

Pilot-Scale Fluoropolymer Incineration Study: Thermal Treatment of a Mixture of Fluoropolymers under Representative European Municipal Waste Combustor Conditions

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Significance and Motivation

A recent study by Conversio, a consultancy based in Germany, has shown that at its end-of-life approximately 85% of all fluoropolymers end up in waste-to-energy recovery incinerators. A subsequent question of regulators was: Do fluoropolymers get fully incinerated without any formation of short chain or long chain PFAS? A recent project executed by the Karlsruhe Institute of Technology (KIT) in cooperation with Société Générale de Surveillance (SGS) was conducted to assess the same.

Experimental Parameters

Main applications of the four highest volume fluoropolymers (PTFE, PVDF, PFA and FKM) representing more than 80% of commercial fluoropolymer production based on data from Pro-K (German association of polymers processors) were considered. Post-use samples from these applications were incinerated as a mixture under standard operating conditions for municipal and industrial waste incineration. Figure 1 presents the experimental conditions. Experiments were conducted under two sets of conditions over a period of 9 days. The first experiments were conducted at a process setting of 860°C and 2.0 s residence time. These experiments were conducted in three stages. Initially, background tests were performed using natural gas and 100 kg/h wood chips. This was followed by the same fuel conditions with the addition of 320 g/h of fluoropolymer. The final test involved switching back to background conditions. The duration of each of these tests ranged from 9 – 13 hrs. A second set of experiments was conducted at a process setting of 1100°C and 2.0 s residence time. These tests were conducted in the same sequence as the first set of tests. The feed rates for the wood chips and the fluoropolymer mixture were identical to the tests at 860°C and 2.0 s residence time. The test duration for this second set of tests also ranged from 9 – 13 hrs.

test	parameters	number of HF and PFAS sampling	locations	duration [hrs]	RUN	date / remarks		day
start-up with natural gas and oil				24		25.2.23; 10 a.m.	day 1 and 2	
starting solid feeding (wood chips)				24		26.2.23; 10 a.m.		
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips	T _{PCC} : 860 °C; 2.0 s	3	Top of post-combustion chamber (E1b), after boiler, stack	11	1	27.2.2023; 9 am	day 3	Monday
solid fuel: woodchip (100 kg/h) + 320 g/h FP together with oil and natural gas		no		9		feeding of fluoropolymers over night		
		3		11	2	28.2.2023; 9 am	day 4	Tuesday
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips		no		13		stop feeding flouoropolymers in the evening		
		3		11	3	01.03.2023; 9 am	day 5	Wednesday
Change of temperature post combustion chamber				12		over night		
background of rotary kiln / combustion chamber with oil, natural gas and wood chips	T _{PCC} : 1100 °C; 2.0 s	3	Top of post-combustion chamber (E1b), after boiler, stack	11	4	02.03.2023; 9 am	day 6	Thursday
solid fuel: woodchip (100 kg/h) + 320 g/h FP together with oil and natural gas		no		9		feeding of fluoropolymers over night		
		3		11	5	03.03.2023; 9 am	day 7	Friday
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips		no		13		stop feeding flouoropolymers in the evening		
		3		11	6	04.03.2023; 9 am	day 8	Saturday
shut down				24			day 9	

Material	Mass fraction [wt.-%]
PTFE tubes	63,00
PTFE tape	7,00
PVDF	18,00
PFA	6,00
FKM rubber	6,00

mass flow = 320 g/h

Figure 1: Experimental setup

The fluoropolymers were fed as a mixture at relative proportions that correspond to the mass fractions sold in the European marketplace. These data are also shown in Figure 1. Suspension and emulsion polymerized PTFE application samples represented about 70 mass percent of the fluoropolymer feed rate.

