradable polyethoxylate chains. The major products observed were FTEO carboxylates [FTEOC, $F(CF_2CF_2)_x(CH_2CH_2O)_{y-1}CH_2COOH$], but the shorter FTEOCs (y < 9) did not seem to further degrade. It was proposed that biodegradation started from shortening of the ethylate groups through an oxidation to the respective aldehydes, and then followed by second oxidation to form FTEO carboxylates (Frömel and Knepper, 2010b).

3.2. Biodegradation of perfluoroalkane sulfonamido derivatives

3.2.1. N-ethyl perfluorooctane sulfonamidoethanol

EtFOSE was an important product of electrochemical fluorination. It was used to synthesize downstream products such as phosphate esters, which later were employed to manufacture paper protectors (3M, 1999). Similarly to FTOHs, EtFOSE biodegradability impacts the degradability of its derivatives. The aerobic biodegradation of EtFOSE as a PFOS precursor in (diluted) activated sludge has been investigated by Boulanger et al. (2005), Rhoads et al. (2008) and Lange (2000). Benskin et al. (2009) investigated its biodegradation in marine sediment under aerobic conditions. The aerobic biodegradation pathways proposed are illustrated in Fig. 4. All studies have found EtFOSE prone to biodegradation and the major difference was kinetics. As the rate limiting step was degradation of EtFOSAA, consequently, EtFOSAA turned out to be the major degradation product, rather than PFOS. The significant presence of EtFOSAA in landfill leachate and sediment seems to support the finding of laboratory investigations (Benskin et al., 2012b; Higgins et al., 2005; Huset et al., 2011). There were only slight variations of pathways observed. Rhoads et al. (2008) suggested that EtFOSA could undergo direct dealkylation to form FOSA as shown in Fig. 4. Lange (2000) proposed that PFOA could be formed from perfluorooctane sulfinic acid (PFOSI, $C_8F_{17}SO_2H$) through an abiotic one-electron transfer mechanism (Hu et al., 1990), but later studies (Benskin et al., 2013; Rhoads et al., 2008) did not find PFOA to be a degradation product. It is likely that the study done by Lange was conducted at a time when the extent of the interference caused by chemical residuals or background signals (PFOA in this case) was not fully acknowledged, potentially confounding the interpretation of biodegradation experiments.

3.2.2. EtFOSE-based phosphate diester

EtFOSE-based derivatives have not been widely studied probably due to the early phase-out of these products by their major manufacturer, and lack of high-purity chemical standards. SAmPAP diester, an EtFOSE-based phosphate diester, is structurally analogous to fluorotelomer PAPs, and was a high production-volume chemical until 2002 (Benskin et al., 2013). Though a similar hydrolysis reaction was expected for SAmPAP as fluorotelomer-based PAPs (Section 3.1.5), SAmPAP diester was found to be highly recalcitrant to microbial degradation in marine sediments in a laboratory setting (Benskin et al., 2013). The poor biodegradability was attributed to the strong sorption to particulate matter as determined by the large molecular size and high hydrophobicity, as well as the general low microbial activities of sediment (Benskin et al., 2013). The long half-lives (more than 380 days at 25 °C and much longer at 4 °C) in part explains the observed elevated levels of SAmPAP in marine sediments despite its phase-out more than a decade ago (Benskin et al., 2012a). Though SAmPAP is not expected to be a significant PFOS precursor in marine sediments owing to slow microbial biodegradation, its biotranformation potential to form PFOS in benthic biota is largely unknown. In vitro metabolism of SAmPAPs has been shown to produce PFOS by rats and human hepatocytes (Mulvana and Henion, 1996).

