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John R. Parsons, Monica Sáez, Jan Dolfing, and Pim de Voogt

Contents

1   Introduction

In recent years, there has been increasing concern over the levels of perfluorinated and polyfluorinated chemicals, such as PFOS (perfluorosulfonate) and PFOA (perfluorooctanoic acid), in the global environment and their fate and possible adverse effects in the environment. Perfluorinated compounds (PFCs) are substances with the general formula $F(CF_2)_n$-R, consisting of a hydrophobic alkyl chain of varying length (typically C4 to C16) and a hydrophilic end group (Table 1). The partially fluorinated compounds that contain a $-CH_2CH_2-$ moiety between the hydrophilic part and the fully

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Table 1 Examples of perfluorinated compounds

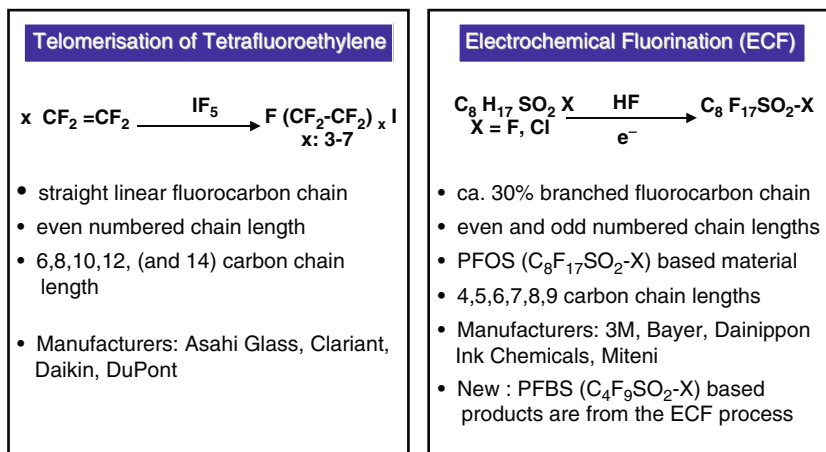| Name	Chemical formula	Acronym	CAS no.[a]
Sulfonates			
Perfluorobutane sulfonate	$F(CF_2)_4SO_3^-$	PFBS	375-73-5
Perfluorooctane sulfonate	$F(CF_2)_8SO_3^-$	PFOS	1763-23-1
Carboxylates			
Perfluorobutanoate	$F(CF_2)_3CO_2^-$	PFB	375-22-4
Perfluorooctanoate	$F(CF_2)_7CO_2^-$	PFO	335-67-1
Perfluorononanoate	$F(CF_2)_8CO_2^-$	PFN	375-95-1
Perfluoroundecanoate	$F(CF_2)_{10}CO_2^-$	PFUn	2058-94-8
Alcohols			
Perfluorohexyl ethanol	$F(CF_2)_6CH_2CH_2OH$	8-2 FTOH	678-39-7
Perfluorooctyl ethanol	$F(CF_2)_8CH_2CH_2OH$	6-2 FTOH	647-42-7
Other			
1*H*,1*H*,2*H*,2*H*-Perfluorooctane sulfonate	$F(CF_2)_6CH_2CH_2SO_3^-$	6-2 FTS	27619-97-2
Perfluorooctyl sulfonamide	$F(CF_2)_8SO_3NH_2$	PFOSA	754-91-6

[a]For acids, the CAS number is for the protonated form, e.g., $F(CF_2)_3COOH$ (=PFBA).

fluorinated remaining carbon chain ($F(CF_2)_n$-CH_2CH_2-X) are called telomer substances and derive their name from the telomerization production process. Telomers are suggested to be precursors of some of the PFCs found in the environment.

The hydrophilic moiety of PFCs can be neutral or positively or negatively charged. The resulting compounds are nonionic, cationic, or anionic surface-active agents, respectively, as a consequence of their amphiphilic character. Examples of neutral end groups are $-CH_2CH_2OH$ (fluorotelomer alcohol) and $-SO_3NH_2$ (perfluoroalkyl sulfonamide (e.g., perfluorooctane sulfonamide, PFOSA). Examples of anionic end groups are the carboxylates ($-COO^-$), the sulfonates ($-SO_3^-$), and the phosphates ($-OPO_3^-$). In cationic PFCs, the fluorinated hydrophobic part is attached to another moiety, such as a quaternary ammonium group.

Perfluorinated compounds show high thermal, chemical, and biological inertness. Fluorochemical products can resist degradation by acids, bases, oxidants, reductants, photolytic processes, microbes, and metabolic processes (Schultz et al. 2003), because the carbon–fluorine bond is the strongest existing covalent bond (450 kJ/mol). Moreover, the presence of three pairs of nonbonding electrons around each fluorine atom and the effective shielding of carbon by the fluorine atoms prevents any significant attack (Kissa 2001). Consequently, these fluorosurfactants as well as other fluorinated alkyl substances are stable under conditions in which their hydrocarbon analogues are degraded.

Two major processes exist (Hekster et al. 2003; de Voogt et al. 2006) for production of PFCs, viz., electrochemical fluorination (ECF) and telomerization (TM) (Fig. 1). The products from the first process (the so-called ECF products) contain a

Telomerisation of Tetrafluoroethylene	Electrochemical Fluorination (ECF)
$x\ CF_2 = CF_2 \xrightarrow[\text{x: 3-7}]{IF_5} F\ (CF_2\text{-}CF_2)_x\ I$	$C_8 H_{17} SO_2\ X \xrightarrow[e^-]{HF} C_8 F_{17} SO_2\text{-}X$ $X = F, Cl$
• straight linear fluorocarbon chain	• ca. 30% branched fluorocarbon chain
• even numbered chain length	• even and odd numbered chain lengths
• 6,8,10,12, (and 14) carbon chain length	• PFOS ($C_8 F_{17} SO_2\text{-}X$) based material
	• 4,5,6,7,8,9 carbon chain lengths
• Manufacturers: Asahi Glass, Clariant, Daikin, DuPont	• Manufacturers: 3M, Bayer, Dainippon Ink Chemicals, Miteni
	• New : PFBS ($C_4 F_9 SO_2\text{-}X$) based products are from the ECF process

