

## **Analysis of the unknown pool of PFAS: Total Oxidizable Precursors (TOP), PFOS Precursor (PreFOS) and Telomer Degradation**

*Patrick van Hees, Eurofins Environment Testing Sweden AB and Man-Technology-Environment Research Centre, Örebro University*

### **Abbreviations:**

AFFF = aqueous film forming firefighting foam; di-SAmPAP = bis-[2-(N-ethylperfluorooctane-1-sulfonamido)ethyl] phosphate; ECF = Electrochemical fluorination; EtFOSA = N-ethylperfluoro-octanesulfonamide; EtFOSAA = N-ethylperfluorooctane-sulfonamide acetic acid; EtFOSE = N-ethylperfluorooctanesulfonamidoethanol; FTAA = Fluortelomer sulfonamide alkylamine; FTAB = Fluortelomer sulfonamide alkylbetaine; FTAC = Fluortelomer acrylate; FTB = Fluortelomer betaine; FTCA = Fluortelomer carboxylic acids; FTUCA = Fluortelomer unsaturated carboxylic acids; FTEO = Fluortelomer ethoxylates; FTMAC = Fluortelomer methacrylates; FTOH = Fluortelomer alcohols; FTS = Fluortelomer sulphonates; FTSAS = Fluortelomermercaptodimethylamido sulfonate; MeFOSA = N-methylperfluoro-octanesulfonamide; MeFOSAA = N-methylperfluorooctanesulfonamide acetic acid; MeFOSE = N-methylperfluoro-octanesulfonamidoethanol; PAP = Poly- and perfluoroalkyl phosphate; PFAS = Poly- and perfluoroalkyl substances; PFBA = Perfluorobutanoate; PFCA = Perfluorinated carboxylic acids; PFHxA = Perfluorohexanoate; PFHxS = Perfluorohexane sulfonate; PFHxSA = Perfluorohexanesulfonamide PFPeA = Perfluoropentanoate; PFOA = Perfluorooctanoate; PFOS = Perfluorooctane sulfonate; PFOSA = Perfluorooctanesulfonamide; PFSA = Perfluoroalkyl sulfonic acids; PreFOS = PFOS precursors; TOF = Total organic fluorine; TOP = Total oxidizable precursors; WWTP = Waste water treatment plant

### *Introduction*

In current research and risk assessment of PFAS it has become apparent that a wider evaluation including also so called precursors is necessary. Precursors are compounds, both known and unknown, which have the potential to form perfluorinated PFCAs and PFSA (Houtz and Sedlak, 2012) at degradation. Thus these substances are of interest to study to elucidate both present and future exposure for biota and humans as well as levels in environmental matrices (Martin et al., 2010). Besides risks and toxicological effects associated with precursors it may also be important to know about their presence at remedial actions (McGuire et al., 2014). Among the “known” precursors, those forming PFOS (so called PreFOS) as the major end-product have attracted much attention, and in many cases these have been produced in large quantities. Moreover, a number of studies demonstrating biodegradation of telomer precursors yielding intermediates and PFCAs have been performed in recent years (Liu and Avendaño, 2013). Besides the “known” ones there are also numerous “unknowns”, not included in conventional analyses or potentially not identified. To cover these, fully or to a great extent, alternative methods have been developed such as the TOP assay.

### *Characteristics of PFOS Precursors - PreFOS*

PreFOS are substances that in animals or in the environment can be degraded to PFOS and to a minor extent PFOA (Martin et al., 2010; Liu and Avendaño, 2013). Their presence has also been shown in human blood and serum. Chemically all PreFOS are characterized by a PFOS moiety (with the exception of PFOSI) to which another molecular part, most commonly an amide group, is linked by the sulphonate. In turn this amide is substituted with various alkyl, alkyl amine, alcohol and/or carboxylic groups etc. Typical examples include PFOSA (simplest amide), Me/EtFOSA and Me/EtFOSE.

PreFOS have been used directly or as building blocks for more advanced active substances in products such as Scotchgard (PFOSA etc), surface treated paper (EtFOSE/ MeFOSE), waterproofed textile (MeFOSE) and insecticides (sulfuramide; EtFOSE). Among the higher molecular weight compounds, MeFOSE acrylates and Me/EtFOSE phosphates can be mentioned. Moreover, MeFOSE derivatives have frequently been employed as side chains in various copolymers (Martin et al., 2010). In addition to PFOS itself, compounds such as PFOSA based alkyl amine oxides have been used in AFFF formulations. Moreover, as for PreFOS precursor, compounds with the ability to form other perfluorinated sulphonates e.g. PFHxS do also exist. Older foams may contain PFHxS derivatives such as the amide amine and amide amino carboxylate (Houtz et al., 2013). In addition, other precursor compounds have been identified and discussed in the context of AFFF (Houtz et al., 2013 and references within).

