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Substitution of PFAS chemistry in outdoor apparel and the impact on repellency performance

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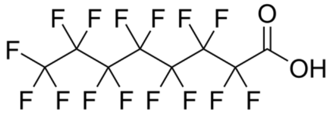
Intensifying legislation and increased research on the toxicological and persistent nature of per- and polyfluoroalkyl substances (PFASs) have recently influenced the direction of liquid repellent chemistry use; environmental, social, and sustainability responsibilities are at the crux. Without PFAS chemistry, it is challenging to meet current textile industry liquid repellency requirements, which is a highly desirable property, particularly in outdoor apparel where the technology helps to provide the wearer with essential protection from adverse environmental conditions. Herein, complexities between required functionality, legislation and sustainability within outdoor apparel are discussed, and fundamental technical performance of commercially available long-chain (C8) PFASs, shorter-chain (C6) PFASs, and non-fluorinated repellent chemistries finishes are evaluated comparatively. Non-fluorinated finishes provided no oil repellency, and were clearly inferior in this property to PFAS-finished fabrics that demonstrated good oil-resistance. However, water repellency ratings were similar across the range of all finished fabrics tested, all demonstrating a high level of resistance to wetting, and several non-fluorinated repellent fabrics provide similar water repellency to long-chain (C8) PFAS or shorter-chain (C6) PFAS finished fabrics. The primary repellency function required in outdoor apparel is water repellency, and we would propose that the use of PFAS chemistry for such garments is over-engineering, providing oil repellency that is in excess of user requirements. Accordingly, significant environmental and toxicological benefits could be achieved by switching outdoor apparel to non-fluorinated finishes without a significant reduction in garment water-repellency performance. These conclusions are being supported by further research into the effect of laundering, abrasion and ageing of these fabrics.

Keywords: Per- and polyfluoroalkyl substances; PFOA and PFOS; consumer products; outdoor apparel; sustainability; SEM- EDX.

1. Introduction

A ubiquitous part of everyday life, liquid repellent finishes are used within a variety of sectors, both within consumer products and technical applications for oil and water resistance.[1-3] Use of polymeric per- and polyfluoroalkyl substances (PFASs) has vastly grown since first use in the 1950s due to the high level of repellent functionality they provide;[4] PFASs are used in many applications, such as food-packaging, fire-fighting foams, cookware, electronics, medical products and within consumer textiles.[3,5-9] Repellent properties are essential for protection against harmful liquids, for example within medical textiles and protective clothing in the oil and gas industry, and are vital for health, safety and comfort of outdoor enthusiasts in inclement weather or extreme environmental conditions.[10] The woven fabric used for outdoor repellent apparel, for both extreme environments and casual leisure activities, is coated with an aqueous emulsion based on PFASs or side-chain fluorinated polymers that imparts a durable water and stain repellent finish.[6] PFASs comprise a polymeric backbone with branching fluorinated side-chains, where on one more carbon atoms and all hydrogens have been replaced by a perfluoroalkyl moiety (C_nF_{2n+1}).[11] There are two main manufacturing processes to produce PFASs. In electrochemical fluorination (ECF) the organic substance is reacted with anhydrous hydrogen fluoride (HF) by electrolysis, substituting all hydrogen atoms with fluorine and creating a mix of linear and branched perfluorinated isomers and homologues.[6,11-13] In telomerisation, perfluoroethylene (CF_2=CF_2) and perfluoroethyl iodide (C_2F_5I) are reacted together to produce perfluorinated iodides with various chain lengths; these intermediates are used in subsequent reactions to synthesize fluorotelomer-based products, which find use in food packaging, surfactants and textile treatments.[6,11,12] In all compounds the degree of fluorination, backbone chain length, and the packing of the side chains affects the characteristics of the compound.[6,11,12,14] The high level of hydrophobicity and oleophobicity provided by PFASs is due to the low surface energy provided by the orientation and packing of the terminal $–CF_3$ end groups within the side-chains.[14,16] The wetting potential is dependent on the adhesive interaction between the liquid surface, solid surface and the air interface. The structure of the fluorinated polymer side-chain, with clustered hydrophobic groups, reduces the surface energy of the fabric; a $–CF_3$ surface construction has a surface tension of 6 dyn cm^{-1} at 20 °C, which repels liquids with a greater surface tension, including polar liquids (*e.g.* water with surface tension of 73 dyn cm^{-1} at 20 °C) and non-polar liquids (*e.g.* octane with surface tension 22 dyn cm^{-1} at 20 °C).[6,17]

