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EFFECTS OF WEATHERING ON PFASS USED IN DURABLE WATER REPELLENCE OF OUTDOOR CLOTHING

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Introduction

Per- and polyfluoroalkyl substances (PFASs) are increasingly attracting attention of environmental scientists. The wide application possibilities together with the persistence of these substances have caused that these compounds occur basically everywhere in the global environment [1]. On top of that, background values several PFASs in human blood have established worldwide. For example, for perfluorinated octanoic acid (PFOA) a background level of 4 ng/mL, and for perfluorinated octylsulfonate (PFOS) a background level of 21 ng/mL is reported for human blood in the USA [2]. In addition to that, around production sites, local populations have in several cases accumulated higher levels of for example PFOA, whereas due to occupational exposure laborers in the Netherlands appear to have accumulated PFOA levels of orders of magnitude higher [3], which no doubt will have caused health effects. These examples show how much risk is associated with the production of these fluorinated compounds and how long it took before we have become aware of their effects. Among the multitude of applications, PFASs are used in textiles [4]. Their oil and water repellent properties make PFASs excellent compounds for the protection of various garments and upholstery. Because PFASs with long perfluorinated chains have been shown to be persistent in the environment, bioaccumulative and (eco)toxic, the textile industry is phasing-out the long-chain PFASs and is replacing those compounds with alternative chemicals that also deliver the desired durable water and soil repellent (DWR) effect. Those alternative chemicals can be divided in three main groups: fluorocarbon-based, silicon-based and hydrocarbon-based polymers. During our research in the SUPFES (Substitution in practice of prioritized fluorinated compounds for textile applications) project (Figure 1), the alternative chemicals are studied to assess (i) their structural properties and related performance, (ii) loss and degradation processes resulting in diffuse environmental emissions, and (iii) hazard profile of the emitted substances. As part of the SUPFES project the influence of weathering conditions on the different types of DWR treatments is assessed. Here the effect of weathering on the PFASs concentrations in nine textiles of outdoor clothing is presented.

Materials and methods

To assess the effect of weathering on the type of PFAS and their concentration in outdoor clothing during the life time of the clothing, nine textile samples of different types of outdoor clothing were exposed in an ATLAS weather-o-meter Cr 3000 to elevated UV radiation, humidity, and temperature in an aging device for 300 h (Table 1), which can be compared to the life time of the outdoor clothing. Before and after the weathering experiment, the textile samples (sample intake 10 cm2) were extracted with methanol and analysed by LS-MS/MS (Agilent 6410 Triple quad) with a validated method for perfluoroalkyl acids (PFAAs) in textiles [5].

Studied were the ionic PFASs: perfluoroalkane sulfonic acids (PFSAs), perfluoroalkyl carboxylic acids (PFCAs), Fluorotelomer sulfonic acids (n:2) (FTSAs), Fluorotelomer carboxylic acids (n:2) (FTCAs), Perfluorooctane sulfonamide (FOSA), and the neutral PFASs: Fluorotelomer alcohols (n:2) (FTOHs), Fluorotelomer acrylates (n:2) (FTACs), Fluorotelomer methacrylates (n:2) (FTMACs), N-Methyl perfluorooctane sulfonamide (MeFOSA), N-Ethyl perfluorooctane sulfonamide (EtFOSA), N-Methyl perfluorooctane sulfonamidoethanol (MeFOSE) and N-Ethyl perfluorooctane sulfonamidoethanol (EtFOSE).

Results and discussion

Outdoor clothing contains polymers with side chains of fluorinated alcohols and acrylates. During the production various PFAAs are being used. Due to weathering, degradation of those alcohols and acrylates into PFAAs is possible. The original nine samples studied contained different levels of PFAAs and showed different patterns before they were exposed in the weathering experiments. They were selected from a set of 50 samples that were all analysed on PFASs (Table 2).

Two of the nine samples did not contain any PFAAs above the limit of quantification (LOQ), in two samples only perfluorooctanoic acid (PFOA) was detected above the LOQ (0.03 and 0.11 µg/m2), while the other samples contained four to thirteen different PFAAs above the LOQ in concentrations varying from 0.03 to 6.4 µg/m2, and one sample contained seven different PFAAs with PFBA (28 µg/m2) and PFBS (45 µg/m2) in the highest concentration. Visual observation of the samples showed a difference in color of the fabrics before and after aging (Figure 2), indicating that indeed some degradation or transformation of compounds occurs.

Results after aging differ between all nine samples. One of the two samples that did not contain any PFAA before aging, still did not contain any PFAA after aging, while in the other sample after aging two PFAAs (PFHpA (perfluoro-n-heptaanoic acid), 0.16 µg/m2; PFNA (perfluoro-n-nonanoic acid) 0.13 µg/m2) were present. In one of the samples (Figure 3) the concentrations of all PFAAs present before aging increased from a median concentration of 0.21 µg/m2 to a median concentration of 2.7 µg/m2, with the remarkable appearance of odd-chain length PFAAs, which were not present before aging. This formation of odd-chain PFAAs is consistent with the formation of odd-chain PFCAs described in a review by Butt et al. [6], and can also be observed in one of the other samples. In five of the textile samples the mean concentrations of PFAAs increased 5-fold or more, and in one of the samples the concentration increased even more than 100-fold. An explanation of the formation of those PFAAs might come from the transformation of the precursors fluorotelomer alcohols (FTOHs) and fluorotelomer acrylates (FTACs), which are used for the formation of polymers used for DWR, or from the degradation of the polymers themselves. In conclusion, weather conditions, like sunlight, high temperatures, or humidity have an effect on PFASs used in DWR of outdoor clothing. In some samples the concentrations of the PFAAs increased and some PFAAs not present in the original textiles were formed during exposure of weather conditions. Odd-chain length PFAAs, not present before aging, can be produced. More research is needed to clarify the details of these processes and to determine the transformation routes. Neutral PFASs analyses are underway.