### *Biodegradation of PreFOS*

There is a growing consensus how PreFOS is biodegraded in environmental and biotic systems (Liu and Avendaño, 2013). Taking EtFOSE as an example, it is firstly oxidized to the corresponding acetic acid (EtFOSAA) then undergoing steps of dealkylation to form PFOSA. PFOSA is finally degraded to PFOS. The degradation of EtFOSAA seems to be the rate limiting step and thus this metabolite becomes quantitatively important. Although more research is warranted half-lives ( $t_{1/2}$ ) in environmental samples (soil, sludge, sediment) seem to vary from <1 d up to >3400 d (Avendaño and Liu, 2015 and references within). Besides the PreFOS studied, factors such as the protective effect of sorption and the variance in microbiological activity may influence the degradation rates. It is important to note that  $t_{1/2}$  only reflects the disappearance of the original compound not any final yield of PFOS. Copolymers may also be biodegraded over time, but the rate of is debated and  $t_{1/2}$  ranging from 10 to >1000y can be found in the literature (Liu and Avendaño, 2013).

An additional field of interest is to what extent branched (br) PreFOS are preferentially biodegraded. PreFOS manufactured by the ECF technique will contain about 30% branched PFOS moieties (Benskin et al., 2010). Especially human serum samples can have a br-PFOS content higher than that found in technical ECF products. One of the most likely explanations is faster decomposition kinetics for the branched forms of PreFOS (Gebbinck et al., 2015).

### *Environmental concentrations of PreFOS*

PreFOS has been identified in most environmental matrices e.g. surface and waste water, landfill leachate, soil, sludge and sediment. On occasions PreFOS can also be found in drinking water, food, indoor air and dust (Martin et al., 2010; Arvaniti and Stasinakis, 2015; NV, 2016). The most commonly detected substance is PFOSA but other PreFOS are frequently observed as well. Although it should be stressed that especially in older studies PreFOS was not always included in the analytical scope. Concentrations in water samples range from pg/l levels in oceans and remote lakes up to about 10-20 ng/l (PFOSA) in some waste waters in the reviews cited above. In the Swe EPA report 6709 (NV, 2016) a compilation of new and old monitoring results of different kinds of water in addition to soil and sludge were presented. PFOSA was most commonly detected and could be identified in effluent waste water from WWTP (median ~0.5 ng/l; n= 20 sites, no of samples higher) and landfill leachates (median ~7 ng/l; n=18 sites, no of samples higher), and occasionally in surface and groundwater typically at lower concentrations. In a more limited number of samples Et- and MeFOSA, FOSAA and Me- and EtFOSAA could also be determined.

In soil from firefighting exercise sites ( $n = 400$ ; NV, 2016) PFOSA, FOSAA and MeFOSA were found among the 10 most common PFAS. The median concentrations of PFOSA and PFOS were 16 and 70  $\mu\text{g}/\text{kg DM}$ , respectively, demonstrating that the potential contribution of PreFOS was significant (NV, 2016). MeFOSA and FOSAA were found at lower levels, about 1  $\mu\text{g}/\text{kg DM}$ . In sediment from run-off water PreFOS (EtFOSA and Me/EtFOSAA) made up approx. 20% of total PFAS (15-27  $\mu\text{g}/\text{kg DM}$ ) in the top layers while PFOS was the major PFAS determined (Nguyen et al., 2016). In a study of sludge from three Swedish WWTP works PFOSA, Et- and MeFOSE and MeFOSA were identified with levels ranging between  $<0.05$  to 3  $\mu\text{g}/\text{kg}$  with highest concentrations observed for MeFOSE (Eriksson et al., 2017). In comparison the content of PFOS was 1-8  $\mu\text{g}/\text{kg}$ .

Concerning adsorption onto environmental solids work for PreFOS is still limited, but to date most studies indicate that adsorption of PreFOS may be more important than for the corresponding sulphonate (PFOS). Results from different sediment studies compiled by Nguyen et al. (2016) showed that the  $\log K_{oc}$  value was typically 0.5 (range 0-1) units higher for PFOSA, EtFOSA, MeFOSAA and EtFOSAA as compared to PFOS (3.7-4.1 vs 3.9-4.8). In the paper by Chen et al. (2015) PFOSA was found to have a  $\log K_{oc}$  value in sediment about one unit higher than for PFOS (3.3 vs 4.3). Ullberg (2015) calculated a  $\log K_{oc}$  value of 4.6 for PFOSA in soil vs. 4.1 for PFOS.

#### *Characteristics of Telomer Precursors*

Telomer precursors are a very wide family of PFAS compounds, most of them sharing a polyfluorinated  $n:2$  structure ( $n = \text{no. of perfluorinated carbon (C) bound to two C without fluorine (F)}$ ). These substances have been used in numerous industrial and commercial products. Among precursors being analysed on a routine basis 4:2, 6:2 and 8:2 FTS can be mentioned. Moreover various FTOH and PAP are also sometimes studied, though other analytical methods are commonly needed. Precursors in this regard may include more advanced structures with ester, ether, urethane, ethoxylate and phosphate linkages among others (Liu and Avendaño, 2013). Examples of this kind are different FTAC, FTMAC, FTEO and PAP compounds.