3.3. Side-chain fluorinated polymers

Side-chain fluorinated polymers refer to those polymers with polyfluoroalkyl or perfluoroalkyl chains attached to non-fluorinated backbones (Buck et al., 2011). As they represent a high percentage of all PFAS sale products, more than 80% in the case of fluorotelomers (Buck, 2004), understanding their biodegradation potential is crucial for predicting the environmental safety of commercial and industrial products incorporating those polymers. Russell et al. (2008) investigated the biodegradation of a high molecular weight (~40,000 amu, 100–300 nm in diameter) polyacrylate polymer aqueous dispersion product in four aerobic soils during two years. Fig. 1A illustrates the polymer product with 8:2 perfluoroethyl moiety. Since no analytical method was available to directly examine the polymer itself, the only way to determine its biodegradability was through monitoring suspected products of degradation such as 8:2 FTOH, 7:2 sFTOH, 8:2 FTCA, 7:3 Acid, 8:2 FTUCA, and PFOA. Longer chained PFCAs, such as PFNA, perfluorodecanoic acid [PFDA,$C_9F_{19}COOH$], perlfuoroundecanoic acid [PFUnDA, $C_{10}F_{21}COOH$], were also monitored because of the presence of 10:2 and 12:2 perfluoroethyl moieties and their likely breakdown. The measured degradation intermediates were consistent with the proposed degradation pathway for the initial cleavage of the ester bond on the fluoroacrylate moiety to release FTOHs. However, when only characteristic products of 8:2 FTOH were analyzed, there exists the possibility that some type of degradation could have happened and went undetected, such as the breakage of the carbon backbone. Two approaches were used to interpret the results and to estimate the half-life of the polymer. The “molar mass balance” approach showed no evidence that the polymer was degrading because PFOA generated was mostly accounted for by impurity (residual non-polymerized PFAS) degradation. The kinetic modeling approach, based on the data of PFOA, estimated half-lives of the polymer to be around 1200–1700 years among the four soils tested. Russell et al. (2010) further investigated the biodegradation of a low molecular weight (~3500 amu) polyurethane polymer product using a similar approach. Higher

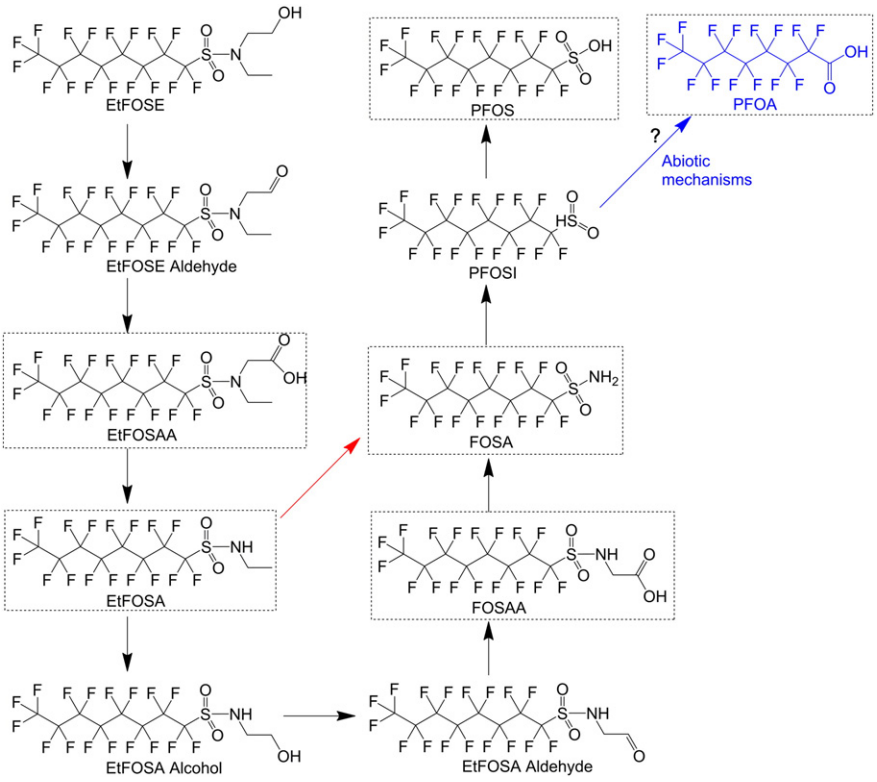

Fig. 4. Aerobic biodegradation of EtFOSE in activated sludge. Blue pathway was observed only by Lange (2000), while red pathway was observed only by Rhoads et al. (2008). Stable and semi-stable compounds are shown inside dashed boxes. PFOA detection might have been due to residuals.
Modified from Lange (2000) and Rhoads et al. (2008).

biodegradability compared to the polyacrylate polymer was demonstrated, as the levels of PFOA produced were several orders of magnitude greater than what the impurities could account for. Through kinetic modeling on PFOA data, the half-lives of the polyurethane polymer were estimated to range from 28 to 241 years among the four test soils.

