1 <u>**Supporting Information**</u>

2 Non-extractable PFAS in functional textiles −
3 Characterization by complementary methods: oxidation,
4 hydrolysis, and fluorine sum parameters

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S1 Chemicals and reagents

LC/MS grade water, methanol (MeOH), ammonium acetate (NH$_4$Ac), and formic acid (FA) were purchased from Thermo Fisher Scientific, as well as hydrochloric acid (32%). Sodium hydroxide (NaOH), tert-butyl methyl ether (MTBE, $\geq$ 99.5%), and Titanium(IV)dioxide (TiO$_2$ anatase, powder, 99.8% trace metal basis) were ordered from Sigma-Aldrich. Hydrogen peroxide solution (H$_2$O$_2$, $\geq$ 30%) was purchased from Fluka Analytical. Potassium persulfate ($\geq$ 99%) and ammonium hydroxide solution (25% NH$_4$OH) originated from Acros Organics. Anhydrous Na$_2$SO$_4$ and n-hexane for gas chromatography were purchased from Merck. PFCA reference standards (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, and PFODA) and, a mass-labelled PFAS extraction standard solution (MPFAC-C-ES) were ordered from Wellington Laboratories.

S2 Instrumental analysis

Table S 1: Gradient elution used for HPLC-QTOF-MS and HPLC-QqQ-MS measurements. Eluent A: 95/5 water/MeOH + 2 mM NH$_4$Ac, eluent B: 5/95 water/MeOH + 2mM NH$_4$Ac.

6550 QTOF-MS			6490 QqQ-MS		
Time (min)	A (%)	B (%)	Time (min)	A (%)	B (%)
0.0	85	15	0.0	60	40
2.0	30	70	1.0	40	60
5.0	10	90	3.5	0	100
10.0	0	100	6.0	0	100
15.0	0	100	6.1	60	40
15.1	85	15	8.0	60	40
22.0	85	15			

Table S 2: Instrument and ESI source parameters used during HPLC-QqQ-MS/MS measurements.

	6490 QqQ	6550 QTOF
Instrument parameters		
Gas Temp (°C)	150	150
Gas Flow (L/min)	16	16
Nebulizer pressure (psig)	45	35
Sheath gas temperature (°C)	380	380
Sheath gas flow (L/min)	12	12
Fragmentor voltage (V)	380	360
Ion source parameter (ESI)		
Capillary voltage (V)	3000	3000
Nozzle voltage (V)	0	300

59 **Table S 3:** Summary of APCI and QTOF parameters used during GC-QTOF-MS measurements.

APCI/QTOF Parameter	Value
Gas Temp (°C)	270
Drying gas (L/min)	11
Fragmentor voltage (V)	150
Capillary voltage (V)	1000
Corona current (μA)	1

60 **Table S 4:** MRM parameters for PFCAs measured by HPLC-QqQ-MS. Precursor and corresponding product ion
61 with the respective collision energy (CE).