AFFF is a product of special interest in relation to PFAS contamination in the environment. In the report by KEMI (2015) a range of modern foams were tested. Besides the presence of limited amounts of perfluorinated PFAS (e.g. PFHxA) and 6:2FTS the investigation identified the main ingredients 6:2 FTSAS and 6:2 FTAB in a number of AFFF. Other PFAS have also been reported such as 6:2 FTAA (D'Agostino and Mabury, 2017), and the list can be further extended.

#### *Biodegradation of Telomer Precursors and Intermediates*

The ability of telomer precursors to biodegrade in environmental systems has been shown in a number of publications (Liu and Avendaño, 2013). Estimated half-lives in soil, sediment and sludge are found in the range  $<2$  up to  $>210$  d for the telomers studied and for side-chain polymers several years. This makes their contribution potentially significant when considering time spans for biological and human exposure as well as remedial actions. Again it should be stressed that  $t_{1/2}$  expresses the disappearance of the original substance not the final perfluorinated products.

In the case of telomers precursors these most commonly degrade to PFCA rather than PFSA. As for PreFOS the pattern of biodegradation seems, by large, be recurring in scientific investigations. Studies of FTOH, both 6:2 and 8:2 show formation of a number of semi-stable intermediates such as FTCAs and FTUCAs. In the case of 6:2 FTOH substances these include 6:2 FTCA/FTCUA but also 5:3 FTCA after a defluorination step (Liu and Avendaño, 2013). Different aldehydes, ketones, alcohols and acids of a more transient nature may also be formed. Further defluorination reactions may take place and thus additional shorter chained PFCA as end products can be observed e.g. for 6:2 FTOH formation of PFHxA, PFPeA and PFBA is possible. In the case of 8:2 FTOH besides PFOA, PFHpA and PFHxA can be identified at least in soil (Wang et al., 2009). Degradation pathways are similar for FTS compounds. In the paper by Zhang et al (2016) rapid decomposition of 6:2 FTS (90 d incubation) was observed in aerobic river sediment with 5:3 FTCA, PFHxA and PFPeA as products (in total 57%). Microbial desulfonation of 6:2 FTS was thought to be the rate-limiting step, and that the impact varied between different environmental samples and microbial populations. No degradation occurred under anerobic conditions. However, in most studies yields of the major PFCA are 10% or less on a molar basis in laboratory experiments with duration of up to approximately 3 months. In longer studies figures of 30-40% can be seen (Liu and Avendaño, 2013).

The biotransformation of AFFF containing telomer precursors in environmental systems such as sludge and soil has also been investigated. In a soil slurry microcosm experiment by Harding-Marjanovic et al. (2015) AFFF, mainly containing 6:2 FTSAS, was added. In line with most other studies, the identified and quantified end products (PFCAs) and intermediate compounds corresponded to about 10% on a molar basis after 60 d with spiking of AFFF at 0 and 18d. The dominant intermediate biodegradation product was 6:2 FTS accounting for 8%. PFCAs made up 1.5% in total. Also 6:2 FTUCA (0.2%) and 5:3 FTCA (0.5%) were determined. In the WWTP sludge experiment by D'Agostino and Mabury (2017) degradation of 6:2 FTAB and 6:2 FTAA was followed over 109 days. Measured degradation products could account for, on a molar basis, ~12-16% (6:2 FTAA) and ~3-6% (6:2 FTAB). As opposed to the 6:2 FTSAS study mentioned, 6:2 FTS was not found to be the major compound formed, instead the 6:2 FTS amide was seen at the highest concentration in both active sludge and in abiotic controls. Significant levels of 6:2 FTS were determined in the abiotic controls only and then especially for 6:2 FTAA (~4%). Other intermediates with notable yields included 6:2 FTOH, 6:2 FTCA/FTUCA and 5:3 FTCA. Notably, 5:3 FTCA peaked after about 90 d (~4%) in the 6:2 FTAA active experiments while it still increasing in the 6:2 FTAB run at the end of the study, but at a lower level (~0.7%). PFCAs (PFHxA, PFPeA and PFBA) as end products were also formed accounting for 2.1% of the 6:2 FTAA additions and 0.6% of the 6:2 FTAB.

#### *Environmental Concentrations of Telomer Precursors*

The presence of especially FTS compounds in water, soil, sediment and sludge is well documented. In the Swe-EPA report 6709 (NV, 2016) 6:2 FTS was found to be the major PFAS in outgoing water from WWTPs (n=20) with a median concentration of around 10 ng/l. 6:2 FTS was also a major compound in landfill leachate with a level of ~220 ng/l (n=18). In a recent study of influent and effluent from three Swedish WWTP plants 6:2 FTS was again observed at similar concentrations (2-6 ng/l). 8:2 FTS was also found but at lower levels (<1 ng/l; Eriksson et al., 2017). Decreases in outgoing water were very moderate or none. In highly contaminated groundwater 6:2 FTS showed an average concentration of 25 000 ng/l while 8:2 FTS were seen in half of the samples but at lower concentrations (Houtz et al., 2013). In the Swe-EPA report (NV, 2016) a compilation of the 30 most contaminated ground waters studied (PFAS<sub>26</sub> = 11-6400

ng/l) demonstrated that 6:2 FTS comprised between 0-100% of the total (mean ~20%) In comparison, for the 30 most contaminated surface waters with PFAS<sub>26</sub> in the range 97-13000 ng/l 6:2 FTS corresponded to 0-62% (mean ~19%). Both ranges for 6:2 FTS stress the impact and importance of the pollution source, at least in highly polluted systems. More advanced telomer precursors are seldom measured and quantified, but in the paper by Boiteux et al. (2017) 6:2 FTAB was measured downstream of a WWTP of a PFAS production facility. Concentrations decreased from nearly 1000 to 250 ng/l over a distance of 62 km. In comparison 6:2 FTS concentrations ranged from 200 down to 100 ng/l. At a water works affected it was shown that ozonation led to removal of 6:2 FTAB largely caused by an oxidation into 6:2 FTS.