However, PFASs have been ubiquitously identified within wildlife, humans and found across the world in the environment;[18,19] they are criticized as being toxic, carcinogenic and persistent within the environment.[20-22] Of high regulatory interest are long-chain PFASs: perfluoroalkyl carboxylic acids (PFCAs) with seven or more fluorinated carbons ($C_nF_{2n+1}COOH$; $n \geq 7$), for example perfluorooctanoic acid (PFOA; **1**); and perfluoroalkane sulfonic acids (PFSAs) with six or more fluorinated carbons ($C_nF_{2n+1}SO_3H$; $n \geq 6$), for example perfluorooctanesulfonic acid (PFOS; **2**).[11,15,19] A wealth of literature exists on the ubiquitous and bio-accumulative nature of PFOA and PFOS and associated increased mortality rates, cancers, and toxic effects on liver and immune systems.[5,12,21,23-27] Bio-accumulation and bio-concentration of PFASs within humans and the food chain are of primary concern,[19] which increases with increasing fluorinated carbon chain length; long-chain PFSAs and PFCAs have a higher bio-accumulation potential than their shorter-chain analogues.[11,19,28,29] PFASs have been acknowledged to have a greater bio-accumulative nature than PFCAs of the same carbon chain length, which is thought to be due to the ability of PFASs to bind more strongly to serum proteins.[29,30,31]



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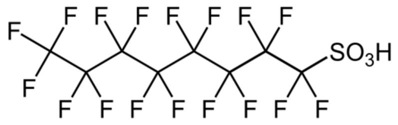

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There is a continuing challenge to find an alternative chemistry and/or physical modifications to provide equivalent liquid repellent functionality to that given by PFAS chemistry. Substitution to ‘short-chain’ PFAS chemistry has taken place with shorter fully fluorinated chain lengths as C6 or C4 analogues. However, there is increasing concern on the persistent and bio-accumulative potential of these short-chain analogues, which have the capability to degrade to short-chain perfluoroalkyl carboxylic acids (PFCAs) or perfluoroalkane sulfonic acids (PFSAs).[32,33] An increasing exposure trend to perfluorohexane sulfonate has been observed, and this compound potentially has a similar or longer serum half-life, within mammals that have been tested, to PFOS.[33] Alternative non-fluorinated chemistries include hydrocarbons, silicones, and dendritic structures, and product developers are increasingly cinched between fulfilment of technical performance for the product, legislative requirements, and social and environmental responsibility.

Recent statistics show that nearly 9 million people in England are active outdoors, with over 250,000 people either climbing or hill-walking at least once a month.[34] An increase in participation and a diversity in the types of activities being undertaken, in terms of terrain, environment and physical activity level, bring an increased and more varied demand on performance clothing functionality; the wearer expects clothing to function and maintain comfort regardless of the climatic conditions encountered.[35] Durable water repellent (DWR) clothing is of high importance for safety and wearer wellbeing in mountainous, often remote, environments during strenuous activity, such as hiking, climbing or mountaineering, and in adverse weather conditions. Rainwear should provide protection, keeping the wearer dry whilst allowing thermoregulation of the body.[10,35,36] Wetting of the garment's outer fabric face, due to decreased repellency, saturates the fabric rapidly, reducing evaporative cooling of perspiration and heat transfer away from the wearer's body;[37-39] this results in a feeling of wearer discomfort, possible wetting of other clothing layers, and accelerated cooling of the wearer,[39-41] consequently, the wearer's physiological responses can be affected, potentially resulting in an issue of health and safety.