The biodegradability of polyacrylate polymer in a solid particle form (~300 μm in diameter) in aerobic soil was examined by Washington et al. (2009). The polymer was much more purified compared to the one used by Russell et al. (2008), yet it still contained low levels of impurities. Based on the experimental data on PFOA, the polymer was estimated to have a half-life of 870–1400 years, which were in the same order of magnitude as the estimate by Russell et al. (2008). Furthermore, Washington et al. (2009) extrapolated based on the theory of surface-mediated degradation of polymer to give estimated half-lives of about 10–17 years for finely grained polymers as used in Russell et al. (2008).

Given the great discrepancy of two studies on half-life prediction, further research is clearly needed to clarify the contributions of polyfluoroalkyl polymers to PFCAs. Several key issues arising from the studies need to be addressed. First, since impurities such as FTOHs, PFCAs, monomers, and FTI greatly complicate data interpretation, their levels should be reduced as much as possible. Second, the issue of poor polymer solubility in organic solvents was raised by Washington et al. (2009) as a likely cause for poor recovery of PFOA. It is likely to be problematic when the study material is a polymer with a diameter of 300 μm and poor solubility; however, it is unclear if solubility could be an issue for the polymer dispersion (100–300 nm in diameter) that has been solubilized prior to dosing (Russell et al., 2008). Therefore, the way in which a polymer of interest is prepared, dosed and extracted needs careful consideration and further validation. Third, it remains unclear if the theory of surface-mediated degradation of polymer can be used for data interpretation and extrapolation. The theory was used by Washington et al. (2009), but no reference was provided to justify the theory. The question is not only important for experimental design and data interpretation, and also critical for understanding the half-life of the polymers embedded in commercial products, which are likely to be of different sizes from those used in laboratory studies. Another issue that has been little discussed is what constitutes a reasonable time frame to test biodegradability of high molecular weight polymers, whose half-lives are likely to be much longer than the duration of a biodegradation experiment. When data collected during a short time frame (such as two years in previous studies) is used to extrapolate for a half-life likely in the magnitude of a thousand years or longer, big uncertainty is sure to rise. A possible solution is to test the biodegradability and half-life of model polymers with similar chemistry but lower molecular weights, and then use the information to extrapolate the half-life of high molecular weight polymers.

3.4. Other polyfluoroalkyl chemicals

Several studies explored structure–degradability relationships of the PFASs that currently are not commercially available. Arakaki et al. (2010) tested the biodegradability in activated sludge of a "fluorotelomer like" compound, DTFA, which has an internal CH_2 group on the perfluoroalkyl chain to improve its biodegradability. Part of the pathways resembled those of 8:2 FTOH and involved the oxidation of the end hydroxyl group to a carboxylic acid group (Arakaki et al., 2010). Though degradation in the internal CH_2 group was expected, it was not fully validated in the study. Dinglasan-Panlilio (2008) investigated the stability of an ether linkage in 8:2 oxetane monomer [8:2 oxetane, $C_8F_{17}CH_2CH_2OCH_2C(CH_2OCH_2)CH_3$]. The compound was found to be highly resistant to biodegradation in a mixed microbial culture inoculated with activated sludge, consistent with what is expected for the stable ether bond. In fact, the use of the ether bond is noted in a couple of newly reported PFASs. Ammonium 4,8-dioxa-3H-perfluorononanoate [ADONA, CF_3OC_3

$F_6OCHFCF_2COO^-NH_4^+$] has recently been assessed as a likely PFOA replacement to be used for emulsion polymerization of fluoropolymers (Gordon, 2011). Chlorinated polyfluorinated ether sulfonate [F-53B, $CClF_2C_5F_{10}OCF_2CF_2SO_3K$] has been used in some industry for about 30 years, and its environmental occurrence, toxicity and persistence are yet to be extensively studied (Wang et al., 2013).