In soil from fire exercise sites (n= ~400; NV, 2016) the concentration of 6:2 FTS was on average 26 µg/kg DM, and thus the second highest measured after PFOS. In the work by Houtz et al (2013) the average level of 6:2 FTS was 68-85 and for 8:2 FTS 42-81 µg/kg for soil and aquifer solids with the higher values recorded for soils. Eriksson et al. (2017) determined 6:2 and 8:2 FTS in sludge, for which sums of 0.8-1.8 µg/kg were found with a tendency for higher levels of the 8:2 compound. In addition to FTS telomers, PAP compounds are sometimes determined in environmental studies and, although not covered here, they are an important group also deserving attention when assessing telomer precursors.

Reports on the occurrence possible degradation products of FTS and molecules such as FTAB and FTSAS are scarcer. This includes various FTOHs, compounds that potentially may exist as both primary contaminants and intermediates. For FTOHs when found in water samples these are often from locations with high levels e.g. production sites. In the paper by Gremmel et al (2017) the influent to an industrial WWTP plant was dominated by 6:2 FTOH (mean ~ 500 000 ng/l) with lower levels of 8:2 and 10:2 FTOH. In the effluent no FTOHs were observed, and the overall PFAS loading had decreased by two thirds. Both volatilization and biodegradation were put forward as explanations for the disappearance. Bach et al (2016) found 8:2 FTOH (100-250 ng/l) in a river 40 km from a PFAS polymer plant. River water in the Osaka area (JP) showed concentrations between <0.2-3.4 ng/l for 8:2 FTOH and <0.2-4.1 for 10:2 FTOH (n=33), though the 8:2 homolog was more frequently detected. WWTP effluent showed a concentration of 17 and 5 ng/l for 8:2 and 10:2 FTOH, respectively (Mahmoud et al., 2009). FTOH substances, incl 6:2 and 12:2 FTOH could be determined also in samples from the North Sea, but at much lower concentrations (mean of sum FTOH 0.013 ng/l; Xie et al., 2013). Eriksson et al. (2017) monitored 5:3 and 7:3 FTCA as well as 6:2 and 8:2 FTUCA in influent and effluent water of three WWTP plants with levels ranging between <LOD to 2.8 ng/l.

In the study by Bach et al (2016), cited above, concentrations in sediment were 1-7 µg/kg DM for 8:2 and 10:2 FTOH. Zhang et al (2015) found 6:2 (31-57 µg/kg DM) and 8:2 FTOH (13-25 µg/kg DM) in two biosolids-amended soils. Degradation products covering 4:3, 5:3, 7:3, 6:2 and 8:2 FTCA in addition to 6:2 and 8:2 FTUCA ranged between <LOD to 0.14 µg/kg DM. In WWTP sludge (3 plants; 2012-15) the sum of FTCA/FTUCA compounds (4-78 µg/kg) exceeded that of PCFA, PFSA and FTS, respectively (1-13 µg/kg). The dominant FTCA/FTUCA was 5:3 FTCA present in the interval 1-68 µg/kg. Low ratios between PFCA:FTCA suggested that PFCA's originated from precursor compounds (Eriksson et al., 2017). Levels of PFAS were monitored in lake and river sediment (n=13) and biota following a railway accident where AFFF was used (Munoz et al., 2017). A number of both betaine and other sulfonamide based precursors were identified e.g. 6:2, 8:2, 10:2 and 12:2 FTAB, and 9:3, 11:3, 9:1:2 and 11:1:2 FTB among others. Concentrations were in the range <0.02-1.2 µg/kg DM. Some of these substances were detected for the first time in fish in the field. Also 5:3 and 7:3 FTCA were detected in some sediment samples ranging between <0.02-0.08 µg/kg DM. FTS compounds were seen in a similar interval (<0.02-0.61 µg/kg DM) with an overall PFAS content 0.1-6.8 µg/kg DM.