The main operational parameters for the two sets of tests are summarized in Figure 2. The temperature of the flue gas outlet exiting the rotary kiln was in the range of 800-900°C. The temperature of the flue gas post-combustion chamber outlet was very close to the targets for these tests (860° and 1100°C in the combustion chamber for setting 1 and 2, respectively). The O₂ and CO measurements for setting 1 and 2 varied somewhat. For setting 1, the values were 11.2 vol % dry and 0.2 mg/m³, respectively, while for setting 2 the O₂ measurements were somewhat lower (7.0 % with an increase in the CO concentration (1.2 mg/m³). The water vapor concentration as measured in the boiler exit ranged from 6.2% in setting 1 to 8.49% in setting 2.

			setting S1	setting S2
		unit	RUN 1, 2, 3	RUN 4, 5, 6
Rotary kiln	mass flow wood chips	kg/h	98	98
	main air	m _N ³ /h	418	423
	mass flow heating oil	kg/h	61	46
	volume flow natural gas	m _N ³ /h	4	4
	volume flow combustion air	m _N ³ /h	872	753
	inclination	°	2	
	rotation speed	rev p.m.	0.2	0.4
	temperature flue gas outlet	°C	800 - 900	
	thermal power	MW	1.1	0.9
combustion chamber	volume flow natural gas to burner D4.1	m _N ³ /h	22	35
	sum of volume flow combustion air to burner D4.1	m _N ³ /h	671	429
	volume flow natural gas to burner D4.2	m _N ³ /h	22	35
	sum of volume flow combustion air to burner D4.2	m _N ³ /h	671	428
	residence time	s	2	
	temperature flue gas post-combustion chamber outlet (with control)	°C	860	1095
	CO (level E2)	mg/m ³	0.2	1.2
	O ₂ (level E2)	Vol.-% dry	11.2	7.0
	thermal power	MW	0.46	0.72
total thermal power rotary kiln and post combustion chamber		MW	1.59	1.67
boiler / fluegas	volume flow	m _N ³ /h	3958	3238
	O ₂	Vol.-% dry	11.9	9.0
	CO	mg/m ³	1.35	1.64
	water vapour	Vol.-% wet	6.20	8.49

Figure 2: Main operational parameters at two experiments

There were multiple sampling locations for this study. Flue gas was sampled near the exit of the combustion chamber (location 1), at the exit of the boiler (location 2), and at the entrance to the stack (location 3), while liquids and residues were also sampled and analyzed after each RUN (see Figure 3, Test facility sampling locations).

The test facility BRENDA comprises a rotary kiln with a post-combustion chamber, a boiler for heat recovery and a flue gas cleaning system, which complies with German emission regulations (17 BImSchV). The thermal power of the rotary kiln is of maximum 1.5 MW, while that of the post-combustion chamber is about 1 MW, which results in a total thermal output of BRENDA of maximum 2.5 MW.

The fluoropolymers mixture after blending with wood chips and consequent weighing was delivered to the rotary kiln. To secure optimal combustion conditions, natural gas and heating oil were supplied additionally to the rotary kiln, while the post combustion chamber was supplied with natural gas only.

The mass flow of the fluoropolymers mixture was set at 320 g/h, which corresponds to a pure Fluorine mass flow of 230 g/h. This level increases the fluoropolymer ratio to fuel, while at the same time keeps the Fluor-concentration below the total halogen limit of 1%, as set by the legislature.

The combustion gases of the rotary kiln enter the post combustion chamber (PCC). It contains two natural gas burners staggered in an antiparallel manner, with a slight shift to each other. The temperature and the residence time in PCC were adjusted mainly with the help of the above mentioned burners, supported by a slight shift of about 200 kW into the post combustion chamber.