Compound	Precursor ion	Product ion	CE (eV)	Compound	Precursor ion	Product ion	CE (eV)
PFBA	212.9	168.8	5	H2PFDA	477	393	15
$^{13}C_4$-PFBA	217	172	5	H4PFUnA	491	367	25
PFPeA	262.9	68.8	45	H4PFUnA	491	387	15
PFPeA	262.9	219	5	PFOSA	498	78	40
$^{13}C_5$-PFPeA	268	70	45	L-PFOS	499	79.7	55
$^{13}C_5$-PFPeA	268	223	5	L-PFOS	499	99	50
L-PFBS	298.9	79.8	40	$^{13}C_8$-PFOS	507	80	50
L-PFBS	298.9	98.9	30	$^{13}C_8$-PFOS	507	99	55
$^{13}C_3$-PFBS	302	80	40	PFDA	512.9	268.9	15
$^{13}C_3$-PFBS	302	99	30	PFDA	512.9	468.8	10
PFHxA	312.9	119	25	$^{13}C_6$-PFDA	519	270	15
PFHxA	312.9	268.9	5	$^{13}C_6$-PFDA	519	474	15
$^{13}C_5$-PFHxA	318	120	25	L-PFNS	549	80	50
$^{13}C_5$-PFHxA	318	273	5	L-PFNS	549	99	50
L-PFPeS	349	80	25	PFUnA	563	519	5
L-PFPeS	349	99	30	PFUnA	563	269	15
PFHpA	362.8	168.7	15	$^{13}C_7$-PFUnA	570	270	15
PFHpA	362.8	318.8	5	$^{13}C_7$-PFUnA	570	525	5
$_{13}C_4$-PFHpA	367	169	15	L-PFDS	599	80	55
$^{13}C_4$-PFHpA	367	322	5	L-PFDS	599	99	55
L-PFHxS	398.8	79.9	45	PFDoA	613	369	15
L-PFHxS	398.8	98.9	45	PFDoA	613	569	10
$^{13}C_3$-PFHxS	402	80	45	$^{13}C_2$-PFDoA	615	369	15
$^{13}C_3$-PFHxS	402	99	45	$^{13}C_2$-PFDoA	615	570	10
PFOA	412.9	168.7	20	PFTrDA	663	169	30
PFOA	412.9	368.7	5	PFTrDA	663	619	10
$^{13}C_8$-PFOA	421	172	15	L-PFDoS	699	80	55
$^{13}C_8$-PFOA	421	376	5	L-PFDoS	699	99	50
H4PFOS	427	81	40	PFTeDA	713	169	25
H4PFOS	427	407	25	PFTeDA	713	669	10
L-PFHpS	449	80	50	$^{13}C_2$-PFTeDA	715	169	25
L-PFHpS	449	99	45	$^{13}C_2$-PFTeDA	715	670	10
PFNA	462.9	218.8	15	PFHxDA	813	169	45
PFNA	462.9	418.8	5	PFHxDA	813	769	10
$^{13}C_9$-PFNA	472	223	15	PFODA	913	169	40
$^{13}C_9$-PFNA	472	427	5	PFODA	913	869	15
H2PFDA	477	63	5				

Non-target screening by HPLC-QTOF-MS and GC-QTOF-MS

Textile extracts and selected PhotoTOP samples were analyzed by HPLC-QTOF-MS (1260 Infinity HPLC system, coupled to a 6550 QTOF mass spectrometer, Agilent Technologies). A Poroshell 120 EC-C_{18} column (2.7 µm, 2.1 × 100 mm) was used at a flow rate of 0.3 mL/min (40 °C) with a 23 min gradient program (for details see Table S1). The ESI source was operated in negative mode (details in Table S2). 5 µL sample was injected with a prior threefold needle wash in isopropanol. Each measurement set included a MeOH and extraction blank. Data acquisition (3 spectra/s) started after a 1 min waste line in the data-dependent acquisition mode (ddMS^2, precursor selection threshold of 1000 counts and 0.5 min exclusion after 3 MS/MS spectra) with a static exclusion list generated from blank injections. The *m/z* range in MS was 100 – 1700 and 70 – 1700 in MS/MS. MS/MS spectra were acquired by using a linear mass-dependent collision energy of $CE(m/z) = \dfrac{3\ m/z}{100} + 15\ \text{eV}$.

For peak finding, the MolecularFeatureExtraction algorithm of the Agilent Qualitative 10.0 Software was used, and Kendrick mass defect analysis was applied to CSV files to find potential PFAS homologues as previously described.[1] FindPFΔS was used to search all MS/MS for fragment mass differences characteristic to PFAS (e.g., ΔCF$_2$, ΔC$_2$F$_4$ ΔHF).[2] Furthermore, chromatograms of suspected PFAS were manually extracted to check for their occurrence. The identical procedure was applied to the GC-QTOF-MS raw data.

TF measurements by combustion ion chromatography

For determination of the instrumental LOQ and LOD values, the standard protocol according to DIN 32645 was followed. Therein, ten repeated measurements of twenty different blank samples (empty sample boats) were conducted. Subsequently, the standard deviation (SD) was calculated, divided by the slope of the calibration curve (1-250 µg/L F$^-$) and multiplied times 3, resulting in the instrumental LOD value of 3 µg/L. Factor ten was used for the determination

86 of the instrumental LOQ (= 10 µg/L). All measured fluoride values per sample were above the

87 determined LOQ.