Multiple factors post-purchase affect the liquid repellent functionality of the garment such as laundering durability, abrasion resistance (rocky terrain for outdoor consumers), and consumer care;[42] only fluorinated repellent finishes have been used ubiquitously throughout consumer repellent apparel achieving a high level of repellency and effective performance. For consumer outerwear in less adverse conditions, a lower level of functionality may be appropriate, where a high level of technical protection is not a key requirement. However, PFAS chemistry has been widely used to fulfil this wide range of requirements and used in abundance due to its capability to be applied to a range of fibre types and fabrics.

Concern on the use of long-chain PFAS chemistry started in the 1960s, notably with the detection of organic fluorine within human serum by Taves in 1968.[43,44] The substitution process away from long-chain PFSAs and PFCAs began in 2000 when the first reports of the ubiquitous occurrence of PFOS within wildlife were published.[11,33] These concerns led to the phase-out of PFOS and related compounds by 3M, whose key components within the manufacture of their Scotchgard stain products produced perfluorooctanesulfonamide derivatives by ECF with PFOS a resulting products from the intermediate perfluorooctanesulfonyl fluoride (POSF) used in secondary synthesis. [11,33,45,46] Industry initiatives moved to shorter-chain analogues of side-chain fluorinated polymers. with non-fluorinated alternatives progressively also being sought.[15,17,33] European legislation and NGO campaigning has driven the move away from long-chain PFSAs and PFCAs; in 2006 the EU imposed a restriction on the use of PFOS to protect health and the environment;[47] in 2009 PFOS was classified as restricted on The Stockholm Convention's list of Persistent Organic Pollutants (POPs); and in 2015 the European Chemicals Agency (ECHA) adopted a proposal to limit the marketing and use of PFOA European-wide.[48-50] The 2013 Helsingør statement[2] raised concerns on the impact of PFASs on health, the environment, and degradation and exposure of fluorinated alternatives, while the Madrid statement[9,51] raised similar concerns on the production and release of PFASs, calling for a limit to its use, and requesting a collaborative effort to develop non-fluorinated alternatives.

Since 2011, Greenpeace have concentrated their campaigning on the use of "toxic chemicals" on the apparel industry. In 2015, Greenpeace launched their 'Detox Outdoor' campaign with specific emphasis on use of PFAS chemistry within outdoor apparel; the 'Footprints in the Snow'[52] study assessed snow and water samples from eight remote locations around the world; the 'Leaving Traces' report[53] utilized social media asking consumers to nominate certain products and brands to be analysed for long-chain PFAS content; and the latest report 'Hidden in Plain Sight'[54] tested air samples from outdoor apparel stores for evidence of PFAS degradation. This increased publicity specifically highlighting the outdoor apparel industry's chemical use has led to many manufacturers and brands seeking a move away from PFAS repellent chemistry.

Despite PFASs being used in a variety of aspects of daily life, the outdoor apparel industry have explicitly been the primary target of this NGO activist attention, yet only a few research studies on the use of PFASs in outdoor apparel have been published, and these have solely focused on exposure pathways and degradation routes;[3,32,55-57] with many being non-peer-reviewed.[53,54,58-60] Whilst knowledge on degradation routes, exposure trends and analytical techniques remains central to research on PFASs, there is sparse comparative literature on the repellent functionality of PFAS chemistry and alternative, non-fluorinated chemistry, in outdoor apparel; one non-peer-reviewed study exists.[61] This functionality is highly important to the end-use of the fabric and the wearer.

The purpose of this work is to communicate the variation in functionality between long-chain (C8) PFAS repellent chemistry, shorter-chain (C6) PFAS repellent chemistry, and non-fluorinated repellent chemistry within outdoor apparel fabrics. The work aims to determine the necessary chemistry of the finish in a DWR treatment by illustrating the user requirements of repellent outdoor apparel and comparing repellent performance of finishes. Criticism has focused on the outdoor apparel industry highlighting repellent performance clothing as a potential route for exposure to PFASs. Considering the complex nature of balancing legislation, sustainability, and functionality, this paper aims to report a novel comparison of currently commercially available repellent fabrics for outdoor apparel and an assessment on their repellent functionality both for water and oil resistance.