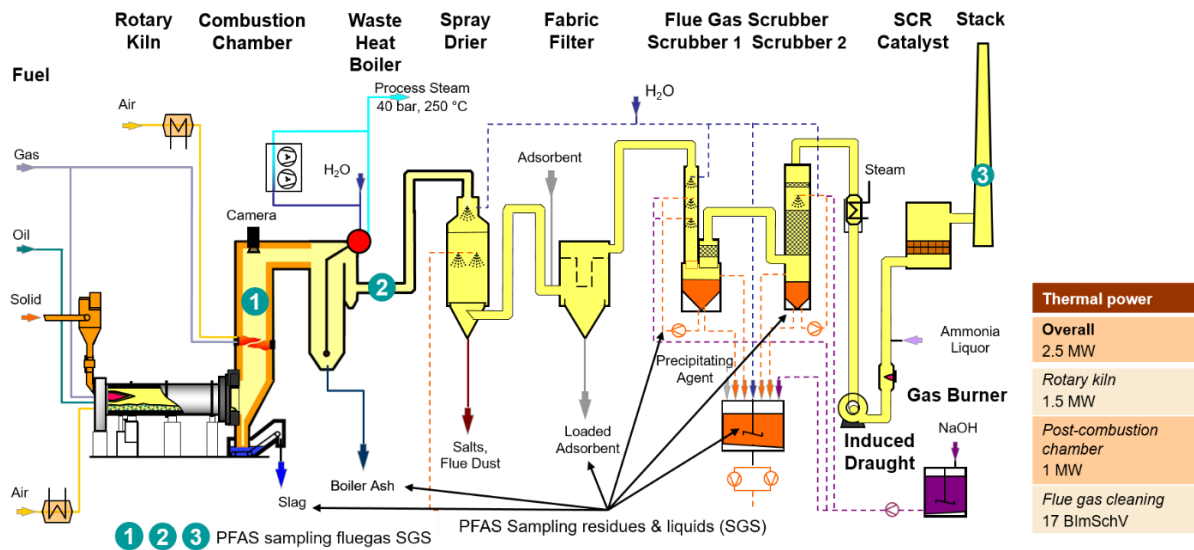


Figure 3: Test facility-BRENDA at KIT

The minimum residence time is calculated according the methodology of the German Technical Supervision Agency ("TÜV") from 2007. The data which were published in the report were re-calculated and then adapted to the operational conditions in this study (Setting 1 and Setting 2). Figure 4 presents the layout of the post combustion chamber with the geometry relevant for the determination of the residence time.

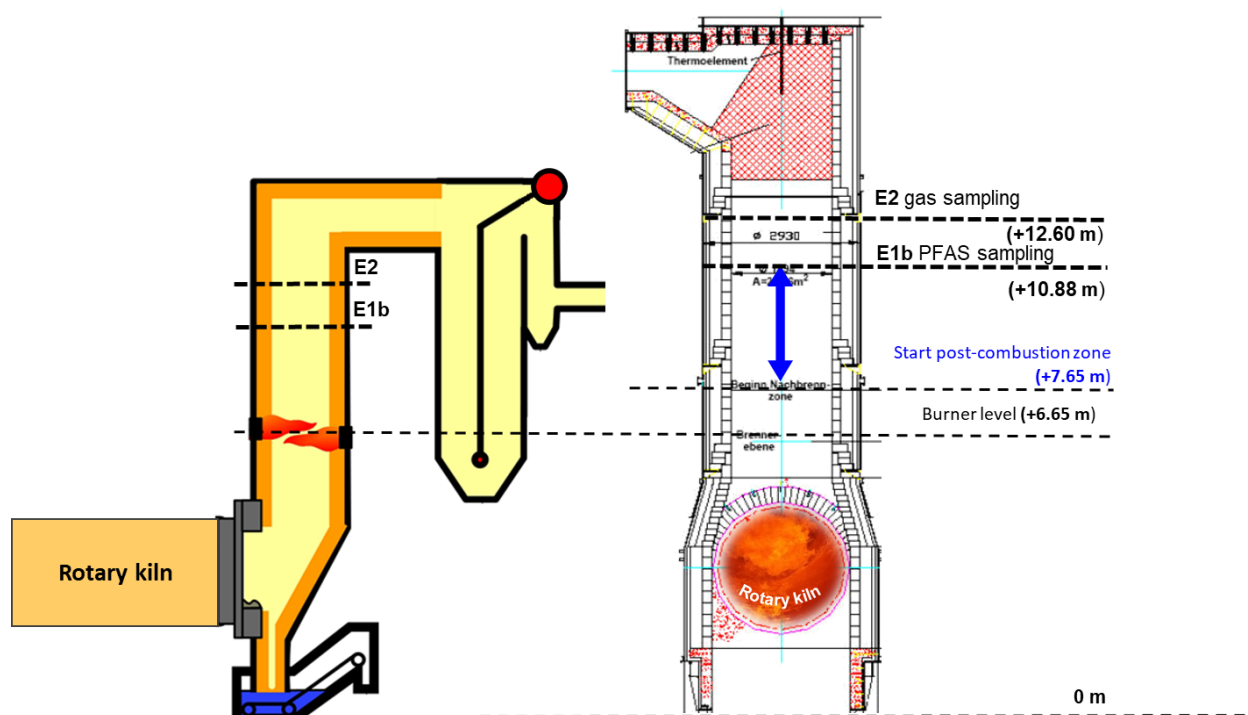


Fig. 4: BRENDA layout with details relevant for the residence time

Table 1 shows the detailed values for the design of the settings.

