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New and old sources of PFAA:

Characterization and biodegradation of two side-chain fluorinated acryl co-polymers

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Abstract

The importance of biodegradation of side-chain perfluoroalkyl polymers as environmental sources of perfluoroalkyl acids remains unclear in comparison to volumes produced. Besides scientific community has not been able to show the changes brought to technical mixtures of polymers to reduce environmental burdens of PFAA from residual leaching. In this paper we report on the analysis of two fluorinated side-chain polymers, one old and one new. Besides, biodegradation experiments with treated wastewater as inoculum were performed. The experiments show that new polymers contain large amounts of PFBA and PFHxA while the old polymers contain a majority of PFOA, PFDA and PFDoA. The analysis of these two polymers specifically shows the shift in production from the longer PFOA based production to shorter chain production of PFHxA and PFBA. Biodegradation experiments showed that short chain PFAAs such as PFHxA and PFBA are produced during biodegradation. The concentrations produced are still well explained by the amount of residuals initially present in the raw polymer mix. The experiments show that the new polymers will be a source of PFHxA, PFBA and FTOH to the environment. Environmental concentrations are therefore expected to increase in the future.

Introduction

The presence of different perfluoroalkyl acids (PFAA) in the environment has instigated research on the different sources of these compounds to the environment. Their ubiquitous presence stems from the strong C-F bond and the deprotonated form they are in at environmental relevant pH, which makes them water soluble. PFAA have been shown to be difficult to remove from water in the production of drinking water [1] and low concentrations in the drinking water can already be responsible for large human exposure to these compounds.

PFAA have been produced for their use as additives (e.g. emulsifiers in the fluoropolymers manufacture) or as part of larger molecules [2]. Two types of emission cause the detection of PFAA in the environment, direct emissions and indirect emissions. Direct emissions to the environment occur during production of PFAA, fluoropolymers, perfluoropolyethers and leaching of PFAA residuals from these polymers e.g. leaching of perfluorooctanoic acid (PFOA) from polytetrafluoroethylene (PTFE) [3, 4]. PFAA have been shown to be present as residuals in polymer mixtures at the μg/mL level [5] and also in consumer products from where they can leach in the environment [6]. However, the use of PFOA as emulsifier should have decreased since more environmental friendly alternatives are available and being used [7]. Indirect emissions stem from the degradation of precursor compounds and side chain fluorinated polymers. An example is the degradation of 8:2 fluorotelomer alcohol (8:2 FTOH) to PFOA [8].

Formation of PFAA has been found to occur in air (via atmospheric degradation of precursors) and in water (wastewater treatment plants). Although much information is available on the role of PFAA precursors and their fate in the atmospheric compartment [9, 10], little information is available on the sources of PFAA precursors, especially new short chain PFAA. A particularly fine example of the importance of precursors in water is the increase of PFOA often observed in wastewater treatment plants. When comparing the influent and effluent concentrations the increase observed has been reported to be significant in several papers. Dramatic increases, up to 50 fold have been observed in the increase of fluoropolymers producing plants.

In general the production of the majority of fully fluorinated moieties starts with the production of perfluoroalkyl iodide (PFAI) from which PFCA and fluorotelomer alcohols can be produced. The fluorotelomer acohols are further used for the production of fluorotelomer acrylates (FTAC) and fluorotelomer mono and di phosphates (mono-

and di-PAPs). FTOH based compounds, the side-chain fluorinated polymers (fluorotelomer based) are of interest in the degradation due to their large production volume. Fluoropolymers (such as PTFE) and fluoropolyethers do not have fluorinated side chains but consist of a fully fluorinated carbon backbone, possibly including Oxygen for the polyethers. The largest part of the fluorinated polymer production (133 000 t per year) is for these polymers.

Global production volumes of perfluorocarboxylic acids (PFCAs) associated are in the order of 3200-7500 t for the period 1960-2004 and 450-2700 t of PFOS for the period 1970-2002 [3]. The calculated emission volumes have been shown to compare relatively well with the amount of PFAA estimated to be present in the environment, showing that the direct emissions still prevail in the overall mass balance of PFAA in the environemnt. It was reported that 33 fluoropolymer manufacturing sites in the world together have a production capacity of about 144000 t [3]. This includes fluoropolymers such as Polytetrafluoroethylene (PTFE). The production of FTOH based fluoropolymers can be estimated from the production of fluorotelomer iodide. Which was estimated to be 5000 to 6500 t per year from 1995 to 2004. About 80% of the fluorotelomer iodide produced is used for the production of fluorotelomer acrylate side chain polymer [11]. It was estimated that the production of sidechain acrylate polymer with a C8 carbon perfluorinated backbone is about 1650 to 2145 t per year from 1995 to 2004, which is considerably higher than the production of PFOA per year which draws the majority of the scientific attention.