Fig. 1 The telomerization (*left*) and electrochemical fluorination (*right*) processes for the synthesis of perfluorinated compounds

sulfonyl group. The products from the second production process (telomers) contain an ethylene group. Perfluorooctane sulfonylfluoride (POSF, $C_8F_{17}SO_2F$) is the most important production intermediate for electrochemical fluorination. Fluorotelomer B alcohol 8:2 (8:2-FTOH, $C_8F_{17}C_2C_2H_4OH$) is a pivotal substance for telomer production. The ECF production process yields even- and odd-numbered, branched, as well as straight perfluoroalkyl chains, whereas telomerization only yields even-numbered, linear chains.

PFOS and other perfluorinated compounds are widely used in industrial and consumer applications including stain-resistant coatings for textiles, leather, and carpets, grease-proof coatings for paper products approved for food contact, fire-fighting foams, mining and oil well surfactants, floor polishes, and insecticide formulations (Renner 2001; Prevedouros et al. 2006).

The production of fluorinated polymers may result in unreacted or partially reacted starting materials or intermediates that end up in the final product. These fluorochemical residuals are typically present at a total concentration of less than 1% in the final commercialized products (Olsen et al. 2005), and may include PFHS (perfluorohexanesulfonate), PFOSA, N-MePFOSE (*N*-methylperfluorooctane sulfonamidoethanol), and N-EtPFOSE (*N*-ethylperfluorooctane sulfonamidoethanol) in the case of the ECF process, and perfluorooctanoic acid (PFOA) and other carboxylic acids in the case of the TM process.

Most PFCs hitherto observed in the environment are known to be possible end products resulting from ECF. Recently, however, more information has become available that suggests TM building blocks or end products may also be precursors of perfluorinated carboxylates and other PFCs in the atmosphere (Ellis et al. 2004).

The major global producer using the EF process, with manufacturing plants in North America and Europe, ceased using the EF production process by 2002.

This decision may have been spurred by findings of PFCs (notably some sulfonates and carboxylates) such as PFOS and PFOA in blood of both occupationally exposed persons and the general population and in terrestrial, estuarine, and Arctic ecosystems (Hoff et al. 2003; Hoff et al. 2004; Martin et al. 2004a; Martin et al. 2004b). Consequently, the TM-based production has increased in importance.

PFCs are reported to be widely distributed in the environment (Giesy and Kannan 2001; de Voogt et al. 2006), originating primarily from anthropogenic sources. Until now, it has not been well understood how, and via which routes, these substances are transported into the environment. The limited information on PFOS blood levels in the general population reveals an increase in levels between 1974 and 1989 but no further change up to 2001 (Olsen et al. 2005); geographic differences exist, probably from variability in sources, levels, and exposure patterns to these chemicals in various countries (Kannan et al. 2004). Moreover, compositions of other perfluorochemicals to which the population may be exposed may vary with country and ethnic group within a country (Kannan et al. 2004; Calafat et al. 2006). Information is lacking, however, on which constitute the most important routes of human exposure. Because PFCs are found in environmental biota, it is likely that food is a human exposure route. The relative contribution of the various foodstuffs to the total human exposure is not known.

In general, degradation by microorganisms (biodegradation) is one of the most important mechanisms by which organic contaminants are removed from the environment. The biodegradation pathways and ultimate fate of PFCs are still largely unknown, however. The strength of the carbon–fluorine bond is generally believed to be the main factor in limiting the biodegradability of PFCs. Although microorganisms are able to remove nonfluorinated functional groups, the central question is whether they are able to successfully attack and remove PFC fluorine substituents to achieve mineralization of perfluorinated molecules. The purpose of this review is to summarize the available literature on biodegradation of PFCs and to present their major degradation pathways. In addition, we briefly address current knowledge on the biodegradation of organohalogen compounds in general, the thermodynamic aspects of the biodegradation of PFCs in comparison with other organohalogens, and the evidence supporting microbially catalyzed cleavage of C–F bonds.

2   Biodegradation of Organohalogen Compounds

In general, organohalogen compounds are characterized by their high stability in the environment. Nevertheless, it has become evident during the past two decades that many of these compounds are susceptible to microbial degradation. It is therefore recognized that microbial degradation of such compounds, although relatively slow, can contribute significantly to their long-term environmental fate (Dolfing 2003; Fetzner 1998; Janssen et al. 2005; Smidt and de Vos 2004).

All organohalogens are characterized by strong carbon—halogen bonds, leading to kinetic stability. It is important, however, to recognize that dehalogenation

is a thermodynamically favorable reaction (Dolfing 2003). Under aerobic conditions, organohalogens are degraded by catabolic pathways similar to those for nonhalogenated analogues (Alexander 1999). Halogenation tends to hinder these reactions, possibly leading to the accumulation of partly degraded metabolites. As a result, aerobic degradation is often a cometabolic process, without apparently yielding useful energy.

A key step in the transformation of halogenated compounds into intermediates in common metabolic pathways is the dehalogenation reaction. A number of dehalogenation mechanisms for both aliphatic and aromatic substrates have been identified (Janssen et al. 2005; Fetzner 1998). These mechanisms include haloacid dehalogenation, halohydrin dehalogenation, haloalkane dehalogenation, and reductive dehalogenation. In a number of cases, the enzymes catalyzing the reactions and the genes encoding these enzymes have been characterized (Janssen et al. 2005; Smidt and de Vos 2004). Such information makes it possible to study how microbes or enzymes have evolved the ability to dehalogenate xenobiotic compounds, which presumably derives from naturally occurring dehalogenation mechanisms, and to identify the presence of dehalogenating activity in the field. There are even a few cases in which information exists on the structure of the active site of the enzyme, which enables computational studies on the mechanism of substrate binding and the subsequent dehalogenation reaction.