3.5. Biodegradability of perfluoroalkyl chemicals

Biodegradability of *polyfluoroalkyl* chemicals is largely owing to its non-fluorinated functionality, whose breakdown precedes the breakdown of the perfluorinated carbons, if the later occurs. In contrast, *perfluoroalkyl* chemicals in general resist biotransformation and defluorination under natural conditions. According to thermodynamics of microbial metabolic processes, perfluorinated chemicals, because of their relative higher oxidation states, could be utilized as electron acceptors to provide energy for anaerobic microorganisms. Though reductive defluorination is expected in theory, the mechanism has rarely been observed, probably due to the less available enzymatic systems in nature, high C–F bond strength, and the absence of structures that are susceptible to electrophilic or nucleophilic attack.

Earlier anaerobic and aerobic biodegradation studies observed decreasing PFOA or PFOS concentrations, but most likely due to sorption, which was supported by the lack of fluoride or metabolite generation (Remde and Debus, 1996; Schröder, 2003). Liou et al. (2010) further confirmed that PFOA was highly resistant to microbial degradation in natural environments using ^{14}C-labeled PFOA [$C_7F_{15}^{14}COOH$], through examining five different microbial communities, a range of electron donors for reductive defluorination processes, and the possibility of co-metabolism during reductive dechlorination of trichloroethene. A likely PFOA aerobic degradation product *2H*-PFOA [$(CF_3(CF_2)_5CFHCOOH$] has been proposed in two prior studies (Wang et al., 2009; Washington et al., 2009), but Liou et al. (2010) concluded *2H*-PFOA was more likely to be an impurity. Though PFOA and PFOS are persistent under the natural environment, there are evidences that when reactions are catalyzed under laboratory conditions, PFOA and PFOS do degrade in enzymatic systems. Colosi et al. (2009) showed that PFOA could be reduced to a mixture of shorter-chain fluorinated compounds through novel horseradish peroxidase (HRP)-catalyzed degradative reactions (rather than polymerization) in the presence of hydrogen peroxide and 4-methoxyphenol. Ochoa-Herrera et al. (2008) has reported reductive defluorination of PFOS in a biomimetic system, where PFOS was reduced by Ti(III)-citrate in an anoxic aqueous solution while catalyzed by vitamin B_{12} at 70 °C and pH 9. Recently, Lee et al. (2012) reported the first in vivo biotransformation of a perfluoroalkyl acid in juvenile rainbow trouts, though the perfluoroalkyl moiety remained intact. It was observed that the carbon–phosphorus (C–P) bond in perfluoroalkyl phosphinic acids [PFPIAs, $O = P(OH)(C_nF_{2n+1})(C_mF_{2m+1})$] could be cleaved in fish to form perfluorohexyl phosphonic acid [PFPA, $O = P(OH)_2C_nF_{2n+1}$]. Mechanisms involving α-oxidation or free-radical dephosphorylation (Frost et al., 1987) have been proposed for in vitro enzymatic cleavage of C–P bond in non-fluorinated organic phosphonate and phosphinate compounds, yet it is unclear what mechanisms are responsible for the phenomenon where the carbon atom is perfluorinated. Whether the same biotransformation can occur in microbial systems is yet to be tested.

4. The issue of bound residues

The formation of bound residues is not limited to PFASs, and is commonly observed for many organic chemicals such as pesticides (Gevao et al., 2000). The bound residues often represent a significant fraction of mass of the chemicals dosed into soils (Gevao et al., 2000). In PFAS soil biodegradation studies, the time-dependent decrease of the total mass balance, or the total solvent extractable fraction, has been noted in multiple studies irrespective of chemical type or soil type (Dasu et al., 2012; Liu et al., 2007, 2010a, 2010b; Wang et al., 2009). For [3-^{14}C] 8-2 FTOH, 35% of ^{14}C dosed was irreversibly bound to soils and was only recoverable by soil combustion by 7 months (Wang et al., 2009). For 8:2 FTS, 38% of the total mass dosed was solvent extractable by 80 days while the rest was not accounted for (Dasu et al., 2012). The use of ^{14}C-labeled 8:2 and 6:2 FTOHs confirmed that the reduced extractability in FTOH biodegradation was mainly caused by the formation of soil bound residues (Liu et al., 2010a; Wang et al., 2009), which were catalyzed by microbial actions based on the lack of bound residue in sterile controls.

