

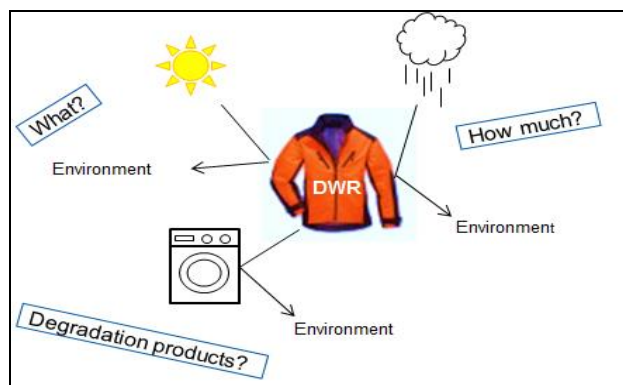
# Leaching of chemicals from the durable water repellence layer of textiles with aging

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## Introduction

Among the multitude of applications, PFASs are used in textiles. Their oil and water repellent properties make PFASs excellent compounds for the protection of various garments and upholstery. In order to obtain the desired durable water repellency (DWR) for outdoor wear, per- and polyfluoroalkyl substances (PFASs) have been used for years. However, because PFASs with long perfluorinated chains have been shown to be persistent in the environment, bioaccumulative and (eco)toxic [1], 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. Within the SUPFES (Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources) project the alternative DWRs are assessed in comparison with the long-chain PFASs with regard to their functionality and their impact on the environment. As part of SUPFES the influence of weather conditions on DWR treatments are assessed, as well as emissions of chemicals during washing and wearing (Figure 1).



**Figure 1. Design of the study on PFASs and alternative chemicals used in the DWR of outdoor clothes.**

Following last year's study on the effect of weathering on several ionic PFASs concentrations in nine textiles of outdoor clothing, now the full study on the effects of weathering on the ionic and volatile PFASs concentrations 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, 13 textile samples of different types of outdoor clothing were exposed in an ATLAS weather-ometer Cr 3000 to elevated UV radiation, humidity, and temperature 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 cm<sup>2</sup>) were for the analyses of ionic PFASs extracted with methanol and analysed by LS-MS/MS (Agilent 6410 Triple quad) with a validated method for perfluoroalkyl acids (PFAAs) in textiles [2]. For the analyses of the volatile PFASs, the samples were extracted with ethylacetate, cleaned with active carbon, and analysed with GC-MS. 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).

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

Method	Exposure period	Broadband (300-400 nm) W/m <sup>2</sup>	Narrowband (340 nm) W/m <sup>2</sup> ·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

## 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.

**Table 2. PFASs present in outdoor clothing samples (n=13) before the weathering experiment.**

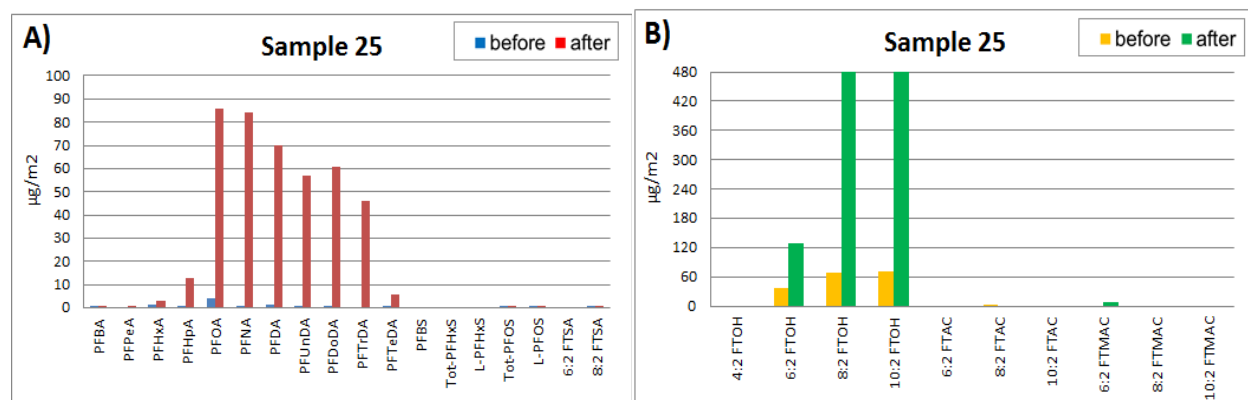
Compound	Detection %	Range (µg/m <sup>2</sup> )	Median value (µg/m <sup>2</sup> )
PFBA	46	0.14-28	4.9
PFHxA	62	0.31-6.4	1.3
PFOA	62	0.03-3.8	0.44
PFBS	23	9.6-45	43
6:2 FTOH	92	1.9-350	43
8:2 FTOH	92	1.1-69	2.5
10:2 FTOH	85	0.38-73	2.7
6:2 FTMAC	69	4.1-180	10

The original samples contained different levels of PFASs and showed different patterns before they were exposed to weather conditions. Volatile PFASs were present in higher concentrations (median 4.8 µg/m<sup>2</sup>) than ionic PFASs (median 0.84 µg/m<sup>2</sup>). The highest concentration detected for PFAAs was 45 µg/m<sup>2</sup> for PFBS, and 28 µg/m<sup>2</sup> for PFBA. For all other compounds the highest concentration PFAAs quantified was 6.4 µg/m<sup>2</sup> for PFHxA. For the volatile PFASs the highest concentration quantified was 350 µg/m<sup>2</sup> for 6:2 FTOH.

Concentrations and patterns after aging differed for all samples. One of the samples, which did not contain any PFAA before aging, still did not contain any PFAA after aging, while in another sample after aging two PFAA (PFHpA, 0.16 µg/m<sup>2</sup>; PFNA 0.13 µg/m<sup>2</sup>) appeared. In most of the samples the concentration of all PFAAs present before aging increased 5 times or more, and in two samples the concentration amplified even more than 100 times. In some samples odd-chain length PFAAs which were not present before aging appeared. This formation of odd PFAAs is consistent with the formation of odd-chain length PFCAs described in a review by Butt et al. [3]. An explanation of the forming of those PFAAs might come from the transformation of the precursors FTOHs, FTACs, and FTMAC, which are used for the formation of polymers used for DWR, or from the degradation of the polymers themselves.

Results of the volatile PFASs show an increase in concentrations after aging up to a factor of 20. As is being modeled and described by Li et al. [4] fluorotelomer-based polymers can degrade to FTOHs and FTACs. This is also experimentally proven by Washington et al. [5]. Considering the research of Li et al and of Washington et al., a possible explanation of the increase in the concentration of volatile PFAS during aging might come from the degradation of the polymers themselves. Another possibility would be that other PFASs, than the analysed ones were present in the original sample, which could possibly degrade to volatile PFAS.

In conclusion, weather conditions, weather conditions, like sunlight, high temperature, or humidity can have an effect on compounds used in DWR of outdoor clothing. In some samples the concentrations of PFAAs increased and PFAAs not present in the original textiles were formed during exposure to weather conditions. In all samples except one the concentrations of volatile PFASs increased. More research is needed to clarify the details of these processes and to determine the transformation routes.



**Figure 2: Concentrations of PFASs in one of the textile samples before and after aging.**

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