While precursor compounds such as fluorotelomer alcohols (FTOH), perfluoroalkyl iodides (PFAI) and fluorotelomer iodides (FTI) have been found in the µg/mL range in polymer mixtures [6], little evidence is available for the contribution of PFAA from side-chain fluorinated polymer (see fig 1) degradation to environmental loads. A complicating element in fluorinated side-chain polymer degradation studies is often that differentiation between residual precursor degradation and actual polymer degradation (often expected to be via esther bond degradation) is hard to make [12].

As a result of voluntary PFOA phase out program instigated by the US-EPA [13] the manufacturing industries moved the production from longer chained PFAA (i.e. ≥C8 PFCA) to shorter PFCA (i.e. ≤C6). Several scientific publications observed increasing levels of the short chained PFAA and decreasing levels over time of the longer chained in various media. While environmental concentrations of PFOA and PFNA fit modelled concentrations based on emission data well, discrepancies between modelled and

measured concentrations for the shorter chain PFAA such as PFBA and PFHxA are much larger [14, 15]. A considerate proportion of the measured environmental concentrations were not explained by known sources. This can be attributed to less monitoring data available and to less information available on the sources of the short chain PFAA.

The purpose of this work is twofold, one to investigate the sources of short chain PFAA and two to show the production shift of C8-C10 based chemistry to C4-C6 based chemistry. We therefore selected two side-chain fluorinated acryl co-polymers and analysed these for the presence of PFAA and FTOH residuals and subjected the entire polymer to a biodegradation setup.

Materials and methods

Polymers analysed and degraded. Two cationic side-chain fluorinated co-polymers were obtained: Capstone (DuPont) and Cartafluor CFI (Clariant). While Capstone is a relatively new product with C4-C6 based chemistry, the Cartafluor CFI is older and still C8-C10 based. Both polymers have side chains manufactured according to the fluorotelomerization process. It is therefore expected that the even chained PFAAs and FTOHs will prevail in the mixtures.

Capstone was provided as a 20% purity aqueous dispersion well dissolvable in water. The polymer is cationic. Cartafluor-CFI is a viscous cationic polymer dissolvable in MeOH.

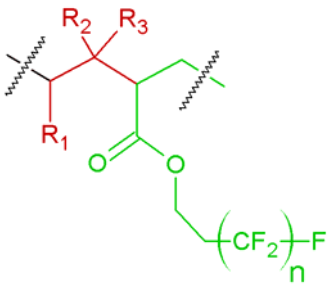

Figure 1 General formula of a side-chain fluorinated acryl co-polymer. R1 can be a non-fluorinated side-chain while R2 and R3 have been shown to be Hydrogen or Chloride. N refers to the number of $-CF_2-$ units and ranges between 6 and 12 for the polymers in the present study.

Residual analysis. Residual FTOH and PFAA were analyzed by carefully pipeting 10 µL polymer in a 2 mL PP cryo vial and filling up with 1 mL MeOH. Mix was Vortex mixed for 1 min and shaken on a shaker for about one hour. The mixture was diluted an appropriate amount of times in order to be quantifiable within the linear dynamic range of the analysis method. After the final dilution step 500 µL of the mixture was spiked with 10 µL internal standard (0,1 ng/µL) and filtered over a 0,45 µm regenerated cellulose filter in a PP insert vial. Although the Capstone polymer was shown not to dissolve in MeOH, it is known that FTOH and PFAA readily dissolve in MeOH. Since for the residual analysis we were mainly interested in the PFAAs and FTOHs this method was used. Possibly the method underestimated the residual concentration due to trapping of the residuals in the polymer.

Oxidation experiments. A 0,1% water solution of the polymer was prepared in a 100 mL PP vial. pH was increased to >12 using NaOH. To the solution 40 gr of Persulfate was added and the sample bottle was placed in a water bath at 80 ˚C for 6 h. After 6 h the bottles were placed in an ice bath and the solution pH was neutralized. Samples were analyzed by direct injection (1:1 MeOH:sample) The experimental method used was described and validated before [12].