There are relatively few studies on the adsorption of telomers onto environmental solid matrices. Liu and Lee (2007) estimated a soil log  $K_{oc}$  values for a range FTOH with values for 4:2 (0.9), 6:2 (2.5), 8:2 (3.8-4.1) and 10:2 (6.1). For comparison the value for 8:2 FTOH is higher than what is typically seen for PFOA and similar or higher than for PFOS. In the paper by Nguyen et al (2016) a log  $K_{oc}$  range of 2.2-4.4 for 6:2 FTS in sediment was compiled, values comparable to PFHxS. A value in the same range  $\sim$ 2.9 was estimated for 6:2 FTS using data in Boiteux et al (2017). Eriksson et al. (2017) calculated  $K_D$  values for WWTP sludge for a number of telomers and intermediates. Re-calculation assuming a  $f_c$  of 30% estimates of log  $K_{oc}$  were obtained for 6:2 FTS (2.6), 8:2 FTS (3.9), 6:2 FTUCA (3.7), 5:3 FTCA (4.3) and 7:3 FTCA (4.8).

#### *Determination of Total Oxidizable Precursors (TOP)*

Today thousands of PFAS compounds exist and it is not analytically possible to determine all. In addition to these individual substances, there is a need to assess the total pool of PFAS that with time may decompose to perfluorinated compounds.

It is known that precursors can be chemically oxidized to corresponding perfluorinated substances and under strongly oxidizing conditions also PFCA/PFSA may degrade. This fact forms the foundation for a number of emerging treatment techniques (Park et al., 2016 and references within). Houtz and Sedlak (2012) developed a laboratory method, which was coined TOP (Total Oxidizable Precursors), based on oxidation using hot persulphate in an alkaline solution. Under these conditions hydroxyl radicals are formed reacting with both telomers and sulfonamide precursors. The parameters were selected in a way so PFCA and PFSA initially present were not affected.

In comparison to naturally occurring biodegradation in the TOP assay sulfonamide containing precursors form a corresponding  $C_n$  PFCA e.g. in the case of PreFOS, PFOA is the resulting product. As in the environment telomer (n:2) oxidation is more complex and a series of PFCAs are produced, which includes the  $C_{n+1}$ ,  $C_n$ ,  $C_{n-1}$  etc down to the  $C_4$  acid. For the telomers investigated the greatest yield was seen for the  $C_{n-1}$  PFCA followed by the  $C_n$  and then  $C_{n-2}$  compounds (Houtz and Sedlak, 2012). Total molar yields ranged from 73-110%, with a tendency that shorter substances (6:2) summed up to lower percentages. It can be speculated that formation of C2 and C3 PFCAs not measured is one likely cause for this (Harding-Marjanovic et al., 2015).

#### *Total Oxidizable Precursors (TOP) measurements*

The TOP assay has been used for a number of environmental matrices such as effluent waste water, run-off, river and ground waters as well as soil and, as mentioned above AFFF. Most of the publications are written by Houtz and co-workers (Houtz and Sedlak, 2012; Houtz et al., 2013, 2016; McGuire et al., 2014; Harding-Marjanovic et al., 2015), but additional work has been performed by Ye et al. (2014) for Japanese river and effluent waste water and Boiteux et al (2017) for French river water. It is also highly likely that further studies will be published in the coming years as the method becomes more wide spread. Unless stated, percentages of increases in PFCAs after TOP oxidation given below are relative to the original content of PFCA plus PFSA.

In the study by Houtz and Sedlak (2012) 33 urban run-off water samples were subjected to TOP oxidation. Analysis before oxidation showed that PFOS was the major PFAS with a mean of ~15 ng/l followed by PFOA (7 ng/l) and PFHxA (5 ng/l) with sums of PFCA and PFSA in the range 6-42 ng/l and 3-35 ng/l, respectively. After oxidation PFCAs were seen to increase by on average 69% (= 14 ng/l), relative to initial PFCA content. This corresponded to an approximate rise of ~35% compared to the sum of PFCA and PFSA. The largest additions were measured for PFHxA and PFPeA implying that 6:2 telomer based precursors made a significant contribution, although additional shorter precursors also may have existed. The new PFOA generated at oxidation could not primarily be explained by the PreFOS determined before, which accounted for 23% of the increase.

Effluent waste water was investigated by Ye et al. (2014) and Houtz et al. (2016). Ye et al. (2014) also included the river receiving the effluent in their study. For six of the effluents analysed by Houtz et al. (2016), PFHxA showed the highest concentration (mean 24 ng/l) followed by PFOA, PFBA and PFOS (15-23 ng/l). Two WWTP effluents showed much higher levels (~400-600 ng/l) for the PFAS mentioned and in addition at one plant 6:2 FTS was detected at a similar high range. These two plants most likely obtained water contaminated with AFFF. TOP results demonstrated a rise in PFAS ranging from 50 up to almost 150%. The precursors determined on beforehand accounted for a minor part of the increases seen at oxidation. A comparison was also made between samples collected in 2009 and 2014 (non-oxidized) which showed a large decrease in PFOS, and to some extent PFOA, while shorter chain (C≤6) PFAS were found at higher levels, probably reflecting shifts in PFAS production.