The volume flow of the required flue gas amount to reach the two seconds was calculated with a target value search.

Table 1. Parameters calculated for the residence time in the PCC

PFAS Project, Level E1b		
	setting 1	setting 2
Start post combustion zone [m] 1 meter above the burners	7.65	7.65
Temperature in the post combustion chamber (PCC) [°C]	860	1100
Volume flow V_{PCC} [m_N^3/h wet] after boiler	3947	3257
Cross section PCC [m^2]	2.82	2.82
Volume flow V_{PCC} [m^3/h]	16,382	16,382
Height h [m] level E1b	10.88	10.88
Residence time from start PCC zone to level E1b [s]	2.00	2.00

The two seconds are the residence time of flue gas from start of post-combustion zone until PFAS sampling point E1b, calculated with calibrated temperature measurements on the top of post combustion chamber (PCC).

The flue gas was sampled for both short-chain and long-chain PFAS in addition to organic and inorganic fluoride. Volatile organic C_1 - C_4 fluorocarbons were also sampled using a tedlar bag at all three sampling locations. At location 2, gas-phase HF was measured in near real-time using a tunable diode laser (TDL). The purpose of the three gas-phase sampling locations was to assess the potential emissions of PFAS at different locations in the system and to use this data to assess potential sources of PFAS in this system. PFAS sampling of residues and liquids is also shown in Figure 3. In addition to these three sampling points, flue gas scrubber water upstream of the SCR catalyst was collected and analyzed for PFAS.

Table 2 provides a list of analytes measured in this study and the Limit of Quantification (LOQ). In addition to PFAS and fluoride ion, volatile C_1 - C_4 fluorocarbons and trifluoroacetic acid (TFA) were also measured. The C_1 - C_4 fluorocarbons were measured by gas chromatography coupled to mass spectrometry (GC-MS). Adsorbable organic fluoride (AOF) was measured using Combustion Ion Chromatography (CIC) and inorganic fluorine in impinger samples were measured by Ion Selective Electrode. TFA was measured using Ion chromatography (IC) and long chain PFAS from impinger samples were measured using Ultrahigh-Performance Liquid Chromatography coupled to tandem Mass Spectrometry (UPLC-MS/MS). HF was also measured at the post-combustion zone location using TDL spectroscopy.

Appendix 1 presents a list of long-chain PFAS measured in this study.

Table 2. Analytes and reporting limits

Analyte	LOQ
Volatile C1-C4 Compounds (CF ₄ , CHF ₃ , C ₂ F ₆ , C ₂ H ₅ F, CF ₂ =CF-CF ₃ , cy-C ₄ F ₈)	5-30 ug/m ³
Adsorbable Organic Fluorine	2 ug/L
Inorganic Fluorine	0.1 ug/L
Trifluoroacetic Acid	0.02 ug/L
PFAS (see Appendix for list of compounds measured)	0.02 ug/L

Note: LOQ for AOF, Inorganic fluorine, TFA, and PFAS are for aqueous samples.

Experimental Results

Fluorine Recoveries

Fluorine recoveries ranged from 69 to 84% using the TDL (at sample location 2). The variability in these data from run to run was low. In contrast, the impinger data analyzed at the same sample location showed about 10 to 20% lower fluorine recoveries. The data are summarized in Table 3. The TDL data provide strong evidence for complete mineralization of fluoropolymer feed mixture.

Table 3: Fluorine Recovery (TDL Measurement)						
Run	Settings	HF (TDL)	volume flow @standard wet conditions	volume flow @270 °C	Fluorine	Fluorine Recovery
		mg/m _B ³ wet Gas	[m _N ³ /h]	[m _B ³ /h]	g/h	%
2	860°C, > 2s, oil + nat. gas + wood chips + 230 g/h F	23.50	3,956	7,866	175.64	76%
		23.93	3,952	7,859	178.62	78%
		25.80	3,943	7,841	192.16	84%
5	1100°C, > 2s, oil + nat. gas + wood chips + 230 g/h F	25.44	3,299	6,560	158.53	69%
		26.58	3,231	6,424	162.23	71%
		26.93	3,217	6,397	163.64	71%

Long-chain PFAS

A large majority of the PFAS measured in impinger samples were near or below reporting limits (>98% of data collected at 860°C and >96% of data collected at 1100°C). Table 3 presents PFAS data for 4 compounds where measurements exceeded reporting limits in several cases. Of particular note is a HFPO-DA measurement which exceeded reporting limits by a factor of 47. Maximum PFBA, PFBS, and 6:2 FTS measurements exceeded reporting limits by much lower factors, ranging from 9 – 12.

