PFAS IN SYNTHETIC OUTDOOR WEAR FROM CHINA, INDONESIA AND RUSSIA

Straková J[1,2], Grechko V[2], Brosché S[1], Speranskaya O[3], Ponizova O[3], Ismawati Y[4], Annisa A[4]

[1]International Pollutants Elimination Network (IPEN), Gothenburg, Sweden, 402 35; jitkastrakova@ipen.org
[2]Arnika – Toxics and Waste Programme, Prague, Czech Republic, 170 00
[3]Eco-Accord Programme on Chemical Safety, Moscow, Russia 127521
[4]Nexus for Health, Environment, and Development Foundation, Denpasar, Indonesia, 80223

Introduction

The PFAS problem

PFAS (per- and polyfluoroalkyl substances) is a large group of more than 4.700 synthetic organic substances[1] used ubiquitously in consumer- and professional products. They all contain a strong C-F bond that makes them very persistent, leading to accumulating levels in the environment[2-3]. PFAS are emitted to the environment at every stage of their life cycle, including production [4-6], use in products[7] and final disposal[8-10]. When PFAS-treated products are recycled, PFAS can spread uncontrollably and contaminate new products, which compromises the circular economy. PFAS have been being detected in air[11], soil[12], water[12-13] (including drinking water sources)[13-14], and household dust[15-16]. They can also be transported over long distances in the environment and have been found far from their places of origin, including the Arctic[17-19.] To date, human biomonitoring studies have detected PFAS in human breast milk, urine and blood samples, including serum, plasma and whole blood[20-27]. This has raised severe concerns since PFAS have been shown to be associated with a range of health effects, including negative impacts on female fertility, thyroid hormone function[28-29] , the immune system[30] and fetal development[31].

PFAS in textile and outdoor wear

PFAS are used in many different applications, including production of fabrics and textiles, since they are both water- and oil repellent. However, most of these uses are not essential for the functioning of society and alternatives are available[32]. Their use in the textile sector accounts for about 50% of global use of PFAS[8], where they are widely used as water and dirt repellents and impregnations[7,33,34] in outdoor wear and in accessories for outdoor sports (e.g., waterproof shoes, jackets, backpacks or tents)[7,35,36]. During the production phase, textile factories pollute the surrounding environment [5,37] and expose workers to PFAS[38]. Moreover, PFAS are volatilized, weathered and washed out from the textile product during their use[8,35]. Up to 30 times higher FTOH concentrations were determined in the interior of sportswear stores compared to outdoor stores[39]. Unfortunately, conventional wastewater treatment plants do not typically have technologies for PFAS capture and destruction, thus PFAS coming with the laundry water are being emitted into the waterways[40-42]. When PFAS treated articles are disposed of at the end of life, PFAS migrate from the waste into the landfill leachates[9,43], are emitted with incineration fumes and ashes[43-44] or are being recycled into new product[45-46].

Aim of study

This study was conducted to assess PFAS utilization in synthetic outdoor- and sportswear products in China, Indonesia and Russia by analysing the presence of 55 targeted PFAS in waterproof and stain resistant clothes. It was conducted by IPEN together with partner organizations Arnika (Czech Republic), Toxics-Free Corps (China), Nexus 3 (Indonesia) and EcoAccord (Russia).

Materials and methods

Sample collection

In total, 41 products made of synthetic textiles were purchased from clothing stores or e-shops. Each product constituted one sample. 18 and 15 winter gloves were purchased in China and Russia, respectively. In Indonesia, 2 samples of sport gloves and 6 additional samples of outdoor wear were purchased. 25 samples were randomly selected for laboratory analysis out of the 41 collected items for budgetary reasons (10 winter gloves from China, 10 winter gloves from China, and 2 sport gloves, one t-shirt, a pair of trousers, and a hijab from Indonesia).

Detection and quantification of targeted PFAS

The 25 selected samples were analysed at the Department of Food Analysis and Nutrition of the University of Chemistry and Technology in Prague, Czech Republic for the presence of 55 PFAS. The following targeted substances were selected based on the availability of standards: <u>Perfluorinated carboxylic acids</u>: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA. PFUnD, PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFODA (LOQ 1.7 ng/g); <u>Perfluoroalkyl sulfonic acids</u>: PFPrS, PFBS, PFPeS, PFHxS, PFHpS (LOQ 1.7 ng/g), br-PFOS (LOQ 0.3 ng/g), L-PFOS (LOQ 1.3 ng/g), PFNS, PFDS, PFDoS, PFOSA (LOQ 1.7 ng/g); <u>Perfluoroalkane sulfonamide and derivatives</u>: N-MeFOSA, N-EtFOSA (LOQ 1.7 ng/g); <u>Perfluoroether carboxylic acid (PFECA)</u>: ADONA, HFPO-DA (LOQ 1.7 ng/g); <u>Chlorinated polyfluorinated ether sulfonates</u>: 9Cl-PF3ONS (LOQ 1.7 ng/g), 11Cl-PF3OUDS (LOQ 1.7 ng/g); <u>Fluorotelomer alcohols</u>: 4:2 FTOH (LOQ 0.8 ng/g), 6:2 FTOH, 8:2 FTOH (LOQ 1.6 ng/g), 10:2 FTOH (16 ng/g), 12:2 FTOH, 14:2 FTOH, 16:2 FTOH, 18:2 FTOH, 20:2 FTOH (detected/not