The average PFAS content in the effluents and river waters investigated by Ye et al. (2014) were in the range 4-110 ng/l before TOP analysis with the highest concentrations found for PFOS, PFOA (0.5-31 ng/l) and in WWTP effluent also PFHxS (up to 24 ng/l). Oxidation achieved increases of 28% (n=9) for main river samples, 69% for tributaries (n=3) and 21% (n=3) for WWTP effluents. In absolute numbers PFHxA and PFOA increased the most while the largest relative rise was seen for PFBA. The overall picture was the same for the three different types of sites. The higher percentage for the tributaries could indicate alternative sources of PFAS as discussed by the authors. Measured potential C8 precursors (MeFOSA, PFOSA, di-SAmPAP) could not account by far for the PFOA measured in the TOP assay. Boiteux et al (2017) used TOP to assess river water and three connected water wells for drinking water production, affected by PFAS in the effluent from a WWTP belonging to a production site. In the river water the initial PFCA content was between 10-17 ng/l (PFHxA, PFHpA, PFOA; n=8), while PFSA levels were not significant. At oxidation there was a rise of +270-830% (or +46-127 ng/l) and of this increase 18-53% could be explained by known precursors, in particular 6:2 FTS. On one sampling occasion 6:2 FTAB was determined and when this compound was taken into account the degree of explanation rose to 68-82%. In raw and treated drinking water (n=24) overall levels of PFCA was lower after oxidation (13-50 ng/l) with the exception of one raw water well. A larger part of the rise could also be explained for most samples (66-114%) of this type.

Firefighter training sites where PFAS containing AFFF has been used might be the most common kind of large scale contaminated areas. Houtz et al. (2013) and McGuire et al. (2014) analysed groundwater, soil and AFFF products from the same military site applying the TOP method. For groundwater (n=22) the sum of PFAS before TOP was ~180 000 ng/l (median value), but at hotspots values of individual compounds could be >300 000 ng/l. Concentrations generally decreased with distance to the burn pit. The major PFAS identified was PFHxS (median 71 000 ng/l; Houtz et al., 2013). Oxidation raised the PFCA+PFSA content with approximately one third, and about 60% of the rise could be attributed to precursors initially measured, especially 6:2 FTS and PFHxSA. However, significant concentrations of PFBA and PFHxA could not be explained.

The contributions of PFAS from various AFFF were discussed in relation to the compositions of the foams and the groundwater samples. Although one type of AFFF (3M in this case) seemed to dominate it was likely that other foams had been used too as seen on the TOP pattern. In the parallel publication by McGuire et al. (2014) it was shown that the largest amount of additional PFAS formed in groundwater by the TOP method spatially coincided with PFOS contamination rather than PFHxA and PFOA. This observation was interpreted to reflect a more intense aerobic activity near an oxygen biosparging well located away from the highest PFOS/TOP area. This was further supported by the finding that the greatest PFHxS:PFOS ratio was found near this well suggesting biodegradation of e.g. C6 sulfonamides.

Soil concentrations of PFAS and TOP from both the saturated and unsaturated zones were also reported by Houtz et al. (2013) and McGuire et al. (2014). As opposed to groundwater PFOS was the PFAS present at the highest level with median values of 2400 and 270 µg/kg for unsaturated soil and aquifer solids, respectively. Also PFHxS, 6:2 and 8:2 FTS were found at relatively high concentrations though PFCA (incl PFOA and PFHxA) were less abundant. TOP increased the PFCA+PFAS content by ~25% for low contaminated soils and up to 65% for highly contaminated saturated/unsaturated soils. Considering the increase, the smallest proportion (~20%) explained by precursors already determined (e.g. 6:2, 8:2 FTS and PFOSA) was observed for the low contaminated soils (approx. 50-500 µg/kg), while the fraction attributed to known precursors in the samples with higher levels ranged between 40-70%. It should be noted that due to the complex pattern of AFFF contamination correlation was not seen between PFAS determined in the different matrices.

In the soil slurry microcosm study by Harding-Marjanovic et al. (2015) TOP was used to estimate the overall mass balance of an added AFFF, which was dominated by 6:2 FTSAS. Comparing to the spiked amount of 6:2 FTSAS the TOP method gave a recovery of 75-85% after the first addition and 80-100% after the second (0 and 18 d). These numbers are in a range similar to known 6:2 telomer standards (see above). From this observation it was concluded that abiotic removal (e.g. volatilization and adsorption to vessels) probably was of minor importance. The intermediates and end products (PFCAs) determined comprised about 10% on a molar basis after 60 d incubation (see above).

TOP assay of seven AFFF showed that a range of PFCAs at high concentrations (6-11 g/l) were formed (Houtz et al., 2013). Before oxidation measurable levels of PFAS appeared in only two old foams with PFOS (3M products). For all formulations but one the composition of PFCA produced by the TOP method was dominated by C5 and C6 PFCA suggesting various 6:2 and 6C PFSA based precursors (e.g. 6:2 FTAB, 6:2 FTSAS and PFHxSA amine). This finding was also supported by earlier studies of similar AFFF by other authors. For one make a comparison between older and newer foam demonstrated a shift away from C8 based precursors, which is a general observation that can be made concerning AFFF (e.g. KEMI, 2015).

