

## PER- AND POLYFLUORINATED ALKYL SUBSTANCES (PFAS) EXTRACTED FROM TEXTILE SAMPLES

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### Introduction

Per- and polyfluorinated alkyl substances (PFAS) have been produced for several decades and they are used in a wide range of applications. These include surface treatment of textiles, leather, carpets and paper, as well as the fluoropolymer industry. Two main production processes for PFAS are applied: Electrochemical fluorination and telomerisation. In the electrochemical fluorination process, a technical mixture of hydrocarbons (different carbon chain lengths including branched isomers) with a functional group is usually subjected to fluorination, leading to a mixture of perfluorinated products. Telomerisation involves coupling of tetrafluoroethene, leading to straight-chain products with an even number of carbon atoms. Fluorotelomer products often possess two carbon atoms adjacent to the functional group that are not fluorinated, but also perfluorinated compounds can be synthesised through the telomerisation process.

For many applications, easy-to-clean textiles are desired (upholstery, table-cloths, car seats), or the textiles must be waterproof but breathable (tents, ski clothes, rain jackets, shoes). PFAS repel both water and oil, and are therefore ideal chemicals for surface treatment of such textiles. Furthermore, polytetrafluoroethylene (PTFE)-based membranes are often used in rain coats due to their water resistance and ability to breathe. However, these membranes are not strong enough to be employed as outer layers of outdoor clothes. They are attached on the inside to a robust textile, which is often additionally surface treated with fluorinated polymers or co-polymers.

Fluorotelomer alcohols (FTOHs) are such fluorochemicals that are used in the production of polymers. The alcohol group is bound to the polymer backbone and the fluorinated carbon chain sticks away from the treated material to yield the desired water and stain proofing. During the production, use or destruction of the textile, FTOHs could be cleaved off the polymer and evaporate to air, due to their high vapour pressure. Alternatively, free FTOHs might remain in the coating as non-bound residuals from the production process of the polymers and eventually leak out to the environment.<sup>1</sup> Indeed, FTOHs have been found in air samples.<sup>2,3</sup> Perfluorocarboxylates (PFCAs) are used in the production of PTFE. Residuals of PFCAs might remain in PTFE membranes and enter the environment through waste water after washing of the textile. Furthermore, it has been hypothesised, that PFCAs are degradation products of FTOHs.<sup>4</sup> PFCAs have been detected in water samples from landfill effluents, sewage treatment plants, lakes and the sea.<sup>5</sup>

The aim of this study was to identify PFAS used in the production of different types of textiles from the Swedish and Norwegian market. The selection of test materials should cover most of the commonly used brands in Scandinavia, focusing on outdoor clothing and rain jackets. A rough estimation of the amount of freely extractable fluorochemicals was also attempted. So far, literature data on this subject is very scarce and mainly comprises determination of residual FTOHs from polymeric and surfactant materials<sup>1</sup> or extractable perfluorooctanoate (PFOA) from textile and carpet samples.<sup>6</sup>

### Materials and Methods

*Test materials.* A total of 17 textile samples from 15 different producers were purchased in shops in Sweden and Norway or directly obtained from manufacturers of outdoor clothing. The 15 producers covered all important brands on the Scandinavian market. More details about the type of the different textiles are given in Table 1 in the Results and Discussion section.