88 The CIC was controlled by the software Chromeleon 7.2.10 (Thermo Fisher Scientific GmbH,

89 Dreieich, Germany). The combustion unit consisted of an autosampler (ASC-270LS)

90 connected to the induction furnace (AQF-2100H) operating between 1000 and 1050 °C. Prior

91 to combustion, all ceramic boats were prebaked for at least 5 min at 1000 °C to avoid organic

92 contamination. All samples were hydro-pyrolyzed in the horizontal combustion furnace

93 operating at 1050 °C under a flow of O_2 (300 mL/min), Ar (150 mL/min) using sample specific

94 boat programs (Table S7). Combustion gases were absorbed in a freshly prepared 3 mM NH_3

95 absorption solution, added with an internal standard for monitoring the exact absorption

96 volume by ion chromatography. For TF measurements, the water supply level was set to "4"

97 and the medium absorption volume of the GA210 (~16 mL) was selected. A 5 µL aliquot was

98 injected into the ion chromatography using Dionex IonPac AG20 (2 × 50 mm) as guard column

99 and Dionex IonPac AS20 (2 × 250mm) as analytic column, both maintained at a constant

100 column temperature of 30 °C. Chromatographic separation was directed by an automated

101 KOH eluent generator, controlled by an optimized gradient program (5 mM to 50 mM) at a

102 constant flow rate of 0.25 mL/min (Table S8). Fluoride ions were sensed by a conductivity

103 detector using 50 mM H_2SO_4 as suppressor regenerant. For calculation of detected peak areas

104 and fluoride concentrations chromatography data system Chromeleon 7.2.10 (Thermo Fisher

105 Scientific) was used. After combustion of the samples and subsequent quantification of the

106 fluoride amount by IC, the collected raw data were transferred to an external computer for

107 more detailed evaluation in Origin 2020 (OriginLab Corporation).

108 **Conversion of fluorine from PFCAs and FTOHs to mass fluorine**

109 To convert PFCAs and FTOHs to mass of fluorine, the measured mass concentration (µg/L)

110 of each compound (e.g., PFPeA, PFHxA and PFHpA) was converted into moles of substance

111 per textile mass (e.g., μmol/kg). Then, by using the number of fluorine atoms, the mass of

112 fluorine per mass of textile was calculated (e.g. mg/kg).

113 **Table S 5:** Combustion parameters used for TF measurements.

Combustion component	
Combustion device	AQF-2100H, A1 Enviroscience, Mitsubishi Chemical Analytech Co., Ltd.
Operating temperature	1050 °C
Ar carrier gas flow	150 mL/min
Ar flow of water supply	100 mL/min
O_2 flow	300 mL/min
Absorption solution/internal standard	3.0 mM NH_3 solution + 2.2 mg/L $MeSO_3H$
Starting Absorption volume	8.5 ml (TF)
Final Absorption volume	16 (TF)
Sample amount	5-10 mg (TF)
Water supply level	4 (TF)

114

115 **Table S 6:** Ion chromatography parameters.

Ion chromatography component	
IC-device	ICS Integrion, Thermo Fisher Scientific
Detector	conductivity detector
Guard column	AG20 2x50mm guard column
Analytical column	Dionex IonPac AS20 2x250mm
Eluent	gradient KOH
Flow rate	0.25 mL/min
Run time	22 min
Column temperature	30 °C
Injection volume	5 μl (TF)
Suppressor regenerant	50 mM H_2SO_4

116

117 **Table S 7:** TF boat program.

Pos	Time (s)	Pos	Time (s)	End Time (s)	Cool Time (s)	Home Time (s)	Ar Time (s)	O_2 Time (s)
100	90	210	60	300	60	200	0	600

118

119 **Table S 8:** IC eluent gradient program.

Time (min)	Eluent concentration (mM)
0	Start, 1.0
0.1	1.0
0.2	2.0
1.0	2.0
10.0	5.0
10.5	5.0
11.0	80.0
14.0	80.0
14.5	1.0
22.0	stop run

120

S3 Supporting figures
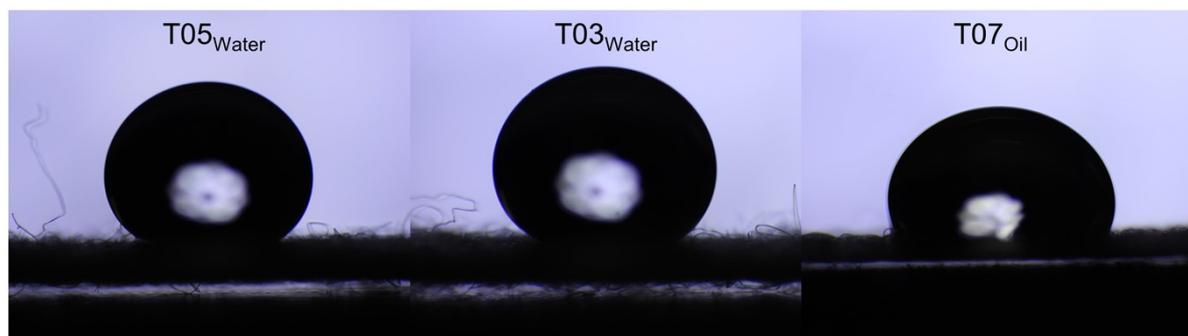

Figure S 1: Examples of photos taken of water and sunflower oil droplets on textile surfaces to determine the contact angle.