Many organohalogen compounds are hydrophobic and therefore tend to accumulate in sediments after they enter the aquatic environment. Other organohalogens such as the chlorinated solvents and perfluorinated surfactants are more water soluble and consequently are groundwater contaminants. As sediment and groundwater environments are predominantly anaerobic, reactions not involving molecular oxygen are required to degrade these compounds. In a number of cases, anaerobic catabolic reactions similar to those occurring aerobically have been identified (Fetzner 1998). These reactions are performed by bacteria presumably using alternative electron acceptors to oxygen, such as nitrate and sulfate. However, of more importance are the reductive reactions leading to dehalogenation. Reductive dehalogenation is thermodynamically favorable under reduced conditions and yields more energy than the reduction of most other electron acceptors (Dolfing 2003; Smidt and de Vos 2004).

The voluminous research done on anaerobic biodegradation of organochlorine compounds has demonstrated that many highly chlorinated compounds that were initially considered to be environmentally persistent do, in fact, undergo reductive dehalogenation at polluted locations. The most extensively studied class of compounds are the chlorinated aliphatic solvents such as tetrachloroethene. Evidence for the reductive dechlorination of chlorinated aliphatic compounds has been found at many contaminated groundwater sites and, in some cases, information is available on the bacteria performing this reaction (Fetzner 1998; Smidt and de Vos 2004). Dehalogenating bacteria have been isolated from a broad range of habitats and characterized using modern methods (Smidt and de Vos 2004). These microorganisms belong to different phyla, and many are able to utilize the energy released by the dehalogenating reactions. Therefore, reductive dechlorination is a form of

respiration for these bacteria and is sometimes referred to as chlororespiration or halorespiration (McCarty 1997). Probably the most interesting genus of dechlorinating bacteria is *Dehalococcoides*, because these organisms depend on halorespiration for growth and are able to completely dechlorinate tetrachloroethene. Reductive dehalogenation of aromatic compounds has been demonstrated for, among others, chlorinated benzenes, phenols, benzoates, biphenyls, and dioxins by bacteria in sediments (Dolfing 2003; Fetzner 1998; Smidt and de Vos 2004). A number of reductive dehalogenases and their genes have been characterized (Smidt and de Vos 2004). In principle, knowledge of these enzymes makes it possible to detect dehalogenation potential and activity in anaerobic ecosystems.

Comparatively little information is available on the dehalogenation of brominated, iodinated, and fluorinated compounds. Reductive debromination yields more energy than reductive dechlorination (Dolfing 2003), and this is consistent with the observed reductive debromination of, for example, polybrominated biphenyls (PBBs). In fact, brominated biphenyls have been used to induce the reductive dehalogenation of both PBBs and PCBs (polychlorinated biphenyls) in sediment (Bedard et al. 1998). Recent results indicate that reductive debromination is also possible for other compounds such as polybrominated diphenylethers (Gerecke et al. 2005; Skoczynska et al. 2005).

3   Thermodynamic Aspects

Thermodynamics provides a useful tool to evaluate whether organisms can obtain energy for growth from catalyzing a certain reaction. A case in point is the reductive dechlorination of 3-chlorobenzoate. When the first observations of reductive dehalogenation were made, it was tacitly assumed that reductive dechlorination of 3-chlorobenzoate was a fortuitous reaction (Suflita et al. 1982). Subsequent awareness that hydrogen was the source of reducing equivalents for the dechlorination reaction (Dolfing and Tiedje 1986), and that 3-chlorobenzoate therefore acted as the electron acceptor, led to the hypothesis that microorganisms can obtain energy for growth from the use of halogenated compounds as electron acceptors (e.g., hydrogenotrophic methanogenic bacteria can grow with bicarbonate as an electron acceptor). At first, it was difficult to prove this hypothesis because of the fastidiousness of the organisms involved, but thermodynamic calculations indicated that a substantial amount of energy would be available from the dechlorination reaction (Dolfing and Tiedje 1987). With the encouragement of this thermodynamic framework, it was subsequently shown that bacteria can indeed obtain energy for growth from the reductive dechlorination of 3-chlorobenzoate (Dolfing 1990). A wide variety of microorganisms are now known to capably grow from this type of reaction (Smidt and de Vos 2004). Thermodynamics support these observations and indicate that reductive dehalogenation (hydrogenolysis) is exergonic for all classes of chlorinated compounds that have been evaluated, including aromatics such as PCBs, chlorophenols, chlorobenzenes, chlorodioxins, and aliphatics such as

chloromethanes, chloroethanes, and chlorethenes (Dolfing and Harrison 1992; Dolfing and Janssen 1994; Holmes et al. 1993; Huang et al. 1996).

The amount of energy available from reductive dechlorination varies between 100 and 180 kJ/mol (standard conditions, hydrogen as electron donor) (Dolfing 2003). This amount is much more than that available from sulfate reduction and methanogenesis (38 and 31 kJ/mol H_2, respectively), not only under standard conditions, but also under environmentally relevant conditions, i.e., at low hydrogen concentrations. This fact explains why dechlorinating organisms are able to function at hydrogen concentrations too low to sustain methanogenesis (Löffler et al. 1999).

The amount of energy available from dechlorination depends somewhat on the position of the substituents and the presence (and nature) of neighboring groups, although differences between different congeners are generally small (Dolfing 2003). Attempts have been made to rationalize degradation pathways for polychlorinated compounds by assuming that higher energy-yielding steps would take preference over those with a lower yield (Dolfing and Harrison 1993). This approach has seen mixed success (Masunaga et al. 1996), possibly because estimates of the Gibbs free energy of formation values on which these predictions are based are not accurate enough to allow such predictions. However, other explanations can also be envisaged; a major one is that the kinetics of the dehalogenating organisms is also governed by structural and evolutionary factors.