*Chemicals and reagents.* Authentic reference standards of the following analytes (combined to analyte groups in Table 1) were used: 10:2 FTOlefin (1H,1H,2H-perfluoro-1-dodecene, Matrix Scientific, Columbia, SC, USA). FTOHs: 4:2 FTOH, 6:2 FTOH, 8:2 FTOH (ABCR, Karlsruhe, Germany) and 10:2 FTOH (Fluorochem, Old Glossop, UK). Fluorotelomer sulfonates and carboxylates, FTS/FTCAs: 6:2 FTS (1H,1H,2H,2H-perfluorooctane sulfonate, Interchim, Montluçon Cedex, France), 6:2 FTCA, 8:2 FTCA, 8:2 FTUCA (saturated and unsaturated fluorotelomer carboxylates, Wellington, Guelph, Canada) and 8:2 FTS, 6:2 FTUCA (not available). Perfluorosulfonates, PFS: PFBS (potassium perfluorobutane sulfonate, Dyneon, Zwijndrecht, Belgium), PFHxS (potassium perfluorohexane sulfonate, Interchim), PFOS (potassium perfluorooctane sulfonate, Fluka, Buchs, Switzerland) and PFDcS (ammonium perfluorodecane sulfonate, Sigma-Aldrich, Steinheim, Germany). PFCAs: PFBA (C4, Sigma-Aldrich), PFHxA (C6, ABCR), PFHpA (C7, Sigma-Aldrich), PFOA (C8, Fluka), PFNA (C9, Sigma-Aldrich), PFDcA (C10, Fluka), PFUnA, PFDcA, PFTeA (C11,C12,C14, Sigma-Aldrich), and PFPA, PFTriA, PFPDA (C5, C13, C15, not available). Fluorooctane sulfonamides/sulfonamidoethanols, FOSAs/FOSEs: PFOSA (perfluorooctane sulfonamide, ABCR), N-Et-FOSA (N-ethyl heptadecafluorooctane sulfonamide, Lancaster Synthesis, Lancashire, UK) and N-Me-FOSA, N-Me-FOSE, N-Et-FOSE (N-methyl heptadecafluorooctane sulfonamide, N-methyl and N-ethyl heptadecafluorooctane sulfonamidoethanol, donation Mabury group, University of Toronto, Canada). As internal standards for GC and LC analysis 7:1 fluorinated alcohol (1H,1H-perfluoro-1-octanol, ABCR) and PF-3,7-diMe-OA (perfluoro-3,7-di-methyl-octanoic acid, ABCR) were used, respectively. As volume standards for GC and LC analysis TCN (1,2,3,4-tetrachloronaphthalene, Dr. Ehrenstorfer, Augsburg, Germany) and 3,5-BTPA (3,5-bis(trifluoromethyl) phenyl acetic acid, ABCR) were used. All solvents and reagents were of highest commercially available purity.

*Extraction.* From each textile sample, two squares (10 x 10 cm) were cut out, cut in small pieces and extracted. One square was spiked with 200 ng 7:1 fluorinated alcohol and extracted with ethyl acetate for GC analysis of volatile compounds. The other square was spiked with 200 ng PF-3,7-diMe-OA and extracted with methanol for LC analysis. Extraction was performed in 50 mL solvent in the ultrasonic bath for 30 min. The extract was then concentrated to 1 mL using a Turbovap evaporator (Zymark, Hopkinton, MA, USA). After addition of 50 ng TCN (ethyl acetate extract) or 200 ng 3,5-BTPA (methanol extract), the extract was centrifuged (14000 rpm, 15 min) and the supernatant clear solution was used for instrumental analysis.

*GC-MS analysis.* For GC-MS analysis a Varian CP-3800 gas chromatograph was coupled to a Varian 1200 triple quadrupole mass spectrometer operated in the selected ion monitoring mode (Varian, Palo Alto, CA, USA). Positive and negative chemical ionization experiments were performed. The method for the 10:2 FTOlefin, FTOHs and FOSAs/FOSEs (confirmation of LC-MS results) was adapted from literature<sup>2</sup> (see also<sup>3</sup>).

*LC-MS analysis.* For LC-MS analysis a 1100 series gradient pump and auto-injector (Agilent Technologies, Palo Alto, CA, USA) were coupled to a time-of-flight high resolution mass spectrometer operated in electrospray negative ionization mode (LCT, Micromass, Manchester, England). Analysis of PFS, PFCAs, FTS/FTCAs and FOSAs/FOSEs was conducted as described in literature.<sup>7</sup> Furthermore, to confirm the free extractability of FTOHs, these were also analysed by LC-MS as described earlier.<sup>7</sup>