Extraction recovery test

An extraction recovery test was performed to verify that the applied extraction technique quantitatively extracts PFAAs from the textiles. Two 4 cm^2 textile pieces and a control without textile (T07, T10) were spiked with a methanolic mixture of PFHpA, PFOA, and PFOS (50 ng each) and left until the MeOH was evaporated. Afterwards, those textiles were extracted by our used extraction procedure (Figure S2) and measured by HPLC-QTOF-MS. The recoveries ranged from 88% up to 102%.
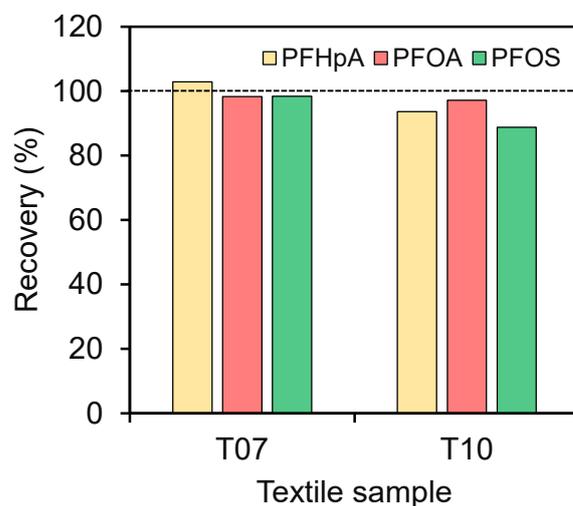
**Figure S 2:** Extraction recoveries for PFHpA, PFOA, and PFOS from spike experiments with two textiles.
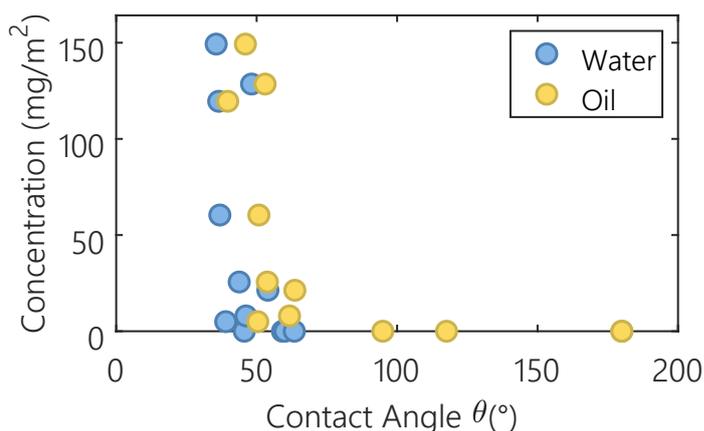
135

136 **Figure S 3:** Concentration of ΣPFCAs after 5 h PhotoTOP oxidation in different textiles vs. water and sunflower
137 oil contact angles. Three textiles were completely oil wetting and no PFCAs formed after PhotoTOP oxidation.
138 Water repellency was observed for all textiles.