2. Materials and Methods

2.1. Consumer survey

To illustrate consumer use of repellent apparel and their requirements, a consumer survey was designed and launched through Bristol surveys, in affiliation with The University of Leeds. The questions included demographic descriptors, indicators of the respondent's participation in outdoor activities, inquiry on the preferences in purchasing decisions and user requirements of personal apparel during activity. Respondents gained access to the survey through a URL address. Completion was voluntary and respondents could withdraw at any time. It was believed that the group of consumers targeted would have some knowledge of the criticism through brand marketing, retailers or NGO literature. The survey was promoted within outdoor recreation Internet forums and featured on an outdoor magazine's online website. The survey ran for 15 months from 15th May 2015 to 19th August 2016 and received a total of 575 responses.

2.2. Materials

Woven fabric samples were kindly supplied for the study by various manufacturers and brands: according to manufacturer details, three of these fabrics were stated to be finished with long-chain (C8) PFAS repellent chemistry, nine fabrics were stated to be finished with shorter-chain (C6) PFAS repellent chemistry, nine fabrics were stated to be finished with non-fluorinated chemistry, and one fabric was untreated. The non-fluorinated chemistries were, at the time of the study, relatively new to the market, supplier information stated that samples ***P*** to ***U*** were hydrocarbon hyper-branched polymers (dendrimers) with a polyurethane backbone, sample ***N*** was a fat-modified resin, and sample ***V*** was a hyper-branched polymer. All fabrics were commercially in use at the time of the study, intended for use in repellent outerwear, with the majority either 100% polyester (PET) or polyamide (PA) fibre content; some samples contained a laminate or membrane (see Table S.1). The fabrics display a range of commercially used fibre and fabric types, within outdoor apparel; all were synthetic monofilaments and the majority plain weave (only samples ***B*** and ***Q*** differ being twill weaves). The sample size stated within standard test methods to be used throughout the experimental work were compared; the specimen size needed to be cross-functional was calculated as 165 mm x 165 mm.

2.3. Energy-dispersive x-ray spectroscopy (EDS/EDX)

SEM-EDX (Jeol JSM 6610LV coupled to Oxford Instrument INCA X-Max 80 EDS system) was used to indicate elemental composition of the fabric sample surface, and therefore define the repellent finish type. Semi-quantitative elemental analysis (magnification x50, accelerating voltage 20 kV, spot size 50, working distance ~10 nm, and aperture 2) determined the elemental content of each fabric sample by weight percentage. Two specimens of each fabric sample, from different areas of the fabric, were analysed using ~1 cm^2 specimens.

2.4. Water repellency

AATCC 22-2014[62] (similarly BS EN ISO 4920:2012[63]) is a widely used test method to determine the resistance of a fabric to surface wetting by water. The procedure set out in the standard was followed using three different specimens, cut from separate places of the fabric sample, with 5 repeat tests. Each specimen was assessed according to the AATCC rating scale; intermediate ratings can be used for evaluation above water repellency grade of 50. Evaluation was carried out according to the water repellency grades as shown in Table 1 with inclusion of intermediate rating

95. According to AATCC 22-2014, a rating of '100' should be given where there is no sticking or wetting of the specimen, however, in preliminary testing it was observed that there is always some sticking to the fabric surface and therefore determined that a rating of 100 was unfeasible; a rating of 97.5 was given, as a substitute, when few small sparse droplets were seen.

