CHEMISTRY FOR ANY WEATHER: PER- AND POLYFLUORINATED CHEMICALS IN TEXTILE PRODUCTS AND AMBIENT AIR

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Introduction

Since 2011, Greenpeace's Detox campaign has been working to ensure that hazardous chemicals are removed from textile production processes. By testing samples of wastewater[1] and textiles[2,3], Greenpeace has revealed that the textile industry releases chemical compounds that are harmful to human health and environment. The chemicals discovered included Nonylphenol ethoxylates (NPEs) which can break down to form endocrine disrupting Nonylphenols (NPs) when released into the environment as well as phthalates and poly- and perflourinated chemicals (PFCs). Over the last three years, the Detox campaign has mobilised hundreds of thousands of people around the world to challenge major clothing brands to eliminate all releases of hazardous chemicals from their supply chains and products. So far, the campaign has been able to secure public commitments from twenty international fashion companies. As global players, international brands are perfectly placed to eliminate the negative environmental impacts of their production. They can do this through the suppliers they choose to collaborate with, the design of their products, and the control they can exert over the chemicals used throughout the production processes.

PFCs are used in many industrial processes and consumer products due to their unique chemical properties, including textile products, primarily due to their stability and ability to repel both water and oil[4]. Although limited studies into their presence in textiles have been conducted, the most commonly found PFCs to date were Perfluorocarbonic and Perfluorosulfonic acids (ionic PFCAs and PFSAs), as well as Fluorotelomer alcohols (FTOHs) and Fluorotelomer acrylates (FTAs). The manufacture and use of PFCs, including for textiles, can result in releases to the environment, either directly from manufacturing facilities, or indirectly when products containing PFCs are used, washed and disposed of. Many PFCs are highly persistent or form very persistent degradation products once released to the environment. This has led to their ubiquitous presence in the environment, even in remote regions[5]. Furthermore, their ability to bioaccumulate has led to PFCAs and PFSAs being reported in a wide range of both aquatic and terrestrial biota[6,7,8], in human blood[9] and also in breast milk[10]. Precursor PFCs, such as FTOHs, have the potential to degrade to PFCAs either through biotransformation[11], or abiotically in the atmosphere[12]. They are volatile and have frequently been detected in air samples, even in remote areas[13]. 8:2 FTOH can form C8 compounds including PFOA, while 6:2 FTOH can result in C6 compounds including PFHxA. Humans occupationally exposed to high levels of 8:2 FTOH have been found to have high concentrations of PFOA in their blood[14]. In addition, there are indications that biotransformation can form intermediate products in the body that can be more harmful than the PFCA end product[15].

Greenpeace has recently published a number of investigations showing that a wide range of textile products, manufactured and sold in many countries around the world, can contain residues of highly persistent per- and polyfluorinated chemicals: Greenpeace has found PFC in waterproof jackets and trousers[16], in leather gloves[17], and, most recently, in swimwear[18], luxury textile products and footwear[19].

In the current study outdoor clothes were assessed for their PFC contamination. In addition chamber tests were conducted for assessing if and to what extent some of these compounds evaporate.

Materials and methods

Outdoor wear items were assessed for the presence of a range of ionic and volatile PFCs. The products tested (the majority of which were waterproof jackets and gloves for adults but also included two children's jacket), were sold by 12 outdoor brands, with one product per brand (apart from 3 products by The North Face, 2 by Mammut, 2 by Jack Wolfskin and 2 by Vaude). They were purchased in Germany, Austria, Switzerland, China and the United States. The majority were made in China (8), followed by Vietnam (5), Indonesia (2) and Thailand (1); for one product, the country of manufacture was undisclosed.

Textile product samples were sent to an accredited commercial laboratory and tested for a wide range of perfluorinated and polyfluorinated compounds, such as PFCAs, PFSAs, FTOHs and FTAs. The analyses did not include PFCs which cannot be extracted using solvents, e.g. polymeric PFCs. PFCAs and PFSAs were extracted with methanol and analyzed using high-performance liquid chromatography combined with tandem mass spectrometry (HPLC-MS/MS). The FTOHs and FTAs were extracted with methyl tertiary butyl ether (MTBE) and analyzed using gas chromatography coupled with mass spectrometry (GC-MS).