Through the observation that 6:2 FTOH and several of 6:2 FTOH biotransformation products showed enhanced recovery after the soil solvent extract was subject to NaOH treatment, Liu et al. (2010a) hypothesized that these compounds were conjugated to dissolved soil components to lead to non-detection. The authors further proposed that such conjugate formation between fluorinated compounds and dissolved soil components resembled the types of interactions as those responsible for bound residue formation observed elsewhere in soils, except for the differences being types, sizes and mobility of organic matter. Liu et al. (2010a) also found at the end of the study, 5:3 acid was the only remaining transformation product that may be irreversibly bound to soil components to form bound residues. Recently, Longstaffe et al. (2010, 2012) applied nuclear magnetic resonance (NMR) spectroscopy techniques to examining interaction mechanisms between fluorinated compounds and soil components. PFOA was found to predominantly interact with the protein-derived domains or protein structures in dissolved humic acids in a peat soil, while heptafluoronaphthol was found to interact with lignin-like components (Longstaffe et al., 2010, 2012). The studies demonstrate that highly heterogeneous organic matter in soils contains different domains, each with different propensity to capture and release organic contaminants to varying extent. The results are not yet sufficient to support observed low yields in soil biodegradation studies, because PFOA almost always shows satisfactory recoveries. Yet the approaches may be applied for compounds that show time-dependent recoveries, such as 5:3 Acid, to elucidating possible binding mechanisms that can be directly related to low yields of biodegradation studies.

The issue of bound residues is expected to be subject to continuous and intensive scientific debates regarding the ecological impacts of organic contaminants sequestered in soils. As far as PFASs are concerned, the bioavailability and toxicity of bound residues to soil biota need to be determined. In addition, further studies are needed to explore in situ chemical profile of the soil bound residues, complexes formed between soil components and fluorinated compounds, and the mechanisms of binding.

5. Conclusions and recommendations for future work

A main purpose of performing biodegradation studies is to evaluate whether PFCAs, PFSAs or other PFAAs are formed from precursor chemicals, which account for the majority of PFASs ever produced or used. Drawn on the studies performed so far on a number of precursors (as summarized in Table 1), it has been demonstrated that the half-life of precursors, degradation kinetics and quantitative contributions to PFAAs vary dramatically, and depend on both chemical structures and environmental conditions, such as the size of the perfluoroalkyl chain, the type of internal chemical linkage connecting to non-fluorinated functionalities, the type of non-fluorinated functionality, molecular size, type of microbes or microcosms and other environmental factors (e.g. temperature). Given the high number of possible precursors that have been manufactured (OECD, 2007), biodegradability and contribution to PFAAs of the majority of PFASs remain completely unknown. Aside from a few precursors that have been mentioned in the review, such as polyfluorinated amides and PFPIAs, here we propose additional PFASs of highest priority to be studied in the near future, which in no means are inclusive.

(i) *Perfluorooctane sulfonamide-based side-chained polymers.* Given the high production of those polymers prior to 2002, lack of any biodegradation data, and a wide range in predicted half-lives of fluorotelomer-based side chain polymers, it remains unknown if those high molecular weight precursors significantly contribute to PFAAs, in particular PFOS, in the environment. It is also undecided whether they should be included in emission models. The high stability in marine sediment of SAmPAP, whose molecular weight is much lower, implies that these side-chained polymers are likely to be more resistant to biodegradation, yet experimental studied are indispensable to test such hypothesis.

(ii) *Zwitterionic, cationic, and anionic fluoroalkyl surfactants used in AFFFs.* The direct release of AFFFs through firefighting activities into soil and groundwater has been shown to give rise to a wide range of highly mobile and persistent PFASs, and sometimes at very high levels (Backe et al., 2013; Moody and Field, 2000; Schultz et al., 2004). The question is not whether those polyfluoroalkyl precursors could degrade into more problematic compounds such as PFOS or PFOA, but rather how quickly and under what geochemical conditions. The ten tentative identified classes of AFFF chemicals show that new formulations also include C8 perfluoroalkl moiety (Place and Field, 2012), which could lead to PFOS or PFOA.