Table 1. Spray test water repellency grades, according to AATCC 22-2014 (BS EN ISO 4920).[62,63]

Repellency grade	Description
97.5	Sparse small droplets visible on the specimen surface.
95	Few random sticking of water droplets clinging to the surface fibrils.
90	Slight random sticking or wetting of the specimen face
80	Wetting of specimen face at spray points
70	Partial wetting of the specimen face beyond the spray points
50	Compete wetting of the entire specimen face beyond the spray points
0	Complete wetting of the entire face of the specimen

The mode value of the repeat spray tests, for each fabric sample, was calculated. In addition, the amount of water that adhered to each fabric sample, either by sticking to the surface or by absorption by capillary action, was calculated as % change in comparing mass before and after testing; this method has previously been used to discriminate between similar rated fabrics.[61] The mass of each dry and conditioned fabric sample was measured using a Precisa 310C-3010D balance, and the mass of the sample following testing to two decimal figures. % Water adherence (A) was calculated according to equation 1, where mi and mt are the mass of the sample before and after testing, respectively. Average percentage mass increase was calculated for each fabric sample.

$$A = \frac{m_i - m_t}{m_i} 100 \tag{1}$$

2.5. Aqueous and oil repellency

BS ISO 23232:2009[64] determines aqueous liquid repellency using eight grades of water and isopropyl alcohol solutions with surface tension values between 24.0-59.0 dyn cm^{-1}. BS EN ISO 14419:2010[65] determines oil repellency using eight test solutions of hydrocarbons with surface tension values between 19.8-31.5 dyn cm^{-1}. These tests provide a wider range for greater discrimination between similarly performing samples. Wetting was evaluated and assigned a grade number 0-8, and assessed as a 'fail', 'pass' or 'borderline pass', where the grade was expressed to the nearest 0.5 value. The grade number in agreement from two specimens was recorded, with a third specimen tested where necessary.

3. Results and Discussion

3.1. Consumer survey

Of all the respondents, 526 were living within the UK (91.5%) with 35 other respondents from Europe and 14 from other countries worldwide. All age groups were represented. On a monthly basis, 83 respondents participated in outdoor recreation daily (14.4%), 76 participated 21-30 times per month (13.2%), 244 participated 6-20 times per month (42.4 %) and 170 respondents participated 5 or fewer times per month (29.5%). Two respondents did not participate in outdoor recreation at all (0.3%). The main outdoor activity undertaken by respondents was hiking, trekking, mountaineering and hill-walking.

384 respondents (67%) said they participated in outdoor recreational activities in all weathers, including rain and snow, with 268 respondents being outdoors in the rain more than 20 times per year; advocating the need for a high, sustained level of water repellency on their apparel. Respondents ranked purchasing factors by importance (Figure 1). None of the factors were ranked as 'unimportant' but respondents, overall, stated water repellency, breathability, fit, durability and wind resistance to be very important. Overall, the majority of respondents (82%) considered water repellency to be the most important factor, compared to the majority of respondents being indifferent to stain resistance (48%) and dirt and oil repellency (42%). Respondents were more concerned with performance factors than appearance. This highlights the primary consumer demand of a water repellent garment: protection from the rain and inclement conditions.