Biodegradation experiments. The biodegradation of entire polymer mixture was studied in labscale bioreactors using municipal wastewater treatment plant effluent as inoculum. Figure 2 shows the biodegradation setup. The method used was described in detail before [16]. Briefly, 4.5 L of wastewater effluent was taken for each tank. Three tanks were run, one biodegradation tank, one blank tank and one sterile control tank. Samples were taken daily in the first week and sampling interval gradually decreased after the first week. Air was pumped with an aquarium pump into the tank and effluent air stream was run over a C18 SPE-cartridges in order to catch the volatilized compounds. Microbial activity was checked using a microscope.

Figure 2 Labscale bioreactors setup showing the Biodegradation tank, Blank, and sterile control.

Instruments used.

A linear ion trap quadrupole LC-MS/MS mass spectrometer (Applied Biosystems 3200 Q TRAP, software Analyst, version 1.5.1) in MRM mode with negative ESI was used for determination of the PFASs. Two MS/MS methods were used during this study. The

PFAS-a MS/MS method was used for the experiments, which includes the PFCAs (C4 – C14), PFSAs (C4, C6, C7, C8, C10) and FOSAs (FOSA, N-MeFOSA and N-EtFOSA). The PFAS-n MS/MS method was used for the experiments, which includes the FTOHs (6:2, 8:2, 10:2-FTOH) and FOSEs (N-MeFOSE and N-EtFOSE)

A hybrid triple quadrupole/linear ion trap LC-MS/MS mass spectrometer (Applied Biosystems 3200 QTRAP, software Analyst, version 1.5.1) in MRM mode with negative ESI was used for determination of the PFASs. A Perkin Elmer Series 200 HPLC system combined with three reverse phase columns was used: a C18 pre-column (Phenomenex Aqua, 50 x 2.0 mm, 5 µm) was inserted before the injector and retarded the PFAS leaching out of the system. The analytical C18 column (MZ-Aqua Perfect®, 50 x 2.1 mm, 5 µm) was protected by a C18 precolumn (MZ-Aqua Perfect® precolumn, 5 µm).A water/methanol gradient with 5 mM ammonium acetate was used and the duration ofone run was 35 minutes. Eluent A was H2O with 5% MeOH and 5 mM ammonium acetate and eluent B contained 95% MeOH with 5% H2O and 5 mM ammonium acetate. The injection volume was 50 µL at a flow rate of 200 and 300 µL/min depending on the HPLC method.

PFAS-n method

The injection volume was 50 µL at a flow rate of 200 µL/min. A basic scheme of the gradient is presented in Table 1. An overview of the MS/MS method, internal standards and retention times used is shown in Table 2.

Table 1: HPLC gradient of the PFAS-n method

Total Time [min]	Flow Rate [µL/min]	A [%]	B [%]
0	200	50	50
2	200	50	50
8	200	0	100
10	200	0	100
12	200	50	50
25	200	50	50

Table 2: Overview of the MS/MS method, MRM transition and retention time of the PFAS-n MS/MS method

Substance	MW [g/mol]	MRM transition [*m/z*, $[M+Ac]^-$]	Internal standard	Retention time [min]
6:2-FTOH	364.1	423 > 59	M-8:2-FTOH	8.8
8:2-FTOH	464.12	523 > 59	M-8:2-FTOH	10.0
10:2-FTOH	564.14	623 > 59	M-8:2-FTOH	10.8
N-MeFOSE	557.23	616 > 59	M-8:2-FTOH	10.1
N-EtFOSE	571.25	630 > 59	M-8:2-FTOH	10.4

PFAS-acids

The injection volume was 50 µL at a flow rate of 300 µL/min. A basic scheme of the gradient is presented in Table 3. An overview of the PFAS-acids MRM transitions, internal standards and retention times is shown in
Table 4.

Table 3 HLC gradient of the PFAS-a method.

Total Time [min]	Flow Rate [µL/min]	A [%]	B [%]
0	300	100	0
2	300	100	0
15	300	0	100
20	300	0	100
25	300	100	0
35	300	100	0

Table 4: Overview of the MS/MS method, MRM transition and retention time of the PFAS-a MS/MS method