These data was re-analyzed to assess the veracity of data. The results are also presented in Table 4. The results indicate that the high measurement values for HPFO-DA could not be reproduced. The results for PFBA and PFBS were also lower when re-analyzed. The lack of reproducibility of data and the lower

measurement values upon re-analysis suggests that cross-contamination is a possible reason for high measurement values for HPDO-DA, PFBA, and PFBS in the initial analysis.

PFAS analyses of wastewater and ash residue samples indicated a large majority of the samples were below reporting limits. One notable exception was a deslagger water bath sample where HFPO-DA was a factor of 16 above the report limit.

Table 4. PFAS Analysis of Impinger Samples

Initial Analysis

PFAS Compound	RL (ng/m ³)	# > RL	ng/m ³ (max)
PFBA	2.8	5	35.8
PFBS	1.4	22	19.5
6:2 FTS	1.4	17	12.5
HFPO-DA	1.4	31	66.3

Re-Analysis

PFAS Compound	RL (ng/m ³)	# > RL	ng/m ³ (max)
PFBA	2.8	0	2.8
PFBS	1.4	7	10.7
6:2 FTS	1.4	11	16.2
HFPO-DA	1.4	16	25.2

Note: For each data set, the total number of measurements equal 54: 27 for each combustion condition.

Short-chain PFAS

TFA was non-detect for all 76 impinger samples analyzed, at a reporting limit of 14 µg/m³ (ppb).

Volatile Fluorocarbons (FC)

Tetrafluoromethane (CF₄) was the only volatile FC detected in the GC-MS analysis. Values of CF₄ at stack were near detection limits (20-27 µg/m³) and detected in 2 of 14 samples. The results are considered questionable because CF₄ was only detected in one post-combustion sample. There is no plausible reason for larger CF₄ values downstream of the combustion unit unless a non-combustion source is considered.

Discussions

There is one prior published pilot-scale study of the combustion of PTFE (Aleksandrov et al. 2019). Combustion tests were performed at two conditions: 870°C and 4 s residence time and 1020°C and 2.7 s residence time and wood chips were used as the supplemental fuel. The prior study burned 0.3 wt % PTFE. Sampling was performed at a single location, downstream of the waste heat boiler. Thirty-one PFAS compounds were sampled and analyzed (see Table 1 of Aleksandrov et al. for a list of PFAS measured).

Fluorine recoveries were determined indirectly via IR water vapor measurements. The fluorine recoveries ranged from 56 to 78%, with three of the four tests yielding recoveries less than 70%. Eleven PFAS compounds were detected from the combustion and/or control samples and each at a level above 100 ng/m³ in at least one sample. PFOA was detected in all but one sample and at values as high as 2.7 µg/m³ (see Table 3 of Aleksandrov et al.).

The current study differs from the prior test in two important ways. The fluorine recoveries in this study were determined from direct spectroscopic measurements and were above 70% in five of the six tests. Secondly, PFAS reporting limits were on the order of 1 ng/m³ or less and a large majority of samples (>98%) were at or below reporting limits. The current study provides strong evidence that incinerating a mixture of fluoropolymers under representative municipal waste combustion conditions leads to complete mineralization of the C-F bonds, no significant emissions of long-chain PFAS, and no significant emissions of TFA or light fluorocarbons such as CF₄ or C₂F₆. The prior study did not provide evidence that the PFAS detected were from sources other than the combustion of PTFE.