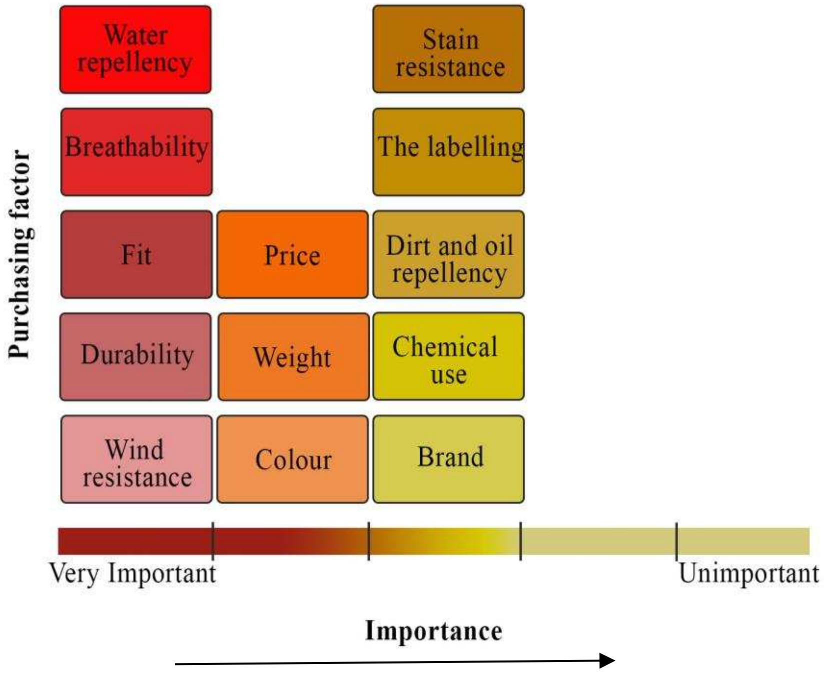


Figure 1. Respondents purchasing factors ranked by importance. No factors were ranked as unimportant. Water repellency was the main requirement for survey participants, ranked as 'very important' by 82% of respondents.

Respondents selected important factors they considered to be important in the 'environmentally friendly production' of a repellent garment. The main priorities of consumer environmental considerations in production were 'functionality to not be lessened' (310 respondents), product to be 'ethically sourced' (255 respondents), a 'repairable product' (252 respondents) and 'non-toxic chemicals' (242 respondents). Whilst this, again, highlights the importance of performance for the consumer, it does suggest that social and environmental impact are of concern to the consumer.

Table 2. Energy-dispersive x-ray spectroscopy analysis of all fabric samples; elemental content shown in weight percentage (%) of elements carbon (C), oxygen (O), fluorine (F), titanium (Ti), sulphur (S), silicone (Si), and chlorine (Cl).

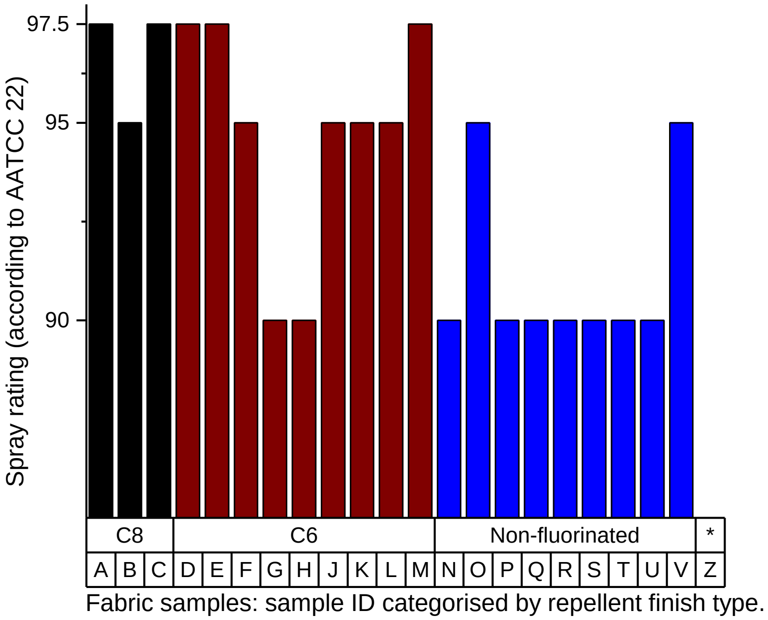
Alleged repellent finish type	**Sample label**	**C (%)**	**O (%)**	**F (%)**	**Ti (%)**	**S (%)**	**Si (%)**	**Cl (%)**
Long-chain (C8) PFAS	**A**	74.2±0.2	22.6±0.5	2.05±0.30	0.78±0.10	0.19±0.00	n.d.	0.23±0.01
	B	73.4±0.1	23.7±0.4	2.11±0.36	0.58±0.04	0.18±0.06	n.d.	n.d.
	C	59.9±0.1	38.9±0.1	n.d.*	1.21±0.01	n.d.	n.d.	n.d.
Shorter-chain (C6) PFAS	**D**	73.8±0.9	22.4±0.8	2.77±0.29	0.84±0.21	0.22±0.05	n.d.	n.d.
	E	75.0±0.2	22.7±0.1	1.38±0.04	0.35±0.05	0.16±0.00	0.12±0.00	0.34±0.05
	F	74.7±1.8	22.6±2.6	2.01±0.64	n.d.	0.22±0.03	0.28±0.08	0.19±0.05
	G	76.2±0.6	21.0±0.3	1.62±0.25	0.85±0.12	0.20±0.01	0.10±0.00	0.13±0.02
	H	77.8±0.4	21.1±0.1	0.74±0.00	0.20±0.01	0.17±0.01	0.14±0.00	0.23±0.02
	J	72.7±0.2	19.7±0.2	5.53±0.51	0.83±0.06	0.52±0.26	0.28±0.02	0.48±0.01
	K	75.0±0.1	24.1±0.1	n.d.	0.57±0.03	0.17±0.01	n.d.	0.19±0.02
	L	74.3±0.2	23.7±0.2	1.43±0.12	0.60±0.14	n.d.	n.d.	n.d.
	M	61.0±0.6	37.8±0.7	n.d.	1.16±0.01	n.d.	n.d.	n.d.
Non-F (fat-modified resin)	**N**	73.4±0.6	25.2±0.5	n.d.	1.48±0.05	n.d.	n.d.	n.d.