detected); Fluorotelomer sulfonic acids: 4:2 FTS, 6:2 FTS, 8:2 FTS, 10:2 FTS (LOQ 26 ng/g), 12:2 FTS, 14:2 FTS, 16:2 FTS (detected/not detected); Fluorotelomer phosphate monoesters (PAPs): 6:2 PAP, 8:2 PAP (LOQ 260 ng/g), Fluorotelomer phosphate diesters: 6:2 diPAP, 6:2/8:2 diPAP, 8:2 diPAP LOQ 26 ng/g); Perfluorophosphonic acid: PFBPA (LOQ 260 ng/g), PFHxPA, PFOPA, PFDPA (lOQ 26 ng/g).
The targeted PFAS were extracted using a methanol: ethyl-acetate mixture and all except the FTOHs analysed using ultra-high-performance liquid chromatography interfaced with tandem mass spectrometry with electrospray ionization in negative mode. The selected FTOHs were analysed using gas chromatography coupled to tandem mass spectrometry operated in positive ion chemical ionization.

Results and discussion
For the complete analytic results (ng/g), please see the table below.

Sample origin	Sample ID	Sample type	8:2 FTOH (ng/g)	12:2 FTOH (screening)	6:2 diPAP (ng/g)	6:2/8:2 diPAP (ng/g)
Russia	RUS-PFAS-01	Teen/adult winter glove	19.3	Not detected	<26	<26
Russia	RUS-PFAS-03	Teen/adult winter glove	1 791	Not detected	<26	<26
Russia	RUS-PFAS-04	Children winter glove	25.8	Not detected	<26	<26
Russia	RUS-PFAS-05	Children winter glove	<1.6	Not detected	<26	<26
Russia	RUS-PFAS-07	Children winter glove	<1.6	Not detected	<26	<26
Russia	RUS-PFAS-08	Children winter glove	<1.6	Not detected	<26	<26
Russia	RUS-PFAS-10	Children winter glove	19.1	Detected	<26	<26
Russia	RUS-PFAS-11	Teen/adult winter glove	54.8	Not detected	<26	<26
Russia	RUS-PFAS-12	Children winter glove	<1.6	Not detected	<26	<26
Russia	RUS-PFAS-15	Children winter glove	12.6	Not detected	<26	<26
Indonesia	IND-PFAS-01	Adult T-shirt	52.4	Not detected	<26	<26
Indonesia	IND-PFAS-04	Hiking glove	4.5	Not detected	<26	<26
Indonesia	IND-PFAS-05	Hijab	252	Not detected	30 178	679
Indonesia	IND-PFAS-06	Sport trousers	31	Not detected	<26	<26
Indonesia	IND-PFAS-07	Adult glove	103	Detected	<26	<26
China	CHN-PFAS-02	Adult winter glove	53.2	Not detected	<26	<26
China	CHN-PFAS-03	Adult winter glove	25.6	Not detected	<26	<26
China	CHN-PFAS-04	Adult winter glove	81.7	Not detected	<26	<26
China	CHN-PFAS-07	Adult winter glove	87.1	Not detected	<26	<26
China	CHN-PFAS-08	Adult winter glove	85.6	Not detected	<26	<26
China	CHN-PFAS-09	Adult winter glove	57.1	Not detected	<26	<26
China	CHN-PFAS-11	Adult winter glove	36.2	Not detected	<26	<26
China	CHN-PFAS-12	Adult winter glove	23.4	Not detected	<26	<26
China	CHN-PFAS-14	Adult winter glove	129	Detected	<26	<26
China	CHN-PFAS-18	Adult winter glove	31	Detected	<26	<26

Identified PFAS – only the tip of the iceberg
Of the 55 targeted PFAS, only 3 (fluorotelomer alcohols 8:2 FTOH and 12:2 FTOH and fluorotelomer phosphate diester 6:2 diPAP) were found to exceed their LOQ (1.6 ng/g for 8:2 FTOH and 26 ng/g for 12:2 FTOH and 6:2 diPAP) and 1 more PFAS (6:2/8:2 diPAP) was detected in the 25 samples analysed. Fluorotelomer alcohols are starting chemicals and intermediate degradation by-products in production of majority commercial PFAS including fluorotelomer-based polymers, and their presence is an indication of treatment with unknown PFAS compounds. The limited number of identifiable PFAS in the textile samples is consistent with previous studies[8,47,48]. This highlights both the current limitations of the employed analytical methods, which are not able to identify PFAS such as fluorinated polymers, and the lack of commercially-available standards to allow identification and quantification of all relevant PFAS used for treating textiles[49-52]. In this regard, the 4 identified PFAS are only the tip of the iceberg. Despite not being identified individually, the other potentially present PFAS cause concern due to their ability to persist and accumulate in the environment. It is not only challenging to identify them, but also to control them once they are in the environment.