To summarize TOP oxidation increase the PFAS content between 20-800% relative to the original sum of PFCA plus PFSA. From the limited number of studies it is difficult to draw any general conclusions on matrix, contamination level and original PFAS composition for which the contribution made by TOP might be more important. The same statement can be said regarding the fraction that can be explained by precursors analysed on beforehand, though there is a possible tendency that unknown precursors may be more important in samples with low total levels (Houtz and Sedlak, 2012; Ye et al., 2014; Houtz et al., 2016) unless the contaminant source can be well explained (Boiteux et al., 2017).



### *Total oxidizable precursors (TOP) - source tracking and regulation*

Although more studies are warranted, the ones published so far show indicate that there, most commonly, is a significant pool of precursors that are not seen in regular PFAS analysis. To further investigate the source also the pattern of PFCAs formed has been employed to gain information about the nature of unknown precursors. Houtz and Sedlak (2012; suppl. material) set up equation systems to calculate the potential contribution of different telomer and sulfonamide precursors. In this way ranges in precursor concentrations can be constructed. Besides providing information on the composition of precursors, computations could be discussed in a context of production shifts, if samples have been impacted by AFFF or biodegradation (McGuire et al., 2014; Houtz et al., 2016). Similar calculations have underpinned reasoning in other papers too. A possibility to use the concentrations of branched and linear PFCA as another means of shedding light on the origin has been put forward (Houtz et al., 2013) since telomers as opposed to ECF sulfonamides are purely linear. It must be stressed that the number of precursors/polyfluorinated compounds, including PreFOS, determined in the original sample is important and will impact the possibility to assess the origin of the PFCA produced by TOP oxidation. Variance in oxidation pattern and yield, although seemingly predictable, as well as LC-MS/MS analysis must be considered as well.

TOP has already, in part, formed the basis for regulation. In the policy by Queensland Dept. Env. and Heritage Protection on AFFF limits are set out (EHP, 2016). This includes limits for foam with respect to PFOS (10 mg/kg) and the sum PFOA + higher homologues + C7-C14 PFAS formed in the TOP assay. Moreover, values for waste water, above which release to soil, waterways etc is not allowed, are given too. Trigger values are for both PFOA and PFOS 300 ng/l (each) and for the sum of C4-C14 PFAS from TOP plus C4-C8 PFSA 1000 ng/l. Also for monitoring purposes a broader approach than measuring a standard suite of PFAS has been discussed. The Swedish EPA comments in the report 6709 upon the need to assess precursors and other potential organic fluorine compounds (NV, 2016), and specifically mentions TOP and TOF as two ways to achieve this.

### *References*

- Arvaniti, O. S., Stasinakis, A. S. Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment. *Sci. Tot. Env.* 2015, 524–525, 81–92
- Bach, C., Boiteux, V., Hemard, J., Colin, A., Rosin, C., Munoz, J-F., Dauchy, X. Simultaneous determination of perfluoroalkyl iodides, perfluoroalkane sulfonamides, fluorotelomer alcohols, fluorotelomeriodides and fluorotelomer acrylates and methacrylates in water and sediments using solid-phase microextraction-gaschromatography/mass spectrometry. *J. Chrom. A*, 2016, 1448, 98–106
- Benskin, J.P., De Silva, A. O., Martin, J. W. Isomer Profiling of Perfluorinated Substances as a Tool for Source Tracking: A Review of Early Findings and Future Applications. *Rev. Environ Contam. Toxicol.*, 2010, 208, 111-160
- Boiteux, V., Dauchy, X., Bach, C., Colin, A., Hemard, J., Sagres, V., Rosin, C., Munoz, J-F. Concentrations and patterns of perfluoroalkyl and polyfluoroalkyl substances in a river and three drinking water treatment plants near and far from a major production source. *Sci. Tot. Environ.* 2017, 583, 393–400
- Chen, X., Zhu, L., Pan, X., Fang, S., Zhang, Y., Yang, L. Isomeric specific partitioning behaviors of perfluoroalkyl substances in water dissolved phase, suspended particulate matters and sediments in Liao River Basin and Taihu Lake, China. *Wat Res.* 2015, 80, 235-244
- D'Agostino, L., Mabury S. Aerobic biodegradation of 2 fluorotelomer sulfonamide-based aqueous film-forming foam components produces perfluoroalkyl carboxylates. *Environ Toxicol Chem.*, 2017, in press (DOI: 10.1002/etc.3750)
- EHP (Dept. Environ. Heritage Protection). Operational Policy, Environmental Management of Firefighting Foam, ABN 46 640 294 485. Queensland Government, Brisbane, 2016
- Eriksson, U., Haglund, P., Kärrman, A. Contribution of precursor compounds to the release of per- and polyfluoroalkyl substances (PFASs) from waste water treatment plants (WWTPs). *J. Environ. Sci.* (2017), in press (<http://dx.doi.org/10.1016/j.jes.2017.05.004>)
- Gebbink, W. A., Berger, U., Cousins, I. T. Estimating human exposure to PFOS isomers and PFCA homologues: The relative importance of direct and indirect (precursor) exposure. *Env. Int.* 2015, 74, 160–169