Conclusions

The study clearly demonstrated that fluoropolymers are converted to inorganic fluorides and carbon dioxide. The inorganic fluorides detected were hydrogen fluoride. A large majority of samples indicated that long-chain PFAS were below levels of 1 ng/m³ (> 99% of samples associated with 860°C condition and > 98% of samples associated with 1100°C condition). There were no short chain PFAS detected post incineration. TFA was non-detectable in all samples with a reporting limit of 14 µg/m³. **The results confirm that fluoropolymers at their end of life when incinerated under representative European municipal incinerators conditions do not generate any measurable levels of PFAS emissions and therefore pose no risk to human health and the environment.**

The main reason to include fluoropolymers in the EU PFAS restriction proposal was persistence (resistance to degradation in the environment) in the environment. The absence of organic fluorides and more specifically PFAS in tests representative of municipal waste incineration confirms complete mineralization of fluoropolymers and provides critical data in support for exempting Fluoropolymers from the EU REACH PFAS restriction proposal.

References

TÜV report from 19th of January 2007: Expert opinion on compliance with and monitoring of the combustion conditions (residence time, temperature) in the afterburning zone of the THERESA test facility at the Forschungszentrum Karlsruhe GmbH

Aleksandrow, K, Gehrmann, H-J, Hauser, M., Matzing, H., Pigeon, D., Stapf, D., and Wexler, M., Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas, Chemosphere, 2019, 226, 898-906.

Appendices

1. List of long-chain PFAS analytes analyzed in this study

Common Name ^a	Abbreviated Name	CAS ^b Registry Number	Isotopic Pre-Extraction Pair
Perfluoroalkylcarboxylic acids (PFCAs)			
Perfluorobutanoic acid ^{1,3,4}	PFBA	375-22-4	¹³ C ₄ -PFBA
Perfluoropentanoic acid ^{1,3,4}	PFPeA	2706-90-3	¹³ C ₅ -PFPeA
Perfluorohexanoic acid ^{1,2,3,4}	PFHxA	307-24-4	¹³ C ₂ -PFHxA
Perfluoroheptanoic acid ^{1,2,3,4}	PFHpA	375-85-9	¹³ C ₄ -PFHpA
Perfluorooctanoic acid ^{1,2,3,4}	PFOA	335-67-1	¹³ C ₄ -PFOA
Perfluorononanoic acid ^{1,2,3,4}	PFNA	375-95-1	¹³ C ₅ -PFNA
Perfluorodecanoic acid ^{1,2,3,4}	PFDA	335-76-2	¹³ C ₂ -PFDA
Perfluoroundecanoic acid ^{1,2,3,4}	PFUnDA	2058-94-8	¹³ C ₂ -PFUnDA
Perfluorododecanoic acid ^{1,2,3,4}	PFDoA	307-55-1	¹³ C ₂ -PFDoA
Perfluorotridecanoic acid ^{2,3,4}	PFTriDA	72629-94-8	¹³ C ₂ -PFDoA
Perfluorotetradecanoic acid ^{2,3,4}	PFTeDA	376-06-7	¹³ C ₂ -PFTeDA
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	¹³ C ₂ -PFHxDA
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	¹³ C ₂ -PFDoA
Perfluorinated sulfonic acids (PFSA)			
Perfluoro-1-butanedisulfonic acid ^{1,2,3,4}	PFBS	375-73-5	¹³ C ₃ -PFBS
Perfluoro-1-pentadisulfonic acid ^{1,3}	PFPeS	2706-91-4	¹³ C ₃ -PFHxS Or ¹³ C ₃ -PFBS
Perfluoro-1-hexadisulfonic acid ^{1,2,3,4}	PFHxS	355-46-4	¹⁸ O ₂ -PFHxS or ¹³ C ₃ -PFHxS
Perfluoro-1-heptadisulfonic acid ^{1,3}	PFHpS	375-92-8	¹³ C ₄ -PFHpA
Perfluoro-1-octadisulfonic acid ^{1,2,3,4}	PFOS	1763-23-1	¹³ C ₄ -PFOS
Perfluoro-1-nonadisulfonic acid ³	PFNS	68259-12-1	¹³ C ₄ -PFOS
Perfluoro-1-decadisulfonic acid ³	PFDS	335-77-3	¹³ C ₄ -PFOS
Perfluorododecane sulfonate	PFDoS	79780-39-5	¹³ C ₄ -PFOS
Perfluorinated sulfonamides (FOSAs)			
Perfluoro-1-octanesulfonamide ^{3,5}	FOSA	754-91-6	¹³ C ₈ -FOSA
N-Methylperfluorooctanesulfonamide ⁵	MeFOSA	31506-32-8	d3-MeFOSA
N-ethylperfluorooctanesulfonamide ⁵	EtFOSA	4151-50-2	d5-EtFOSA
Perfluorinated sulfonamidoacetic acids (FOSAA)			
N-methyl perfluorooctanesulfonamidoacetic acid ^{2,3}	MeFOSAA	2355-31-9	d3-MeFOSAA
N-ethyl perfluorooctanesulfonamidoacetic acid ^{2,3}	EtFOSAA	2991-50-6	d5-EtFOSAA
Fluorotelomer sulfonates (FTS)			
1H,1H,2H,2H-Perfluorohexane sulfonic acid ^{1,3}	4:2 FTS	757124-72-4	M2-4:2 FTS
1H,1H,2H,2H-Perfluorooctane sulfonic acid ^{1,3}	6:2 FTS	27619-97-2	M2-6:2 FTS
1H,1H,2H,2H-Perfluorodecane sulfonic acid ^{1,3}	8:2 FTS	39108-34-4	M2-8:2 FTS
1H,1H,2H,2H-perfluorododecane sulfonate (10:2)	10:2 FTS	120226-60-0	M2-10:2 FTS
Fluorinated Replacement Chemicals			
4,8-Dioxa-3H-perfluorononanoic acid	ADONA ¹	919005-14-4	¹³ C ₄ -PFOS
Hexafluoropropylene Oxide Dimer Acid	HFPO-DA (GenX) ¹	13252-13-6	¹³ C ₃ -HFPO-DA
Additional Targets			
Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate ⁴	PFecHS	67584-42-3	¹⁸ O ₂ -PFHxS