A wealth of data have become available during the past two decades on the Gibbs free energy values of chlorinated compounds. Although less information is available on Gibbs free energy values of fluorinated compounds, available data are clear in showing that the amount of energy available from defluorination is similar to (or slightly lower than) the amount available from dechlorination, as is illustrated in Table 2 for reductive dehalogenation of halobenzoates and halomethanes. The higher energy from dechlorination compared to defluorination is in line with the observation that chlorofluoroalkanes are dechlorinated rather than defluorinated (Hageman et al. 2001; Sonier et al. 1994). However, the substantial energy yield from defluorination also indicates that, from a thermodynamic point of view,

Table 2 Gibbs free energy values for reductive dehalogenation (hydrogenolysis) of selected fluorinated aromatic and aliphatic compounds and their chlorinated analogues[a]

	$\Delta G°$, (kJ/mol)	
	Defluorination	Dechlorination
2-Halobenzoate + H_2 → Benzoate + H^+ + halide$^-$	−132	−145
3-Halobenzoate + H_2 → Benzoate + H^+ + halide$^-$	−138	−137
4-Halobenzoate + H_2 → Benzoate + H^+ + halide$^-$	−142	−144
Halomethane → Methane + H^+ + halide$^-$	−156	−164
Dihalomethane → Halomethane + H^+ + halide$^-$	−107	−161
Trihalomethane → Dihalomethane + H^+ + halide$^-$	−85	−170
Tetrahalomethane → Trihalomethane + H^+ + halide$^-$	−89	−188

[a] All calculations used the following standard conditions: T = 298.15 K, pH 7, methanes and H_2 in the gas phase at 1 atm, benzoates and halides in the aqueous phase at 1 M.
Sources: Dolfing and Harrison (1992); Dolfing (2003).

there is no reason why microorganisms should not be able to obtain energy for growth from reductive defluorination. So far, however, such organisms have not been described (Vargas et al. 2000).

In the foregoing paragraphs, the emphasis is on whether organisms can obtain energy for growth from catalyzing a certain reaction. It should be remembered that microorganisms do not always harness the energy that their activities generate. Reductive dechlorination is stimulated by the presence of, for example, vitamin B_{12} (Assaf-Anid et al. 1992). Methanogenic bacteria possessing vitamin B_{12} catalyze this reaction, but their growth is not stimulated by the energy released (van Eekert et al. 1999). In fact, the dechlorination reaction costs the organisms energy in the form of reducing equivalents that could have been used to generate energy via methanogenesis.

Cometabolic degradation of halogenated compounds by aerobic microorganisms has also attracted a fair amount of attention (Semprini 1997) and is the basis for technology that has been applied in the field for the degradation of trichloroethene, for example (Hopkins and McCarty 1995). However, from a thermodynamic point of view, there is no reason why halogenated compounds such as tri- and di-chlorethene should be degraded cometabolically rather than serve as an energy source. A change in Gibbs free energy indicates that aerobic mineralization of halogenated compounds yields enough energy to sustain growth of the organism involved (Dolfing et al. 1993; Dolfing and Janssen 1994). Whether organisms harness this energy is another question. Nevertheless, in one case, the fact that thermodynamic calculations support the hypothesis that organisms should be able to grow on halogenated compounds assisted in the isolation of a novel dichloroethene-degrading aerobic bacterium (Coleman et al. 2002).

4   Biodegradation of Polyfluorinated Compounds (PFCs)

Despite their high stability, polyfluorinated compounds do undergo degradation in the environment. Atmospheric degradation of fluorotelomer alcohols by OH radicals yields perfluorinated carboxylic acids (Ellis et al. 2004) and has been proposed as a source of the acids present in the Arctic. The acids do react further with OH radicals, but this is considered to be of minor importance (Hurley et al. 2004). The hydroxyl radical also reacts with 8:2 fluorotelomer alcohol in aqueous systems, including Lake Ontario water samples irradiated with synthetic sunlight (Gauthier and Mabury 2005). There was no evidence for direct photolysis of the fluorotelomer alcohol. The main products formed were the 8:2 fluorotelomer aldehyde and acid and PFOA.

The published information on the biodegradation of PFCs is very limited. The earliest study reported was an investigation of the ready biodegradability of three fluorinated surfactants under aerobic and anaerobic conditions (Remde and Debus 1996). Two of the surfactants (of unspecified composition) were degraded under aerobic conditions and one was also degraded anaerobically. The extent of degradation of the first surfactant, expressed as oxygen consumption or carbon dioxide or methane produced, was enough to classify the surfactant as readily biodegradable. However, there was no

evidence for the release of fluoride from the compound. No biodegradation was observed for the third surfactant, PFOS, under either aerobic or anaerobic conditions.

An extensive analytical study of the biodegradation of PFCs was reported by Schröder (2003). Wastewater samples were spiked with a number of perfluorinated surfactants (PFOS, PFOA, and nonionic surfactants including partially fluorinated alkyl ethoxylates, perfluorooctanesulfonyl-amidopolyethoxylate, and perfluorooctanesulfonyl-amido–polyethoxylate methyl ether) and incubated under aerobic and anaerobic conditions. Rapid biodegradation was observed in aerobic wastewater of the partly fluorinated compounds to form carboxylic acids (identified by LC-MS/MS). For the perfluorinated compounds, in contrast, there was a rapid removal of PFOS (within 2 d) under anaerobic conditions followed by a slower removal of PFOA. Of the nonionics, only the sulfonyl compounds were removed. Metabolites were neither detected in the anaerobic incubations nor was there any increase in fluoride concentration observed (Schröder 2003).

A further study of the biodegradation of PFOS and PFOA was performed in aerobic and anaerobic reactors containing sludge from German wastewater treatment plants (WWTPs) (Meesters and Schröder 2004). No primary biodegradation was observed under aerobic conditions, but removal, first of PFOS and subsequently of PFOA, was observed under anaerobic conditions until neither compound could be further detected after 26 d. No metabolites or increases in fluoride ion concentration were detected.