- Gremmel, C., Frömel, T., Knepper, T.P. HPLC–MS/MS methods for the determination of 52 perfluoroalkyl and polyfluoroalkyl substances in aqueous samples. *Anal. Bioanal. Chem.* 2017, 409, 1643–1655
- Harding-Marjanovic, K. C., Houtz, E. F., Yi, S., Field, J. A., Sedlak, D. L., Alvarez-Cohen, L. Aerobic Biotransformation of Fluorotelomer Thioether Amido Sulfonate (Lodyne) in AFFF-Amended Microcosms. *Environ. Sci. Technol.* 2015, 49, 7666–7674
- Houtz, E. F., Sedlak, D. L. Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff. *Environ. Sci. Technol.*, 2012, 46, 9342–9349
- Houtz, E. F., Higgins, C. P., Field, J. A., Sedlak D. L. Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. *Environ. Sci. Technol.* 2013, 47, 8187–8195
- Houtz, E. F., Sutton, R., Park, J.-S., Sedlak, M. Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Wat. Res.* 2016, 95, 142–149
- KEMI (Swe. Chem. Agency). PM 6/15 Chemical Analysis of Selected Fire-fighting Foams on the Swedish Market 2014. Stockholm, 2015.
- Liu, J., Lee, L. Effect of Fluorotelomer Alcohol Chain Length on Aqueous Solubility and Sorption by Soils. *Environ. Sci. Technol.* 2007, 41, 5357–5362
- Liu, J., Avendaño, S. M. Microbial degradation of polyfluoroalkyl chemicals in the environment: A review., *Env. Int.* 2013, 61, 98–114
- Mahmoud, M. A. M., Kärman, A., Oono, S., Harada, K. J., Koizumi, A. Polyfluorinated telomers in precipitation and surface water in an urban area of Japan. *Chemosphere* 2009, 74, 467–472
- Martin, J. W., Asher, B. J., Beesoon, S., Benskina, J. P., Ross, M. S. PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? *J. Environ. Monit.*, 2010, 12, 1979–2004
- McGuire, M. E., Schaefer, C., Richards, T., Backe, W. J., Field, J. A., Houtz, E., Sedlak, D. L., Guelfo, J. L., Wunsch, A., Higgins, C. P. Evidence of Remediation-Induced Alteration of Subsurface Poly- and Perfluoroalkyl Substance Distribution at a Former Firefighter Training Area. *Environ. Sci. Technol.*, 2014, 48, 6644–6652.
- Munoz, G., Desrosiers, M., Duy, S. V., Labadie, P., Budzinski, H., Liu, J., Sauvé, S. Environmental occurrence of perfluoroalkyl acids and novel fluorotelomer surfactants in the freshwater fish *Catostomus commersonii* and sediments following firefighting foam deployment at the Lac-Mégantic railway accident. *Environ. Sci. Technol.* 2017, 51, 1231–1240
- Nguyen, T. V., Reinhard, M., Chen, H., Gin, K. Y. H. Fate and transport of perfluoro- and polyfluoroalkyl substances including perfluorooctane sulfonamides in a managed urban water body *Environ Sci Pollut Res*, 2016, 23, 10382–10392
- NV (Naturvårdsverket). Rapport 6709. Högfluorerade ämnen (PFAS) och bekämpningsmedel. En sammantagen bild av förekomsten i miljön. Redovisning av ett regeringsuppdrag
- Park, S., Lee, L. S., Medina, V. F., Zull, A., Waisner, S. Heat-activated persulfate oxidation of PFOA, 6:2 fluorotelomer sulfonate, and PFOS under conditions suitable for in-situ groundwater remediation *Chemosphere*, 2016, 145, 376–383
- Ullberg, M. Effects of pH and Cation Composition on Sorption of Per- and Polyfluoroalkyl Substances (PFASs) to Soil Particles. MSc thesis, Uppsala University, 2015
- Wang, N., Szostek, B., Buck, R.C., Folsom, P.W., Sulecki, L.M., Gannon, J.T. 8-2 fluorotelomer alcohol aerobic soil biodegradation: pathways, metabolites, and metabolite yields. *Chemosphere* 2009, 75, 1089–1096.
- Xie, Z., Zhao, Z., Möller, A., Wolschke, H., Ahrens, L., Sturm, R., Ebinghaus, R. Neutral poly- and perfluoroalkyl substances in air and seawater of the North Sea. *Environ. Sci. Pollut. Res.* 2013, 20, 7988–8000.
- Ye, F., Tokumura, M., Islam, M. S., Zushi, Y., Oh, J., Masunaga, S. Spatial distribution and importance of potential perfluoroalkyl acid precursors in urban rivers and sewage treatment plant effluent. Case study of Tama River, Japan. *Wat. Res.*, 2014, 67, 77–85
- Zhang, S., Lu, X., Wang N., Buck, R. C. Biotransformation potential of 6:2 fluorotelomer sulfonate (6:2 FTSA) in aerobic and anaerobic sediment. *Chemosphere* 2016, 154, 224–230
- Zhang, H., Wen, B., Hu, X., Wu, Y., Luo, L., Chen, Z., Zhang, S. Determination of fluorotelomer alcohols and their degradation products in biosolids-amended soils and plants using ultra-high performance liquid chromatography tandem mass spectrometry. *J. Chrom. A*, 2015, 1404, 72–80.