Fluorinated Replacement Chemicals			
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS (F-53B Major) ¹	756426-58-1	¹³ C ₄ -PFOS
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid OR 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate ^a	11Cl-PF3OUdS (F-53B Minor) ¹	763051-92-9 83329-89-9	¹³ C ₄ -PFOS

Perfluorinated sulfonamide ethanols (FOSEs)			
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol ⁵	N-MeFOSE	24448-09-7	d7-N-MeFOSE
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol ⁵	N-EtFOSE	1691-99-2	d9-N-EtFOSE

Additional Targets			
Nonafluoro-3,6-dioxaheptanoic acid ^{1,5}	NFDHA	151772-58-6	¹³ C ₅ -PFHxA
Perfluoro(2-ethoxyethane)sulfonic acid ^{1,5}	PFEESA	113507-82-7	¹³ C ₃ -PFBS
Sodium perfluoro-1-dodecanesulfonate ⁵	PFDoS	1260224-54-1	¹³ C ₄ -PFOS
Perfluoro-4-methoxybutanoic acid ^{1,5}	PFMBA	863090-89-5	¹³ C ₅ -PFPeA
Perfluoro-3-methoxypropanoic acid ^{1,5}	PFMPA	377-73-1	¹³ C ₄ -PFBA
3:3 Fluorotelomer carboxylic acid ⁵	3:3 FTCA	356-02-5	¹³ C ₂ -FHEA
5:3 Fluorotelomer carboxylic acid ⁵	5:3 FTCA	914637-49-3	¹³ C ₂ -FHEA
7:3 Fluorotelomer carboxylic acid or 3-perfluoropheptyl propanoic acid ^{4,5}	7:3 FTCA or FHpPA	812-70-4	¹³ C ₂ -FOEA

2H-perfluoro-2-decenoic acid ⁴	8:2 FTUCA or FOUEA	70887-84-2	¹³ C ₂ -FOUEA
2-perfluorodecyl ethanoic acid ⁴	10:2 FDEA	53826-13-4	¹³ C ₂ -FDEA
2-perfluorooctyl ethanoic acid ⁴	8:2 FTA or FOEA	27854-31-5	¹³ C ₂ -FOEA
2H-perfluoro-2-octenoic acid ⁴	6:2 FHUEA	70887-88-6	¹³ C ₂ -FHUEA
2-perfluorohexyl ethanoic acid ⁴	6:2FTCA or 6:2 FHEA	53826-12-3	¹³ C ₂ -FHEA