In addition, the study determined to what extent certain PFCs are emitted from the items of clothing into air. To date, there have been only few studies on the evaporation of PFCs from textiles[20]. The laboratory analysed the quantity of volatile PFCs evaporating from nine items of clothing at room temperature into the surrounding air within a test chamber. Each jacket was put into a 120-liter stainless steel chamber and remained there for six days under ambient conditions.[21]

Results and discussion

Of the fifteen jackets and two pairs of gloves tested, PFC residues were detected in all samples. Therefore the results confirm the findings of previous studies, demonstrating that a high share of the outdoor wear items investigated contained perfluorinated and/or polyfluorinated chemicals.

Key findings:

- PFCAs were detected in all articles tested. 15 of 17 products contained PFOA at concentrations between 0.1 to 6.3 $\mu g/m^2$; concentrations were above 1 $\mu g/m^2$ in one third of the samples. Shorter chain perfluoro-hexanoic acid (PFHxA) was detected in 14 out of 17 samples at concentrations between 0.1 and 11.4 $\mu g/m^2$.
- In 7 products PFSAs were detected, predominantly PFBS. Only one article contained PFOS, but in very high concentrations: A pair of gloves sold by Mammut had a PFOS concentration of 9.5$\mu g/m^2$, exceeding the EU regulatory limit of 1 $\mu g/m^2$ by far.
- Of the 17 products tested, 16 contained residues of volatile FTOHs, at much higher levels than the ionic PFCs in each case. Concentrations for total volatile PFCs ranged between 48.9 and 2090 $\mu g/m^2$. The concentrations of the compound 6:2 FTOH were substantially high compared to former studies: the median concentration increased from 62$\mu g/m^2$ in 2012 to 274$\mu g/m^2$ in 2013. The median level for 6:2 FTOH is also considerably higher than the median for 8:2 FTOH, which remained at a similar level, but with higher variation between samples compared to previous tests.

Table 1: Median and range for key PFC compounds (in $\mu g/m^2$) in outdoor wear.

This test (2013)	PFHxA	PFOA	6:2 FTOH	8:2 FTOH	PFBS	PFOS
In x of 17 products	14	15	14	15	7	1
Min	0,2	0,1	29,4	13,4	0,14	9,49
Max	11,5	6,3	1189,7	1387,3	9,0	9,49
Median	0,5	0,7	274,3	81,9	0,5	-
Previous test (2012)[22]	PFHxA	PFOA	6:2 FTOH	8:2 FTOH	PFBS	PFOS
In x of 14 products	9	14	6	5	0	0
Min	0,1	0,2	27,0	30,0	-	-
Max	26,9	5,0	352,0	229,5	-	-
Median	0,5	0,5	62,0	78,1	-	-

The investigation also found that certain PFC's are released into the air from the items of clothing under ambient conditions. The results showed that all nine tested products released FTOHs and FTAs to the surrounding air at room temperature: between 540 und 9220 ng/d; With one exception products with a higher concentration of 6:2 FTOH than 8:2 FTOH in the material, also emitted more 6:2 FTOH to the ambient air – and vice versa.

The test chamber investigations show that FTOHs and FTAs can evaporate under ambient conditions and therefore demonstrate an additional route for these substances to be released into the environment. It is not possible to estimate the contribution that outdoor clothing makes to the total levels of PFC in indoor air, based on these tests, as a number of other possible sources, such as carpets and shoes, would need to be taken into account. However, previous studies have shown that the indoor air in stores selling weather clothing has considerably elevated concentrations of FTOHs[23].