Non-F (specifics unknown)	**O**	72.6±0.4	26.8±0.4	n.d.	0.59±0.03	n.d.	n.d.	n.d.
Non-F (dendrimers with PU backbone)	**P**	72.8±0.2	25.9±0.1	n.d.	1.30±0.12	n.d.	n.d.	n.d.
	Q	72.4±1.1	25.6±1.0	n.d.	2.01±0.08	n.d.	n.d.	n.d.
	R	65.8±0.4	33.4±0.3	n.d.	0.73±0.08	n.d.	n.d.	n.d.
	S	60.2±0.4	39.4±0.5	n.d.	0.44±0.11	n.d.	n.d.	n.d.
	T	72.8±0.0	24.5±0.7	n.d.	2.73±0.80	n.d.	n.d.	n.d.
	U	72.1±0.3	26.4±0.4	n.d.	1.47±0.06	n.d.	n.d.	n.d.
Non-F (dendrimers)	**V**	58.5±0.5	39.5±0.6	n.d.	1.99±0.03	n.d.	n.d.	n.d.
Untreated	**Z**	75.24±0.3	24.5±0.3	n.d.	0.12±0.00	0.11±0.01	n.d.	n.d.

Detection limit to parts per thousand (1 x 10^{-3}).

Table 2 shows the semi-quantitative elemental composition of the repellent finish by EDX. Twelve samples were allegedly finished with either long-chain (C8) PFAS or shorter-chain (C6) PFAS repellent chemistry, however, no **F** content was detected on samples **C**, **K**, or **M**. On a few samples F was seen as an emerging peak, but was below the levels of detection from the baseline by the software. C, O, and Ti (originating from TiO_2 used for fabric whitening) were detected on all 'non-fluorinated' repellent finished fabric samples suggesting a hydrocarbon-based surface chemistry; no F nor Si was detected on any 'non-fluorinated' repellent finished fabrics. While EDX is a surface analysis technique it is thought that several elements of the fabric bulk were detected; Si detected in sample ***J*** is thought to be the laminate backing and in sample ***F*** it is thought to be the polymeric coating.

All fabric samples showed a good level of resistance to surface wetting, assigned a spray rating of 90 or above (Figure 2). Untreated fabric (Sample ***Z***) was completely wet by the water spray with movement of water by capillary action through the fibres (known as 'wicking') within the fabric structure and penetration of water through the fabric; Sample ***Z*** was assigned a spray rating of 0. Generally, long-chain (C8) and shorter-chain (C6) PFAS repellent fabric samples were rated either 95 or 97.5, with the exception of two shorter-chain (C6) examples (samples ***G*** and ***H***), which were rated 90; for sample ***H***, this may be due to the low fluorine content. In comparison, non-fluorinated repellent fabric samples were generally rated at 90, although two examples (samples ***O*** and ***V***) were rated 95. Directly comparing samples ***C***, ***M*** and ***V***, which have the same fibre and fabric type, the long-chain (C8) repellent sample was rated at 97.5, while the shorter-chain (C6) repellent sample and the non-fluorinated repellent sample had an average spray rating of 95.