### Results and Discussion

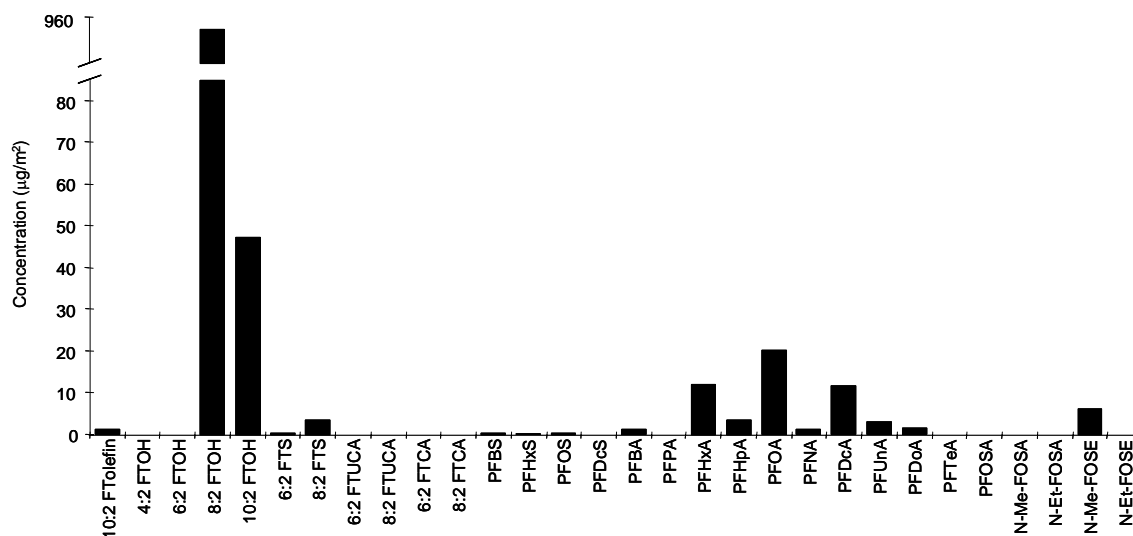
*Extraction.* Since the aim of the study was the identification of extractable PFAS from textiles and only a rough estimation of quantities, an exhaustive extraction of all freely extractable fluorinated compounds was not attempted. Therefore, the results probably underestimate the total amount of PFAS present in the textile samples. Neither did this study attempt to simulate real-use conditions, such as UV radiation from the sun, rain, washing etc. In this respect, the here presented results overestimate the amount of PFAS that would be released to the environment during the life time of the clothes, as has been shown in literature for PFOA.<sup>6</sup> Extraction of the internal standards was controlled, however, and recoveries ranged between 41 and 65% for the GC method (7:1 fluorinated alcohol) and between 51 and 110% for the LC method (PF-3,7-diMe-OA).

*Results for PFAS groups.* Table 1 shows the obtained results for extraction of PFAS from textile samples. The results are summarised for PFAS groups according to the classification given in the Materials and Methods section. To make the table visually easier to read, grey scale backgrounds are added according to the sum

concentration values (higher concentrations have darker background). As can be seen from table 1, FTOHs are the dominating PFAS class extracted from the textiles. FTOHs chemically bound to an oligomeric/polymeric backbone structure might cleave off at high temperatures as used in the GC injector. Therefore, the fluorotelomer alcohols were also quantified in the methanol extracts by LC-MS, and the high concentrations of freely extractable FTOHs were confirmed. However, there were big differences in the concentrations found in different textiles. Whereas FTOHs were not detected in one sample, as much as 11 mg/m<sup>2</sup> were extracted from the jacket with the highest FTOH content. Next to FTOHs, PFCAs were the PFAS group showing highest extractable concentrations. Levels exceeded 0.1 and 0.4 mg/m<sup>2</sup> for a PTFE table-cloth and a cotton textile, respectively. Only minor amounts of PFS (including PFOS) were detected, however, they positively correlated with the values for FOSAs/FOSEs, which are possible precursor compounds for PFOS.