Substance	MW [g/mol]	MRM transition [*m/z*, $[M-H]^-$]		Internal Standard	Retention time [min]
		Quantifier	Qualifier		
PFBA	214.03	213 > 169	-	MPFBA	6.3
PFPeA	264.04	263 > 219	-	MPFHxA[1]	11.1
PFHxA	314.05	313 > 269	313 > 119	MPFHxA	12.5
PFHpA	364.06	363 > 319	363 > 169	MPFHxS[1]	13.3
PFOA	414.07	413 > 369	413 > 169	MPFOA	14.0
PFNA	464.07	463 > 419	463 > 169	MPFNA	14.6
PFDA	514.08	513 > 469	513 > 269	MPFDA	15.2
PFUnA	564.09	563 > 519	563 > 319	MPFUnA	15.7
PFDoA	614.1	613 > 569	613 > 219	MPFDoA	16.1
PFTrA	664.1	663 > 619	663 > 169	MPFDoA[1]	16.5
PFTeA	714.11	713 > 669	713 > 169	MPFDoA[1]	16.9
PFBS	300.10	299 > 80	299 > 99	MPFHxA[1]	11.6
PFHxS	400.12	399 > 80	399 > 99	MPFHxS	13.4
PFHpS	450. 12	449 > 80	449 > 99	MPFOA[1]	14.0
PFOS	500.13	499 > 80	499 > 99	MPFOS	14.6
PFDS	600.14	599 > 80	599 > 99	MPFUnA[1]	15.6
FOSA	499.15	498 > 78	-	MPFDoA[1]	15.6
N-MeFOSA	513.17	512 > 169	512 > 219	MPFDoA[1]	16.4
N-EtFOSA	527.2	526 > 169	527 > 219	MPFDoA[1]	16.7

[No internal standard was available for the substances with an index [1].The application of present labelled compounds with a closed retention time to the analytes compensated those inexistences]

Quality assurance.

Data were only reported when complying with the following criteria: analyte signal to noise ratio was >10; peak area of the sample was within the peak area s covered by the levels and the ratio of the transition 1 and transition 2 of an analyte did not differ by more than 30% from the average tr1/tr2 ratio in the levels.

Recoveries per matrix and experiment are given in table 1.

Table 5 Recovery biodegradation experiments

Samples	Recovery	Stdev	LOQ	Blank
Capstone Biodeg PFHxA	131	26	0.05 ng/mL[a]	nr
Capstone Biodeg PFBA	108	21	0.5 ng/mL[a]	nr
Cartafluor Biodeg PFOA	107	21	0.5 ng/mL	nr
Residual PFBA	101	5	0.5 ng/mL[a]	<LOQ
Residual PFPA	88	10	0.5 ng/mL[a]	<LOQ
Residual PFHxA	88	10	0.5 ng/mL[a]	<LOQ
Residual PFOA	62	25	0.5 ng/mL[a]	<LOQ
Residual FTOH	79	2	10 ng/mL	

[a] LOQ based on the lowest validated level.

[b] LOQ based on the blank concentration.

nr = non relevant since blanks are accounted for by blank in the biodegradation experiment

Additionally the quantification of residual PFAS in the polymer mixes were performed at the DTU in Copenhagen, Denmark and at the FHS in Idstein, Germany.

Results and discussion

Presence of residuals in two polymer mixtures.

The concentrations of the residual FTOHs and PFAAs in the Capstone and Cartafluor CFI polymer mixture were quantified using LC-MS/MS. Figure 3 shows the Capstone polymer which is based on the new short chain FTOH chemistry and the Cartafluor which is based on the longer chained PFAAs.

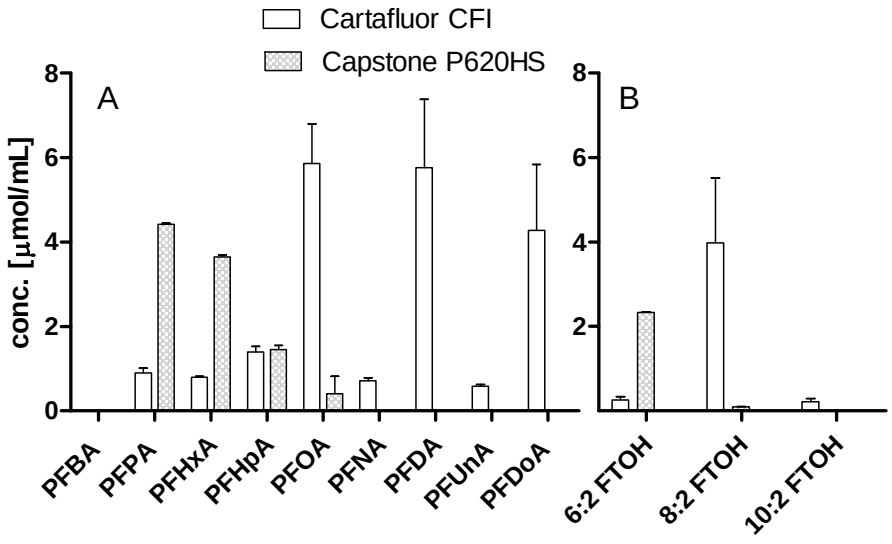

Figure 3 Residual PFAA (graph A) and FTOH (graph B) concentrations measured in the polymer. Concentrations are given per gram polymer.