Fluorotelomer alcohols and polyfluoroalkyl phospfate diesteres – a potential source of globally banned PFOA

8:2 FTOH was quantified in 21 out of 25 samples (84 %) of the analysed outdoor- and sportswear at concentrations from 4.46-1790 ng/g (median concentration 52.4 ng/g and average concentration 142 ng/g). Its presence was confirmed in all samples of winter gloves from China, in all samples of sport gloves and outdoor wear (hijab, trousers, t-shirt) from Indonesia, and in 60% of the winter gloves from Russia. The highest concentration of 8:2 FTOH (1790 ng/g) was found in a pair of winter gloves from Russia.

FTOHs can be released from the investigated products[39], causing concern about the children´s winter gloves from Russia, since children can be exposed to FTOHs in the gloves to a greater extent than adults due to their normal hand-to-mouth contact[53]. There are toxicological concerns regarding FTOHs themselves and their degradation products, which are both associated with hepatotoxicity, mammary gland cancer, negative impacts on the reproductive system, and with developmental disorders[54].

Specifically, 8:2 FTOH degrades to perfluorocarboxylic acids (PFCAs) including shorter chain PFCAs and the globally banned perfluorooctanoate (PFOA)[55-56]. The degradation mechanism was confirmed in a weathering experiment, showing that PFCAs are formed in water repellent outdoor clothing during its wear and aging[35]. In the long run, FTOHs present in waste stocks of end-of-life consumer products, including synthetic outdoor wear, may migrate and degrade into PFCAs (including PFOA) in the environment[55].

In addition to 8:2 FTOH, 6:2 diPAP and 6:2/8:2 diPAP were presented in hijab bought in Indonesia (30 200 and 679 ng/g respectively). This is the first time in many years when presence of diPAPs is reported in textile and clothing. 6:2 diPAP degrades to PFHxA and PFHpA, and 8:2 diPAP to globally restricted PFOA and PFNA[57]. As diPAPs belong among less studied PFAS, their toxicological concerns are so far mainly related to the toxic properties of their degradation products (see above).

Nature of the PFAS treatment – C8-based polymers

Despite of the harmful effects of these substances on human health and the environment, as well as the associated regulatory efforts of the Stockholm Convention, our results suggest that the water repellence of the tested outdoor textiles from China, Indonesia and Russia was achieved by the application of side-chain fluorotelomer-based polymers (FTPs), consisting of a non-fluorinated backbone with C8 polyfluoroalkyl side chains[58]. FTPs are responsible for the 8:2 FTOH presence in the analysed samples and their degradation into PFOA. This fact contradicts the intention of the Stockholm Convention to globally ban PFOA, its salts and PFOA-related compounds via measures to eliminate the production and use of the chemicals under the scope. PFAS extracted from textiles with C8 agents have been indicated in the former studies by Swerea IVF in 2009[59] and Greenpeace in 2013[36], but this practice seems to have been replaced in recent years by the application of polymers with short-chain polyfluoroalkylated side chains in Europe and the U.S[8,60].

Conclusions and Recommendations

The study indicates that the water repellence of the analysed synthetic outdoor- and sportswear from China, Indonesia and Russia was achieved by the application of side chain fluorotelomer-based polymers. The most-frequently identified fluorotelomer alcohol 8:2 FTOH is capable to degrade to the highly persistent pefluorocarboxylic acid PFOA that is listed for global elimination under the Stockholm Convention. To avoid PFOA formation, release and build-up into the environment during the lifecycle of PFAS treated products, application of PFAS needs to be immediately abandoned in the targeted countries.

Only 4 out of 55 PFAS was identified by targeted, compound-specific analysis in 25 outdoor wear samples from China, Indonesia and Russia. Due to the analytic limitations and lack of standards, our survey leaves some PFAS in our samples unidentified. The unidentified PFAS raise concerns due to their ability to persist and accumulate in the environment. Moreover, there are many more PFAS existing and available for use. Nevertheless, use of PFAS in outdoor wear is not essential for the functioning of society and suitable non-PFAS alternatives are available. A class approach to phase out all non-essential uses of PFAS is the only health protective response to the existing environmental health threat.

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