The first detailed report providing evidence for environmental biodegradation of PFCs was a study of the biodegradation of 8:2 fluorotelomer alcohol by a mixed microbial consortium enriched from sediment and soil, using 1,2-dichloroethane and ethanol as carbon sources (Dinglasan et al. 2004). Cell suspensions were spiked with 8:2 FTOH and the aerobic incubation was followed by headspace analysis using GC-ECD and GC-MS. FTOH concentrations declined to undetectable levels over a period of about 17 d. Analysis of the aqueous phase by LC-MS/MS revealed formation of acid metabolites: 8:2 fluorotelomercarboxylic acid (FTCA), 8:2 fluorotelomer unsaturated carboxylic acid (FTUCA), and PFOA as major products. The proposed pathway consisted of the oxidation of FTOH to FTCA and the formation of FTUCA from FTCA, presumably by loss of HF and subsequent conversion of FTUCA to PFOA.

Another extensive biodegradation study with 8:2 fluorotelomer alcohol was carried out by Wang et al. (2005a,b). Microbes in a diluted sewage sludge from a domestic WWTP degraded FTOH to the 8:2 FTCA, the 8:2 FTUCA, and PFOA, consistent with the data reported by Dinglasan et al. (2004). The authors also identified a new transformation product, $2H,2H,3H,3H$-perfluorododecanoic acid ($CF_3(CF_2)6$ CH_2CH_2COOH, also referred to as 7-3 acid), which is a potential substrate for β-oxidation in the degradation pathway (Fig. 2). It was proposed that this compound was formed from the saturated acid by reductive defluorination. Several minor products were identified: 7:2 FTOH, 7:3 FTUCA, and 7:3 fluorotelomer unsaturated amide, as well as PFNA. The release of fluoride to the medium was also significant (about 12% of that present in the telomer alcohol). These results demonstrate that perfluorinated carbon atoms in 8:2 FTOH are indeed defluorinated and the products are degraded by microorganisms from WWTPs to form shorter chain products.
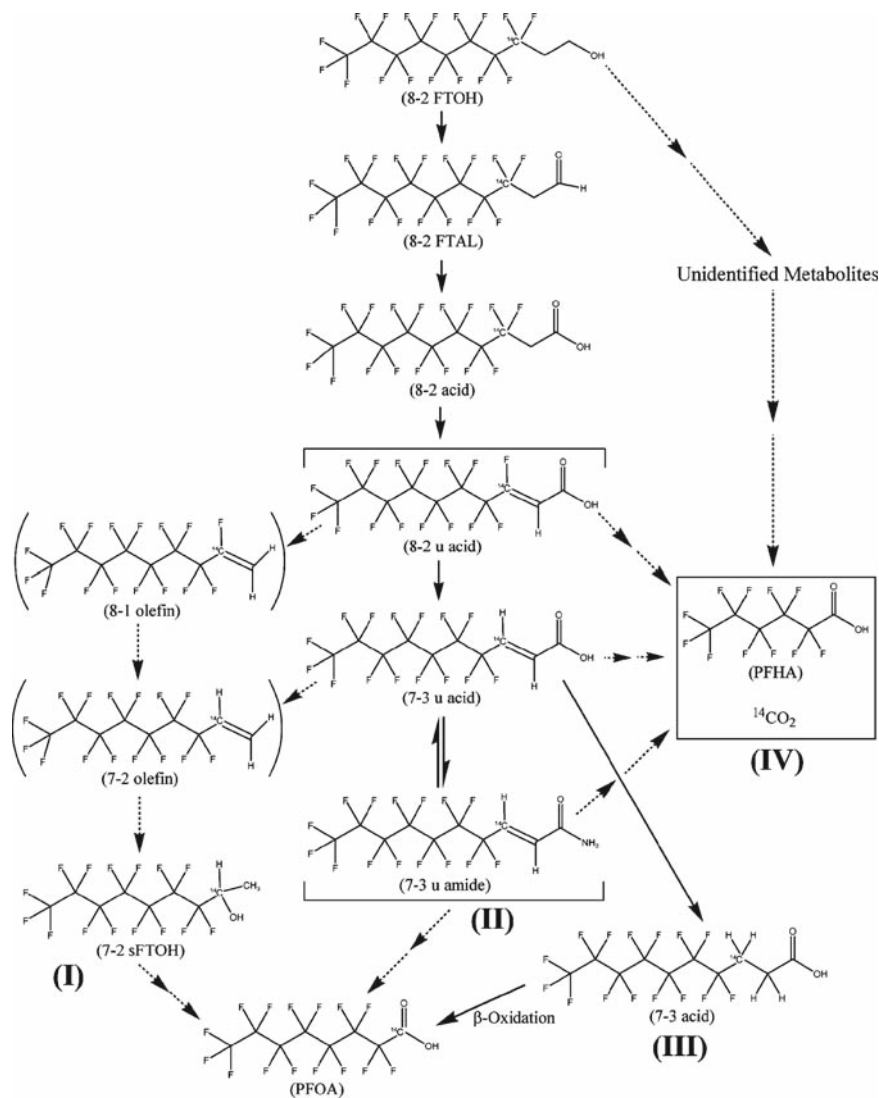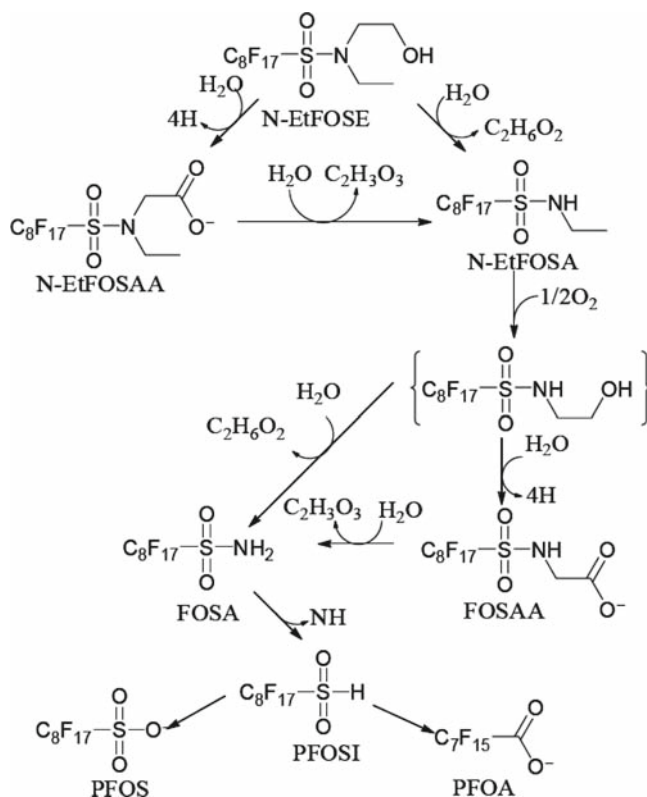
Fig. 2 Proposed pathway for the degradation of 8-2 fluorotelomer alcohol to perfluorooctanoic acid (reproduced with permission from Wang et al. 2005b)