The Capstone polymer contains large amounts of the PFHxA (Figure 3A). Striking is the presence of PFPA, based on the production process via telomerization uneven chains are not expected to be present in the mixture. While PFBA could not be measured it is expected to be present in large concentrations. A similar pattern can be observed for the FTOHs. 8:2FTOH is mainly present in the Capstone mixture while 8:2 and 10:2 are mainly present in the Cartafluor mixture.

The concentrations encountered are in the same order of magnitude as reported by others.

Polymers oxidation

Oxidation experiments show that both polymers give a different result. While Capstone (graph A) shows a dramatic increase in concentration, approximately 500 fold for PFBA and PFBA. The increase is not explainable by the conversion of residual 6:2 FTOH in PFHxA. One possible explanation is that the polymer is degrading to FTOH and subsequently to PFHxA. The oxidation potential of OH radicals is known to be very powerfull. The Cartafluor shows a smaller increase (about tenfold) which is explainable by the residual FTOH present in the polymer. Two reasons can be postulated for the non-dramatic increase: the longer perfluorinated chain present in de polymer gives steric hindrance for the OH radicals to access the weak esther bond or due to the insolubility of the polymer in water, a precipitation occurred during spiking (400 µL in MeOH) and rendered the crystallized polymer inert to the oxidation.

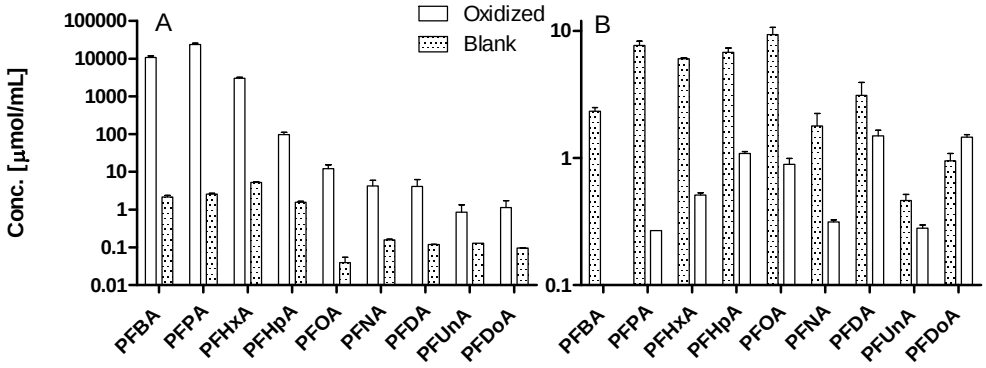

Figure 4 Graphs of oxidized Capstone (A) and Cartafluor (B). Note the difference in scale.

Biodegradation experiments.

The biodegradation experiments were run for a total period of 100 days, Figure 5 shows the results from the first 30 days. On the left y-axis the PFHxA concentration and on the right y-axis 6:2 FTOH concentration in the biodegradation tank are shown. Figure 8 shows that in the culture tank the PFHxA concentration steadily increases to about 4 nmol/L while the sterile cultures remain constant. The point where the y-axis is cut by the sterile and culture line is similar (1 nmol/L) and reflects the PFHxA initially present as residual in the polymer mixture. The PFHxA concentration in the blank tank is reflected by the LOQ. Whether the increase in PFHxA increased is explained by the degradation of the polymer or the residuals is not explained by the figure 8.