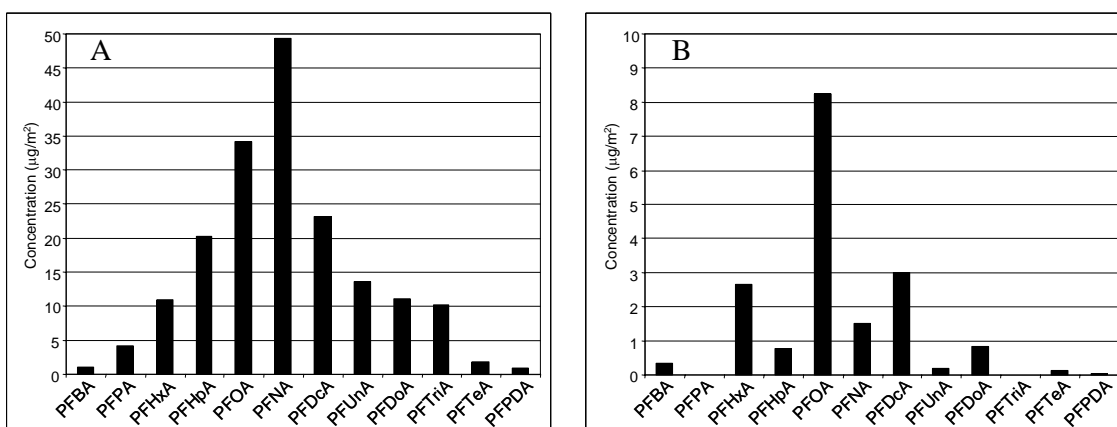
**Table 1.** Freely extractable PFAS from different textile samples summarised in groups (µg/m<sup>2</sup> textile)

	10:2 FTOlefin	Sum FTOHs	Sum FTS/FTCAs	Sum PFS	Sum PFCAs	Sum FOSAs/FOSEs
Alpine trousers for kids	n.d.	n.d.	n.d.	0.06	6.84	n.d.
Overall for kids	n.d.	97.8	n.d.	n.d.	2.97	0.06
Rain and outdoor jacket	n.d.	10700	2.72	30.5	34.9	22.8
PTFE table-cloth	n.d.	285	5.56	0.04	170	0.03
Alpine jacket	n.d.	42.2	0.33	0.03	10.8	n.d.
Sport jacket	n.d.	86.8	0.09	n.d.	18.9	n.d.
Trousers kids	n.d.	426	0.38	0.17	3.41	0.03
Overall for kids	n.d.	207	n.d.	0.07	2.71	0.04
Waterproof jacket	n.d.	155	n.d.	0.07	6.97	1.08
Impregn. and coated jacket	n.d.	33.0	0.06	0.06	17.6	0.36
Mixed synth./cotton textile	n.d.	168	0.97	0.26	94.7	0.74
Cotton textile	0.13	41.1	1.54	23.3	428	107
Synthetic textile	n.d.	73.9	n.d.	0.12	48.5	5.73
Breathable rain jacket	1.11	91.0	1.87	0.02	16.4	1.43
Waterproof rain jacket	0.26	385	1.92	0.28	55.9	14.1
Sailing jacket for kids	0.85	1000	3.87	0.67	53.3	6.10
Waterproof rain jacket	n.d.	27.1	n.d.	0.44	1.89	4.30



**Figure 1.** Freely extractable PFAS from a sailing jacket for kids

*PFAS patterns.* Figure 1 shows the PFAS pattern of a (qualitatively) representative sample of a synthetic textile. The FTOHs are dominated by 8:2 FTOH, followed by 10:2 FTOH. Only in few samples 6:2 FTOH could also be detected, but not 4:2 FTOH. The saturated and unsaturated fluorotelomer carboxylates, degradation products of FTOHs, were hardly ever detected, and the same applies for the fluorotelomer sulfonates. The FOSAs/FOSEs were dominated by N-Me-FOSE in almost all samples, and in particular in the cotton textile, from which 84  $\mu\text{g}/\text{m}^2$  N-Me-FOSE and 21  $\mu\text{g}/\text{m}^2$  N-Et-FOSE were extracted. Two interesting patterns of PFCAs extracted from a table-cloth and a jacket are shown in Figure 2. They probably represent the two main production processes of PFCAs. Figure 2A shows a “Gaussian” distribution of PFCA homologues around PFNA, which leads to the conclusion that this PFCA mixture originates from electrochemically produced PFNA. In contrast, Figure 2B shows predominantly even carbon numbered homologues, dominated by PFOA, as could be expected from a telomerisation production of PFOA. Surprisingly, in both textile extracts PFCAs up to C15 could be detected, which might point to direct sources of long-chain perfluorocarboxylates. So far it was hypothesised, that these must be degradation products of other long-chain fluorochemicals, such as FTOHs.<sup>8</sup>



**Figure 2.** PFCA pattern in the extract from a PTFE table-cloth (A) and an impregnated and coated jacket (B)

### Acknowledgements

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