The formation of PFOA has recently been reported during the aerobic incubation of soil with a fluorotelomer-based polymer. The formation was attributed to the degradation of residual 8:2 FTOH released from the polymer. The half-life of the 8:2 FTOH was estimated as 28 d (Koch et al. 2007).

A preliminary study by the 3M company showed that 2(*N*-ethyl perfluorooctane sulfonamido)ethanol (N-EtFOSE, used to manufacture polymer surface protection products) was degraded in aerobic waste water treatment sludge (3M 2000). Transformation to PFOS and other metabolites occurred within 25 d, and this

compound was not degraded further. A subsequent study of the biodegradation of N-EtFOSE in anaerobic and aerobic sludge showed no degradation in anaerobic sludge but 60% removal in aerobic sludge (Boulanger et al. 2005). The main products identified were 2-(N-ethyl-perfluorooctanesulfonamido)acetic acid (N-EtFOSAA) and perfluorooctanesulfinate (PFOsulfinate), accounting for about 23% and 5.3% of the transformed compound, respectively. The remaining transformation products were not identified but did not include the 2-(perfluorooactanesulfon-amido)acetic acid (PFOSAA), perfluorooctanesulfonylamide (FOSA), and PFOS metabolites identified in the 3M study. Recent results do, however, show the rapid degradation of N-EtFOSE in activated sludge (with a half-life of 0.25 d) to form N-EtFOSAA and other products including FOSA, PFOS, and possibly even PFOA (Fig. 3) (Rhoads et al. 2007). Formation of the latter product would indicate that defluorination must take place.

A recent study of the degradability of a wide range of PFCs in aerobic and anaerobic sediment and activated sludge microcosms showed some evidence for the removal of perfluorinated telomer alcohols under aerobic conditions (Sáez et al., in preparation). There was, however, no evidence of these compounds in anaerobic

Fig. 3 Proposed pathway for the degradation of 2(N-ethyl perfluorooctanesulfonamido)ethanol (N-EtFOSE) in aerobic activated sludge (Rhoads et al. 2007)

incubations or of other PFCs, including carboxylates, sulfonates, and sulfonamides, under either aerobic or anaerobic conditions.

The foregoing literature shows that there is some evidence for biodegradation of PFCs in the environment, but none for complete degradation or dehalogenation of these compounds, probably because of the difficulty of removing fluorine substituents. However, as previously explained, this is a thermodynamically favorable reaction, but one that may be hindered by the kinetic stability of the C–F bond. One could conclude from these results that the C–F bond is microbially inert. Reductive dehalogenation is a well-established reaction for chlorinated and to a lesser extent brominated organic compounds, particularly under anaerobic conditions, but defluorination may be very difficult to accomplish. For example, dechlorination but not defluorination takes place in sewage sludge with mixed chlorinated and fluorinated substrates (Balsiger et al. 2005; Hageman et al. 2001; Sonier et al. 1994).

There are, however, examples of microbially catalyzed C–F cleavage reactions such as the defluorination reported by Wang et al. (2005a,b). An overview of microbial defluorination reactions was published recently (Natarajan et al. 2005). Examples of known microbially catalyzed defluorination reactions include the oxidation of fluoromethane to formaldehyde by a *Nitrosomonas* strain (Hyman et al. 1994) and the degradation of fluorinated acetates by different aerobic bacteria (Marion Meyer et al. 1990). Similar reactions have been observed for other nonperfluorinated compounds such as the defluorination of 4-fluorobenzoate by six bacterial strains able to grow on this compound (Oltmanns et al. 1989) and the liberation of fluoride from fluorobenzoates and fluorobenzene by another aerobic strain (Carvalho et al. 2005). Defluorination of a number of sulfonates has also been observed (Key et al. 1998). A *Pseudomonas* strain defluorinated several nonperfluorinated compounds, such as 1*H*,1*H*,2*H*, 2*H*-perfluorooctane sulfonate, but not PFOS. Although the products of these microbial defluorination reactions have not always been characterized, the mechanism involved appears to be either hydrolytic or oxidative. There have been no reports to date of reductive defluorination, despite the fact that this reaction is thermodynamically favorable under reducing conditions. The lack of data on anaerobic reductive defluorination reactions may be a reflection of the very limited studies that have focused on anaerobic conditions. More studies, using anaerobic microbial communities with a history of exposure to fluorinated chemicals, are required.

5   Perspectives for the Biodegradation of Perfluorinated Compounds

As already mentioned, thermodynamic calculations indicate that reductive defluorination of fluorinated compounds yields sufficient energy for growth of the organisms catalyzing this type of reaction. Estimated amounts of energy range between

80 and 160 kJ/mol fluoride, assuming equimolar concentrations of AF_n and AHF_{n-1} and environmentally realistic conditions (pH 7; $F^- = 0.1$ mM, and $H_2 = 10$ Pa). We do not expect these values to be much different for perfluorinated compounds. This hypothesis is based on lines of evidence presented next.