139
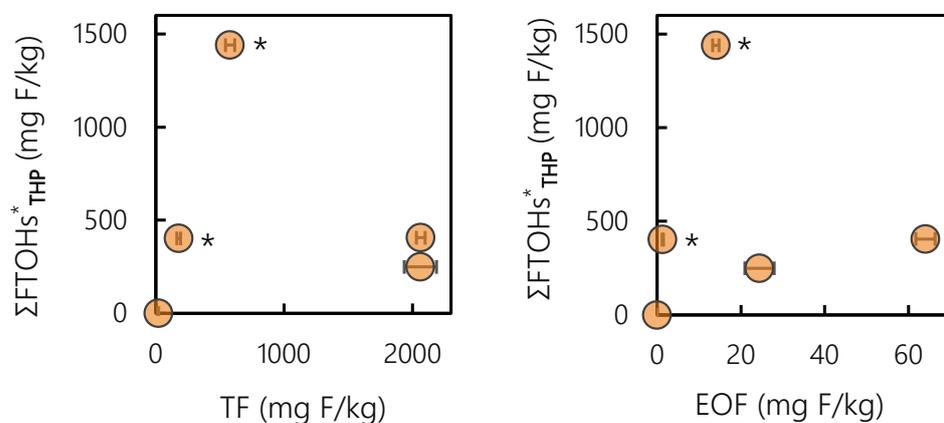
140

141 **Figure S 4:** Correlation of partially semi-quantified ΣFTOHs after the THP assay vs. TF and EOF. Data points
142 marked with asterisks include estimated concentrations of n:2 FTOHs with n ≥ 10. Here, probably an
143 overestimation occurred because more fluorine from hydrolysis than from TF measurements is unlikely.
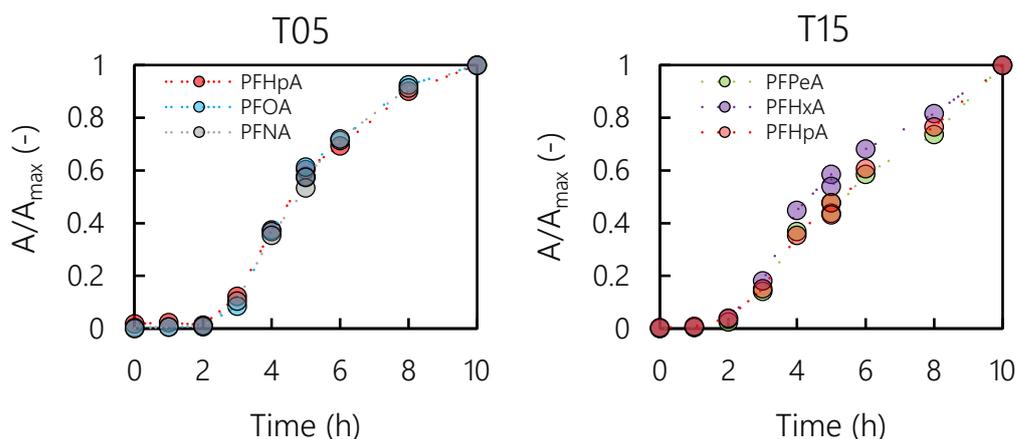
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145 **Figure S 5:** Normalized peak areas of main PFCAs formed from PhotoTOP oxidation of textile T05 and T15
146 over a time of 10 h. Note that although the concentrations still increased after 5 h the formation rates decreased.
147 The data in Table 1 represents concentrations after 5 h of oxidation. Data was acquired by HPLC-QTOF-MS.
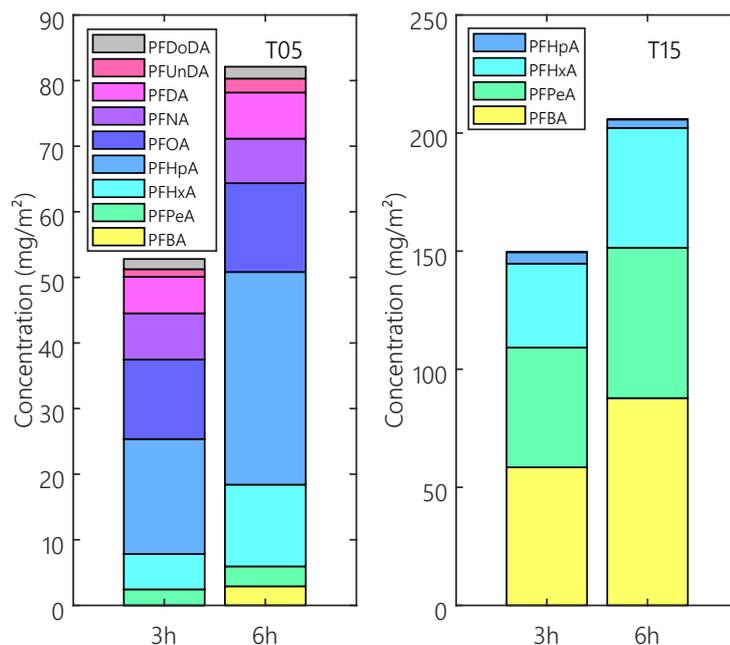
148
149 **Figure S 6:** Concentration of PFCAs after 3 and 6 h of dTOP oxidation in textile T05 and T15 respectively.
150

References

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