

EMISSION OF PERFLUOROALKYL SUBSTANCES (PFASs) FROM TEXTILES

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Introduction

In the past, numerous studies investigated the environmental distribution and fate of poly- and perfluorinated alkyl substances (PFASs) and characterized certain PFASs as being toxic¹, persistent², bioaccumulating³ and/or globally distributed⁴. As result of these findings, some of these compounds have been regulated in manufacturing and use; their production was (partly voluntarily) reduced or completely ceased. Numerous studies were performed to investigate the origins of PFASs in the environment. As result, various sources have been identified including emissions during the life-cycle (production, use, disposal) of products containing PFASs⁵. This study aimed to investigate textiles (here outdoor apparel) as sources for volatile PFASs to ambient air.

Materials and methods

Sixteen outdoor-textile samples (jackets, gloves) were analyzed for their contamination with several PFASs (perfluoroalkyl carboxylates (PFCAs), perfluoroalkyl sulfonates (PFSAs), fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAs), perfluorooctane sulfonamides and -amido ethanols (FOSAs, FOSEs)). About 2 g of each textile sample was used for analysis. For the determination of perfluorinated acids, samples were Soxhlet-extracted with methanol, cleaned-up by solid phase extraction and measured by HPLC-MS/MS. For the determination of volatile PFASs, samples were extracted by ultra-sonication using MTBE and measured by GC-MS using chemical ionization. Compounds-specific mass- labelled internal standards were applied for all analyses. Quantification was performed on the basis of peak areas applying the isotope dilution method.

The selection of textile samples that were tested for their PFAS emissions to air was performed on the basis of the analytical results for volatile PFASs. Overall, eight samples (all of them were jackets) were chosen.

Exposure of the textile samples for the determination of PFAS emission rates was performed according to DIN EN ISO 16000 in 120 L steel chambers. Prior to the use, these chambers were thoroughly cleaned by intensive purging and/or heating and tested for potential contamination with VOC. Samples were placed into the chambers. Active air sampling was performed for 6 days in October 2013 at a temperature of about 23 °C with an exchange rate of 0.5 /h and a total sampling volume of about 7 m³. Target analytes were enriched on ISOLUTE ENV+ SPE columns. One empty chamber was tested to yield a field blank. Additionally, 3 textile samples of potentially high PFAS emission (on the basis of PFAS product content) were used to investigate if break-through occurred with the sampling set-up used. Concentrations of field blank and break-through samples were always below the LOQ. After sampling, SPE columns were sealed and stored refrigerated until analysis.

The SPE adsorption resin was transferred to pre-cleaned centrifuge glasses. Mass-labelled internal standards were added to each sample. Samples were then extracted three times, 30 min each, by ultra-sonication using MTBE/acetone 1:1 as extraction solvent. After each extraction, samples were centrifuged. Samples were measured by GC-MS using chemical ionization. Quantification was performed on the basis of peak areas applying the isotope dilution method.

Results and discussion

Results of textile PFAS contents are presented in figures 1 and 2. All of the investigated textile samples contained PFASs. Concentrations varied strongly between the investigated materials and compounds. The perfluoroalkyl acid which was quantified most often (14 of 16 samples) was PFOA, followed by PFHxA (13 of 16 samples) and PFBA/PFDA (10 of 16 samples). Concentration for individual PFASs were usually between 0.1 and 11 µg/m². Except for three samples, perfluoroalkyl sulfonates were not observed in the textile samples. In one of the three samples containing PFSAs, PFOS was detected in significant amounts.

FTOHs and FTAs were observed in all samples investigated. FOSAs and FOSEs could not be quantified in any sample. Concentrations of volatile PFASs were up to a factor of 100 higher (10 – 1200 µg/m²) than concentrations of the perfluoroalkyl acids. FTOHs were found at highest concentrations with 6:2 FTOH being the predominant compound in most of the samples, followed by 8:2 FTOH. On the basis of these results, samples 1, 3, 8, 9, 10, 13, 14, 15 were chosen for further investigations on PFAS emission rates. These results are presented in table 1.