Yamada et al. (1999) published the thermodynamic properties of a series of mono- to pentafluorinated propanes (Table 3). Analysis (data not shown) of the relationship between the number of fluorosubstituents and $T\Delta S$ values of these compound allowed us to also estimate $S°$ for perfluoropropane (i.e., octafluoropropane) and heptafluoropropane (Table 3). In combination with $\Delta H_f°$ values published elsewhere (Kondo et al. 2002), this also allowed us to calculate $G_f°$ values for octa- and heptafluoroethane. With this information, it is straightforward to estimate the change in Gibbs free energy from reductive defluorination of perfluoropropane to heptafluoropropane: 119 kJ/mol (Fig. 4). This value is similar to the amount achieved from reductive removal of other fluorine substituents in the fluoropropane molecule (Table 4). When we initiated these calculations, we anticipated that the amount of energy available from hydrogenolysis of perfluorinated compounds would be less than the amount available from less fluorinated congeners. However, this turned out not to be the case (Fig. 4). We have made a similar comparison for fluorinated ethanes (Table 5, Fig. 5), and the outcome was essentially the same as for fluorinated propanes.

These calculations imply that the energy yield from hydrogenolysis of perfluorinated compounds is not significantly different than that of hydrogenolysis from less fluorinated compounds and suggests that it is reasonable to pose that reductive defluorination of fluorinated compounds, including the perhalogenated ones, is an energy-yielding reaction. Thus, and despite a lack of published thermodynamic

**Table 3** Thermodynamic properties of fluorinated propanes[a]

Compound[b]	$\Delta H_f°$ kJ/mol	$S°$ J/mol K	$G_f°$ kJ/mol
$CH_2FCH_2CH_3$	−281.9	307	−201.7
$CHF_2CH_2CH_3$	−517.4	324	−431.6
$CF_3CH_2CH_3$	−766.0	330	−671.1
$CH_2FCHFCH_3$	−459.2	325	−373.7
CHF_2CHFCH_3	−689.0	336	−596.1
$CHF_2CF_2CH_3$	−905.3	360	−808.9
$CF_3CH_FCH_3$	−927.0	346	−826.2
$CF_3CF_2CH_3$	−1134.4	360	−1027.1
CF_3CHFCF_3	−1572[c]	390[d]	−1452.2
$CF_3CF_2CF_3$	−1178[c]	404[d]	−1651.5

[a] Properties are for ideal gases at a pressure of 1 atm and a temperature of 298.15 K.
[b] Unless stated otherwise, ΔH_f and $S°$ values are from Yamada et al. (1999).
[c] Data from Kondo et al. (2002).
[d] Calculated based on a correlation between $T\Delta S$ and the number of fluorine substituents (n) in fluoropropane ($T\Delta S = 6.7 \times n + 72.9$; $r^2 = 0.97$) in the data series from Yamada et al. (1999).
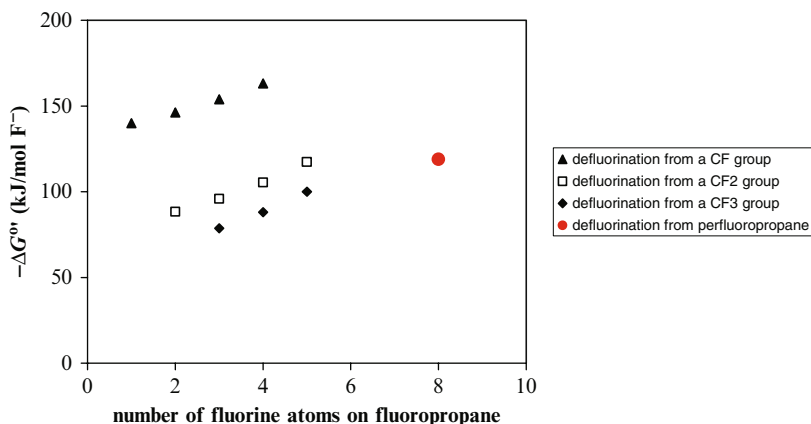
Fig. 4 Change in Gibbs free energy ($\Delta G°'$) values for reductive defluorination (hydrogenolysis) of fluorinated propanes

Table 4 Gibbs free energy changes for reductive defluorination (hydrogenolysis with H_2 as electron donor) of fluorinated propanes[a]

Substrate	Product	$\Delta G°$, (kJ/mol)		n	CF$_3$	CF$_2$	CF
					Defluorination at position:		
CF$_3$CF$_2$CH$_3$	CHF$_2$CF$_2$CH$_3$	−100.0		5	F$_3$F$_2$ → F$_2$F$_2$		
CF$_3$CF$_2$CH$_3$	CF$_3$CHFCH$_3$		−117.4	5		F$_3$F$_2$ → F$_3$F	
CF$_3$CHFCH$_3$	CHF$_2$CHFCH$_3$	−88.2		4	F$_3$F → F$_2$F		
CHF$_2$CF$_2$CH$_3$	CHF$_2$CHFCH$_3$		−105.5	4		F$_2$F$_2$ → F$_2$F	
CF$_3$CHFCH$_3$	CF$_3$CH$_2$CH$_3$		−163.2	4			F$_3$F → F$_3$
CF$_3$CH$_2$CH$_3$	CHF$_2$CH$_2$CH$_3$	−78.8		3	F$_3$ → F$_2$		
CHF$_2$CHFCH$_3$	CH$_2$FCHFCH$_3$		−96.0	3		F$_2$F → FF	
CHF$_2$CHFCH$_3$	CHF$_2$CH$_2$CH$_3$		−153.9	3			F$_2$F → F$_2$
CHF$_2$CH$_2$CH$_3$	CFH$_2$CH$_2$CH$_3$		−88.4	2		F$_2$ → F	
CH$_2$FCHFCH$_3$	CFH$_2$CH$_2$CH$_3$		−146.3	2			FF → F
CFH$_2$CH$_2$CH$_3$	CH$_3$CH$_2$CH$_3$		−140.0	1			F →