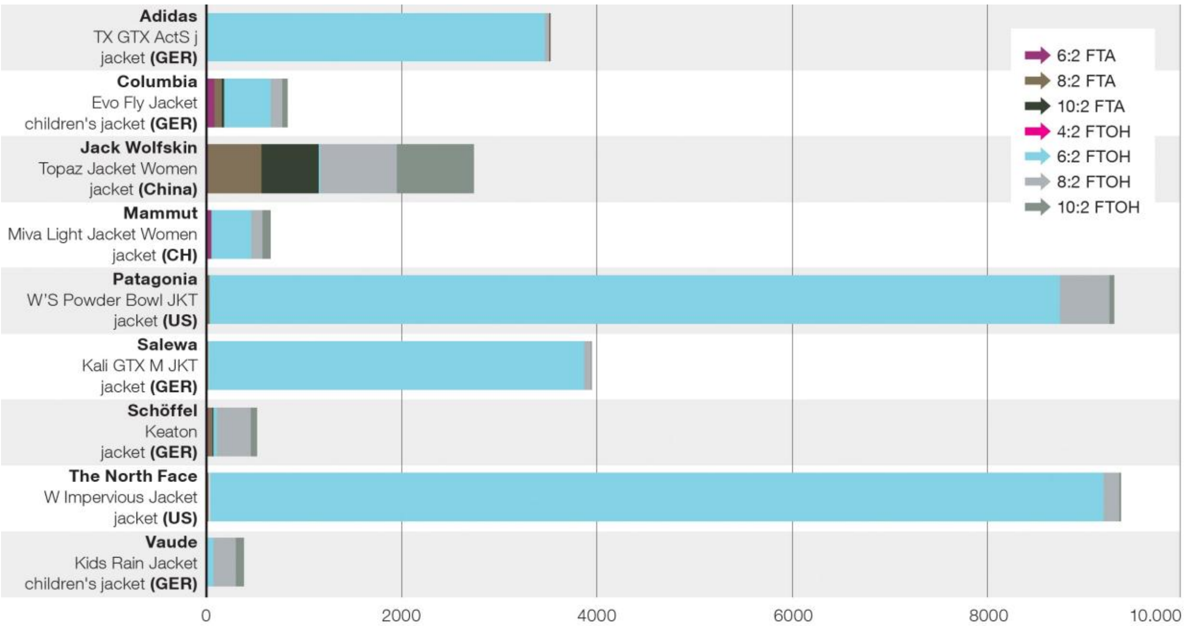

Figure 1: Emissions of polyfluorinated chemicals (FTOHs and FTAs) from Outdoor-Jackets [in ng/d]. Products from The North Face, Patagonia, Adidas and Salewa, emitted the highest levels of total FTOH, in particular 6:2 FTOH. All four jackets also had high levels of 6:2 FTOH in the material. Although Mammut and Vaude products showed similar levels of 6:2 FTOH in the material test, they emitted considerably less FTOH to the air chamber.

A new trend: the use of shorter chain PFCs

This study has found that outdoor clothing contains PFCs which exhibit environmentally harmful characteristics and which can also pose hazard to health. Despite the existence of alternatives which do not have related environmental hazards, outdoor clothing brands are still relying predominantly on PFCs to make their products waterproof and dirt repellent.

Compared to a previous Greenpeace report on PFCs in outdoor wear items[24], shorter chain PFC compounds were detected more frequently and at higher concentrations, in particular 6:2 FTOH. For some brands 6:2 FTOH was the prevalent compound in this study, while in previous tests 8:2 FTOH was prevalent in articles from the same brands. These results suggest that certain outdoor clothing brands are using 6:2 FTOH as an alternative for the longer chain compound 8:2 FTOH – at least for parts of their product range. Although to date there is limited data to support this, the high median concentration of 6:2 FTOH detected in the products suggests that shorter chain PFC compounds are being used in greater quantities compared to 8:2 FTOH. This could be due to the fact, that they are less effective as water repellents. The test chamber analyses show that these shorter chain compounds can easily evaporate from clothing. Once they have been emitted, these volatile compounds can disperse rapidly into the air. In the environment they can be transformed into shorter chain ionic PFCs (perfluorocarbonic acids). These compounds do not degrade in the environment and can easily reach groundwater and drinking water. If the production and commercial use of these highly mobile chemicals increases, this could likely result in higher levels of PFCs in the environment in future, which has already been seen in recent years[25].

Assessment of toxicity: a challenge

One challenge is the toxicological assessment of these findings and of the exposure of people wearing these clothes and those which are otherwise impacted by these releases. Studies indicate that PFCs can cause adverse impacts both during development and during adulthood. PFCs, including PFOA, have been shown to act as hormone (endocrine) disruptors[26], and studies have suggested that PFOS and PFOA exhibit reproductive toxicity, including for humans[27]. Impacts on the immune system have also been reported[28,29], and some are potentially carcinogenic in animal tests[30]. Information regarding the toxicology of FTOH is scarce, though some studies indicate that 6:2 FTOH and 8:2 FTOH show endocrine-disrupting activity, including disturbing fish reproduction[31]. In addition to direct hazards from FTOHs, the potential for FTOHs to transform into other PFCs, including PFCAs, poses an additional hazard. For many of these compounds little toxicological data are available. Furthermore no studies have been conducted on the effects of PFC mixtures on human health. Considering the health effects known and considering the precautionary approach these substances should be substituted by safe alternatives.

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