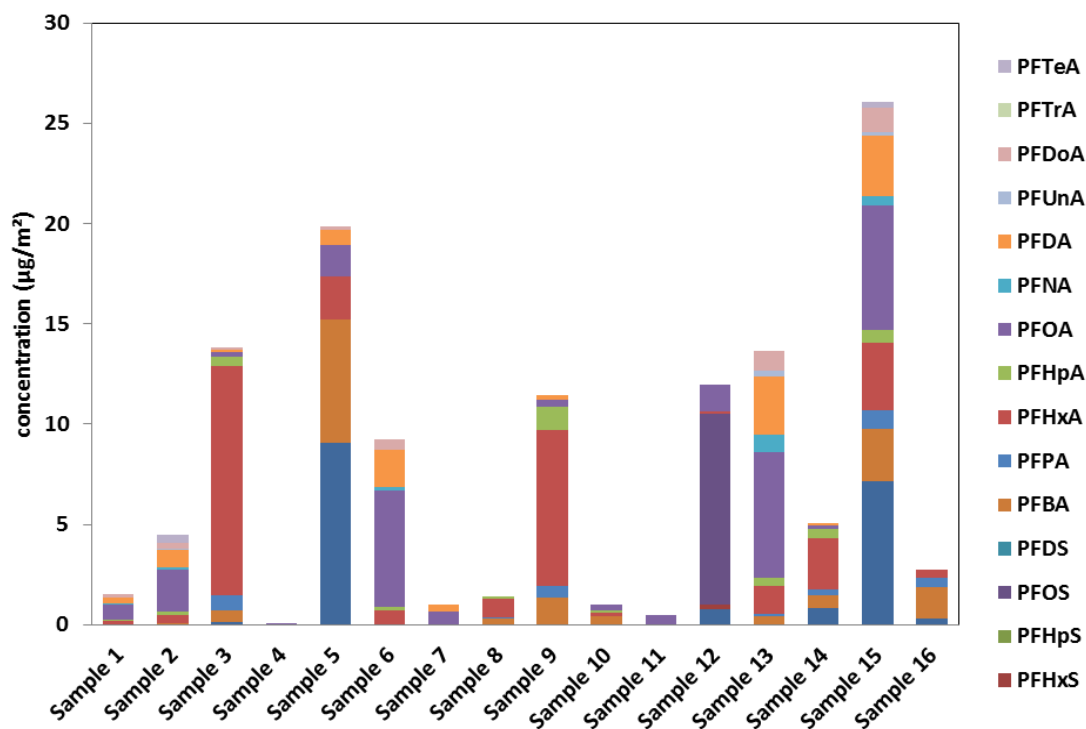


Figure 1: Concentration ($\mu\text{g}/\text{m}^2$) of perfluoroalkyl acids in the investigated textile samples (Sample 11, 12: gloves, remaining samples: jackets)

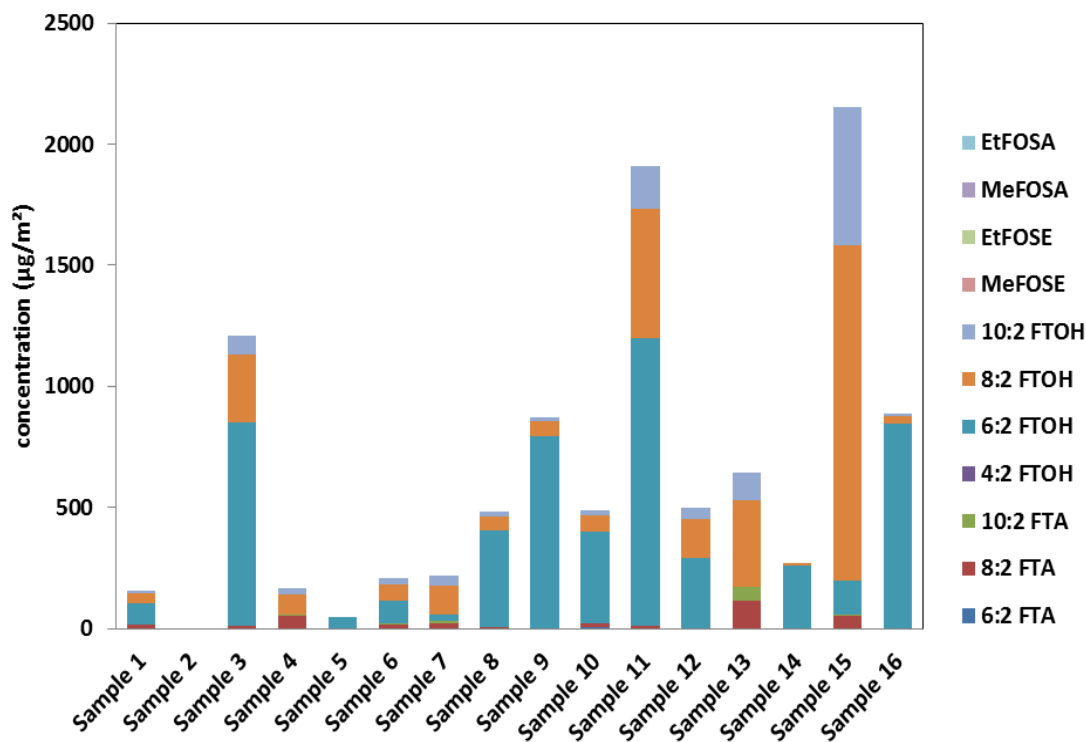


Figure 2: Concentration ($\mu\text{g}/\text{m}^2$) of volatile PFASs in the investigated textile samples (Sample 11, 12: gloves, remaining samples: jackets). Concentrations of FOSA and FOSE were below the limit of quantification.

Table 1: Emission rates of PFASs from textile samples (outdoor jackets) (ng/d).

	Sample 1	Sample 3	Sample 8	Sample 9	Sample 10	Sample 13	Sample 14	Sample 15
6:2 FTA	69	1.0	1.2	3.5	31	7.4	1.5	2.5
8:2 FTA	74	3.9	12	15	4.3	556	5.6	47
10:2 FTA	25	0.8	< 0.6	1.2	2.3	597	1.4	10
4:2 FTOH	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
6:2 FTOH	490	3917	8798	9220	431	17	3505	35
8:2 FTOH	125	68	512	162	121	803	47	372
10:2 FTOH	55	11	53	23	86	803	11	68
MeFOSA	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
EtFOSA	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
MeFOSE	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
EtFOSE	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4

All of the investigated products (now outdoor jackets only) emitted volatile PFASs at room temperature implying that such products are important PFAS sources, particularly for indoor air environments^{6,7}. Similar to the product PFAS contents, emission rates varied strongly between samples and compounds. Emission rates were highest for 6:2 FTOH (up to 9200 ng 6:2 FTOH/d). Emission rates published were in the same order of magnitude, however with maximum emissions observed for 8:2 FTOH.

Acknowledgement:

We are grateful to Manfred Santen and Uli Kallee

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