(iii) Fluorotelomer iodides (FTIs): They have been used as major industrial building blocks in fluorotelomer chemistry, just as important as FTOHs (Buck et al., 2011). They have been present as impurities in commercial products (Buck et al., 2011) and detected in the environment (Ruan et al., 2010). The atmospheric transformation into PFCAs has been shown, and whether FTIs would follow similar degradation pathways or similar kinetics in microbial systems as FTOHs needs to be investigated.

For a few precursors that have been well studied (e.g., FTOHs), the complexity of aerobic biodegradation pathways, high defluorination potential of short-chain homologues, and the ability of pure bacterial cultures to degrade FTOHs, point to continued interests that can be further explored, that is, novel biochemical mechanisms and detailed pathways connecting degradation intermediates to major terminal degradation products. For instance, the novel "one-carbon removal pathways", which are likely routes for mineralization of FTOHs, needs to be further investigated in order to better appreciate degradation mechanisms of highly fluorinated organic compounds in general. In addition, as more pure bacterial cultures capable of breaking down FTOHs have been discovered (Kim et al., 2012, 2013), identification of degrading microorganisms and degrading microbial consortium in key environmental compartments is likely. Furthermore, the types of enzymes or enzymatic reactions that lead to defluorination of perfluoroalkyl moiety in those pure cultures can be further explored. The knowledge generated may be useful for creating novel, environmentally benign fluorochemicals, aside from being used for environmental fate and effect assessment.

Additionally, the novel degradation products discovered can be used for guiding environmental monitoring efforts and ecotoxicological assessment of PFASs. For instance, fluorotelomer carboxylic acids (FTCAs and FTUCAs), x:3 Acids and x:2 sFTOH (Figs. 2 and 3, in dashed boxes) are unique to the biodegradation of fluorotelomer-based chemicals and relatively stable compared to many other transient metabolites, therefore they can be used for differentiating the sources of PFCAs from precursor degradation as opposed to from direct emissions. The high persistence of x:3 Acids and their co-generation with PFCAs in laboratory biodegradation tests suggest they could be suitable marker compounds to indicate the indirect fluorotelomer sources to PFCAs (Wang et al., 2009). The caveat to using the x:3 Acids as potential markers needs to be fulfilled by more field observations in relevant environmental compartments. In comparison, FTCAs, FTUCAs and x:2 sFTOH are much more labile, despite their environmental detection. In the meantime, the toxicity of these degradation products should be evaluated in the environment where their presence could be significant. For instance, the toxicity of fluorotelomer carboxylic acids has been found to exceed those of PFCAs in aquatic environments (Phillips et al., 2007), while the toxicity of x:3 Acids is largely unknown. In contrast, the degradation products of perfluoroalkane sulfonamido derivatives, such as EtFOSAA and FOSA (Fig. 4), are not strong indicator compounds to suggest that PFOS originates from precursors, because PFOS was often produced at much lower yields than EtFOSAA or FOSA in laboratory biodegradation tests (Lange, 2000; Rhoads et al., 2008). The relative stability of the major degradation intermediates (Fig. 4) is less known given the small number of microbial degradation studies performed. Instead, Martin et al. (2010) proposed two PFOS source tracking principles by using PFOS isomer patterns and enantiomer fractions, and applied them to estimate the magnitude of the exposure to PFOS precursors by humans (Benskin et al., 2010) as well as ecosystems (Asher et al., 2012). For example, the finding that *1m*-PFOS was racemic in sediment and water suggested the there was little microbial degradation of PFOS precursors occurred in the sediment investigated in the study (Asher et al., 2012). In addition, different biodegradation and partitioning behaviors of branched versus linear PFOS precursors are expected (Houde et al., 2008), but little study has been performed to date.

In contrast to numerous aerobic biodegradation studies performed (Table 1), little research has taken place to assess anaerobic biodegradability of PFASs. Thus studies are greatly needed to explore the biodegradation potential with other electron acceptors rather than oxygen. It remains largely unknown by what routes or chemical forms the high volume of PFASs present in landfill sites or anaerobic sediment will be re-introduced back into other environmental compartments.

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