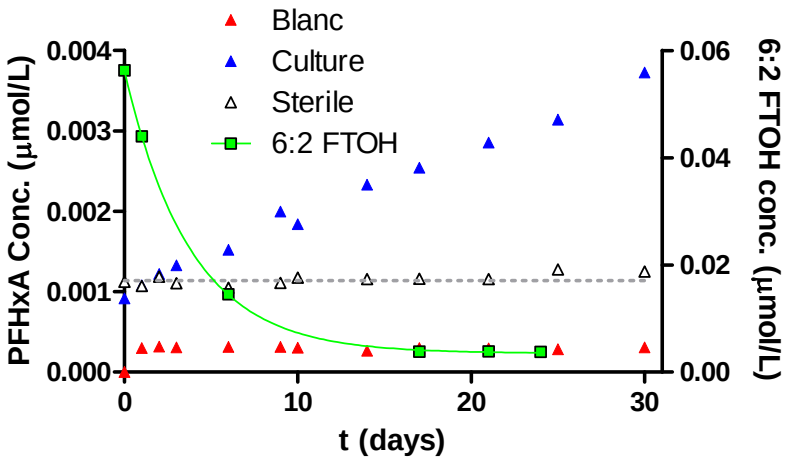

Figure 5 PFHxA concentrations measured in the Blanc, sterile and culture (left axis) and 6:2 FTOH concentration in the Culture (right axis).

Air emissions of the FTOH

Such as explained in the materials and method section the air flow out of the experimental tanks was lead over a C18 cartridge. The first two weeks, two C18 cartridges were placed in series to control for breakthrough of FTOH. Figure 9 shows the cumulative absolute amount of 6:2 FTOH trapped by the C18 cartridges. About 10 nmol escaped from the water phase in total, this is similar for the biodegradation and the

sterile control tank. The black line in figure 8 shows the theoretical increase in the C18 cartridge on the basis of the 6:2 FTOH decrease measured in the aqueous phase. It is shown that about 10% of the initially removed 6:2 FTOH from the biodegradation tank is trapped in the C18 cartridge, 90% is missing. The amount of formed PFHxA (assumed to be 100% stemming from 6:2 FTOH) explains about 0,018 µg (0,004 * 4,5 L (volume of the tank)) of the removed 6:2 FTOH. Summing these up about 28% of the removed 6:2 FTOH is explained by the measurements performed in this work.

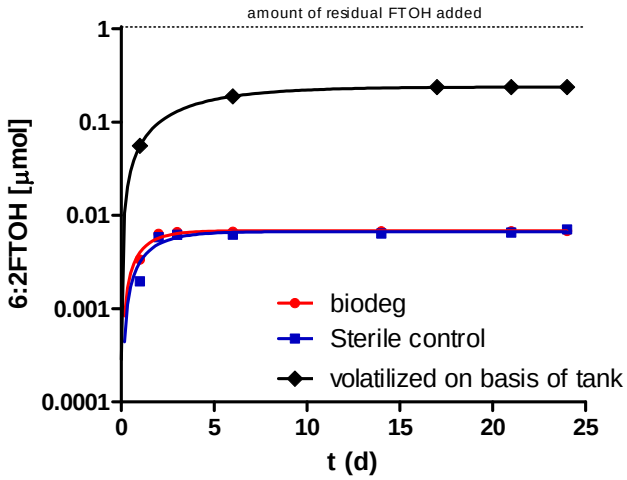

Figure 6 Cumulative trapped absolute amount of 6:2 FTOH in the C18 filters.

Inorganic fluorine concentration

The residuals quantified in the technical mixtures were the FTOH and PFAA. Based on the amount of inorganic fluorine present in the polymer, the amount of PFHxA equivalents in the polymer could be calculated according to a method described in the SI of [8]. Weight percent of fluorine in the etst substance was 12%, which is comparable with the previously measured values by the DuPont cooperation itself in a similar polymer: 12% [8].

Table 6 Characteristics of the Capstone fluoropolymer.

Capstone		
Residual 6:2 FTOH	2,6	nmol
Residual PFHxA	0,005867	nmol
Percentage of Fluorine	12%	g-F/g-polymer

Percentage fluorine in 6:2 FTOH	68%	g-F/g 6:2 FTOH
Percentage 6:2 FTOH of FTOH residuals	61%	g 6:2 FTOH / g ΣFTOH

On the basis of the concentrations and percentages presented in Table 6 it was calculated that the maximum concentration of PFHxA formed on the basis of the polymer degradation would me about 9.3 mg/L. The oxidation experiments performed showed that about 0.667 mg/L PFHxA was formed due to the oxidation of the Capstone polymer (formation of PFHxA was backcalculated to the tank concentration).

The maximum amount of PFHxA formed on the basis of the 6:2 FTOH residual present would be about 82 µg/L. Figure 8 shows the amount of PFHxA produced after 30 days approximately1,2 µg/L. The amount of 6:2 FTOH trapped in the C18 cartridge was about 12 µg/L. These simple calculations show that the formed PFHxA is largely explained by the degradation of precursors and that a large proportion of the residuals will escape via the air and not be converted to PFHxA.

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