[a] $\Delta G°'$ calculations are for ideal gas-phase defluorination based on data presented in Table 2, with $G_f°$ F$^-$ (aq.) = −278.8 kJ/mol and pH =7; n = number of fluorine substituents present on the parent molecule.

properties ($G_f°$, $\Delta H_f°$, $S°$ values) for perfluoroalkylated substances, it seems reasonable to also predict that, thermodynamically, there is no reason why these compounds should not be biodegradable under anaerobic conditions. The question remains, of course, how fast microorganisms will evolve that are able to benefit from this potential source of energy and from where and how they should recruit the enzymatic machinery necessary to catalyze this reaction and harness the energy produced.

Table 5 Gibbs free energy changes for hydrogenolysis and dihaloelimination of fluorinated ethanes with H_2 as electron donor[a]

Substrate	$\Delta G^{\circ}{}'$ (kJ/mol)	
	Hydrogenolysis	Difluoroelimination
CF_3CF_3	−91.0	−2.9
CHF_2CF_3	−108.6	−71.2
CH_2FCF_3	−133.4	−122.4
CHF_2CHF_2	−109.6	−94.9
CH_3CF_3	−75.7	na
CH_2FCHF_2	−126.2	−157.6
CH_3CHF_2	−91.5	na
CH_2FCH_2F	−137.5	−178.0
CH_3CH_2F	−109.0	Na

na, not applicable.
[a]$\Delta G^{\circ}{}'$ calculations are for ideal gas-phase dehalogenation based on data presented in Burgess et al. (1996), Yamada et al. (1998), and Speight (2005) (G_f° F⁻ (aq.) ä −278.8 kJ/mol, pH ä7)
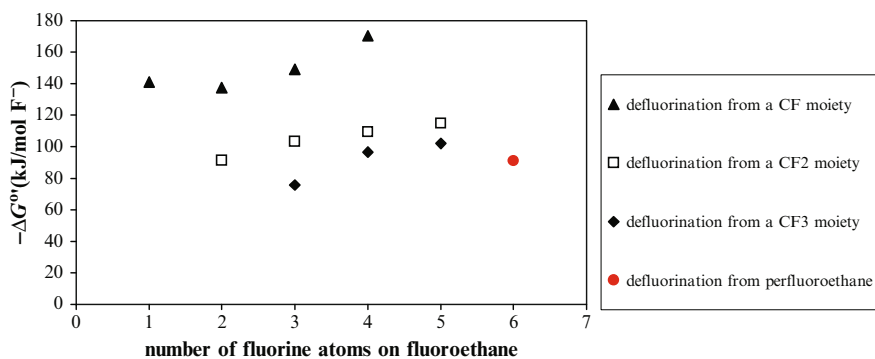
Fig. 5 Change in Gibbs free energy ($\Delta G^{\circ}{}'$) values for reductive defluorination (hydrogenolysis) of fluorinated ethanes (based on data from Yamada et al. 1998 and Speight 2005)

Finally, we expect that the organisms that thrive on anaerobic degradation of perfluorinated compounds will perform a hydrogenolytic defluorination rather than dihaloelimination, because hydrogenolysis of, for example, fluorinated ethanes yields more energy than difluoroelimination. This is different for perchlorinated ethanes, where dihaloelimination yields substantially more energy than hydrogenolysis (Dolfing 2000).

In the preceding paragraphs we have focused on reductive defluorination rather than on aerobic degradation of perfluorinated compounds, largely because perhalogenated compounds are generally only degraded under anaerobic conditions (Bossert et al. 2003). Recently, however, an exception to this rule has been created in the laboratory (Yan et al. 2006). Thus, there are no thermodynamic reasons why perfluorinated compounds such as hexafluoroethane or octafluoropropane should not be degradable under

aerobic conditions, given that the Gibbs free energy yield ($\Delta G^{\circ\prime}$) for mineralization of these compounds is estimated to be 730 and 1132 kJ/mol, respectively.

6 Summary

The information available in the literature provides evidence for the biodegradation of some poly- and per-fluorinated compounds, but such biodegradation is incomplete and may not result in mineralization. Recent publications have demonstrated that 8:2 fluorotelomer alcohol, for example, can be degraded by bacteria from soil and waste-water treatment plants to perfluorooctanoic acid. Similarly, 2-*N*-ethyl(perfluorooctane sulfonamido)ethanol can be degraded by wastewater treatment sludge to perfluorooc-tanesulfonate. It is presently unclear whether these two products are degraded further. Therefore, the question remains as to whether there is a potential for defluorination and biodegradation of PFCs that contributes significantly to their environmental fate.

The lack of mineralization observed is probably caused by the stability of the C–F bond, although there are examples of microbially catalyzed defluorination reactions. As is the case with reductive dechlorination or debromination, reductive defluorina-tion is energetically favorable under anaerobic conditions and releases more energy than that available from sulfate reduction or methanogenesis. Consequently, we should consider the possibility that bacteria will adapt to utilize this source of energy, although evolving mechanisms to overcome the kinetic barriers to degradation of these compounds may take some time. The fact that such reactions are absent for some PFCs, to date, may be because too little time has passed for microorganisms to adapt to these potential substrates. Hence, the situation may be comparable to that of chlorinated organic compounds several decades ago. For many years, organochlorine compounds were considered to be catabolically recalcitrant; today, reductive chlorin-ation reactions of many organochlorines, including PCBs and dioxins, are regularly observed in anaerobic environments. Hence, it is opportune and important to continue studying the potential degradation of perfluorinated compounds in carefully designed experiments with either microbial populations from contaminated sites or cultures of bacteria known to dehalogenate chlorinated compounds.

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