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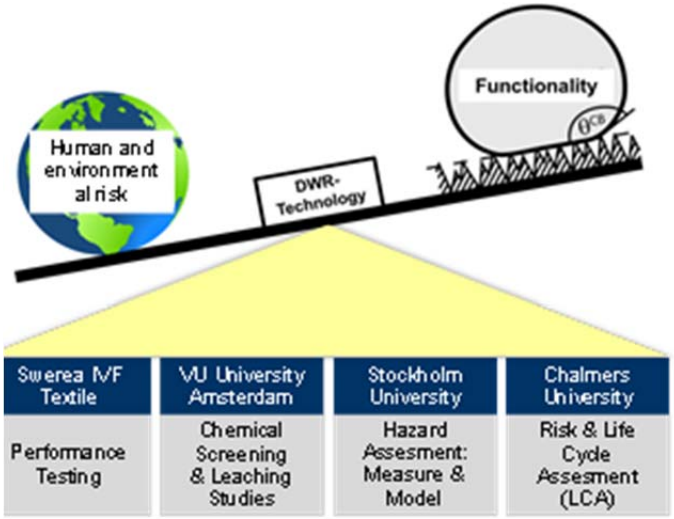

Figure 1. Design of the SUPFES research project.

Table 1. Conditions of weathering experiment (total duration 300 h).

Method	Exposure period	Broadband (300-400 nm) W/m^2	Narrowband (340 nm) W/m^2·nm	Black standard temperature (˚C)	Chamber temperature (˚C)	Humidity (%)
A1 (ISO4892-2)	102 min dry 18 min water spray	60 ± 2 60 ± 2	0.51 ± 0.02 0.51 ± 0.02	65 ± 3	38 ± 3	50 ± 10

Table 2. PFASs present in outdoor clothing samples (n=50) before the weathering experiment.

Compound	Detection %	Range (µg/m^2)	Median value (µg/m^2)
PFBA	47	0.02-28	0.17
PFHxA	76	0.03-6.4	0.21
PFOA	96	0.01-5.1	0.25
PFBS	18	0.02-42	0.69
L-PFOS	18	0.02-3.2	0.09
6:2 FTOH*	88	0.43-360	24
8:2 FTOH*	92	1.5-380	17
10:2 FTOH*	90	0.06-130	4.1
8:2 FTAC*	46	0.3-280	2.6

*Indicative values; PFBA: perfluoro-n-butanoic acid, PFHxA: perfluoro-n-hexanoic acid, PFBS: perfluorobutane sulfonate.

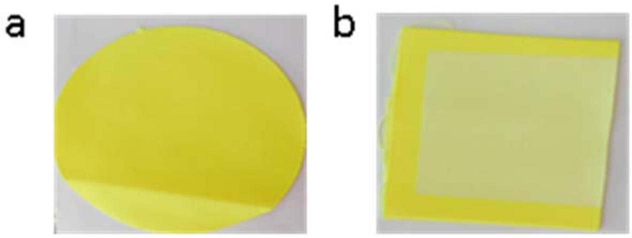

Figure 2. Textile a) before and b) after aging.

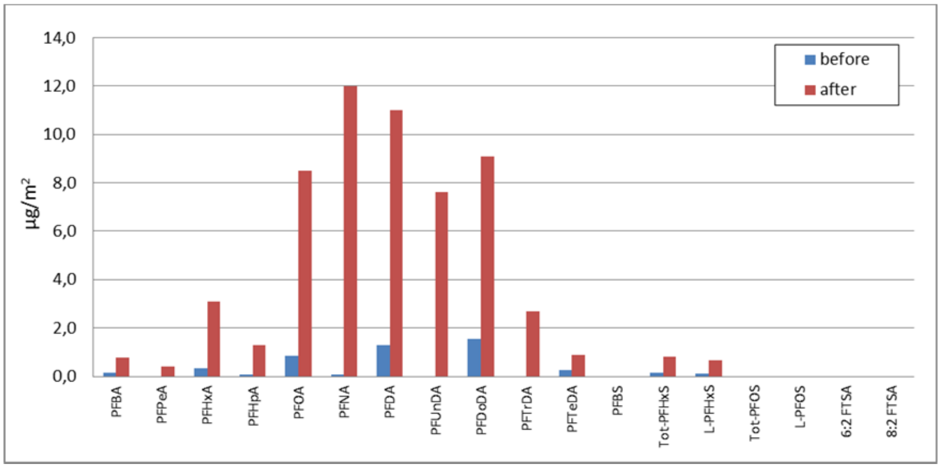

Figure 3: Concentrations of PFASs in one of the textile samples before and after aging.