Fabric samples: sample ID categorised by repellent finish type.
* Sample Z is a untreated fabric.

Figure 2. Spray rating of repellent outerwear fabric samples, measured according to AATCC 22-2014 (BS EN ISO 4920),[62,63] categorized by repellent chemistry type.

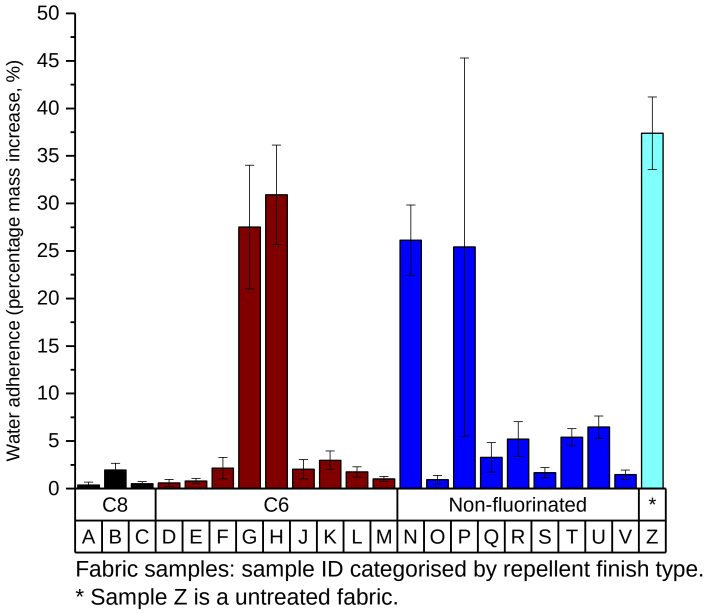


Figure 3. Water adherence measurements of the repellent outerwear fabric samples after spray test. Samples are categorized by repellent chemistry type. Error bars show standard deviation of 5 repetitions.

In terms of water adherence, long-chain (C8) repellent samples all had less than 2% mass increase post-testing with a low standard deviation (0.23-0.72%), suggesting a uniform, highly water-repellent finish (Figure 3). shorter-chain (C6) repellent samples with a spray rating at 97.5 showed low % mass increase, whilst the two examples rated at 90 had a significantly higher % mass increase (sample ***G*** 27.5% and sample ***H*** 30.9%) and greater standard deviation between measurements, suggesting a non-homogenous fabric finish. There was also variation in water adherence for non-fluorinated repellent samples; those assigned a spray rating of 95 had a low percentage mass increase; of those assigned a spray rating of 90, sample ***N*** and sample ***P*** had a relatively high % mass increase (26.1% and 25.4%, respectively) with significant standard deviation between measurements.

Long-chain (C8) repellent fabric sample ***A*** showed the greatest level of repellency to aqueous staining, testing standard BS ISO 23232[64], (Figure 4), with a rating of 6.5 out of 8; shorter-chain (C6) repellent fabric samples varied from 2.5-5.0, and non-fluorinated repellent samples varied from 2.5-4.0, which was expected as the efficacy of repellency to liquids of surface tensions different to water decreased with reduction in fluorocarbon chain length (or presence of fluorine). The untreated fabric sample ***Z*** showed no resistance to aqueous staining.

All non-fluorinated repellent fabric samples demonstrated no resistance to oil-based (hydrocarbon) liquids (Figure 5), which was expected, demonstrating the key differences between repellent functionality provided by PFAS chemistry and repellency provided by non-fluorinated alternative chemistries. The greatest level of repellency to hydrocarbon oil liquids was demonstrated by long-chain (C8) repellent fabric sample ***A***; variation between shorter-chain (C6) repellent fabric samples was seen, with ratings ranging from 1.0-2.5, and shorter-chain (C6) repellent fabric sample ***H*** demonstrated no repellency to hydrocarbon liquids, which may be associated with the absence of fluorine in elemental detection. As expected, untreated fabric ***Z*** demonstrated no resistance to oil-based (hydrocarbon) liquids.

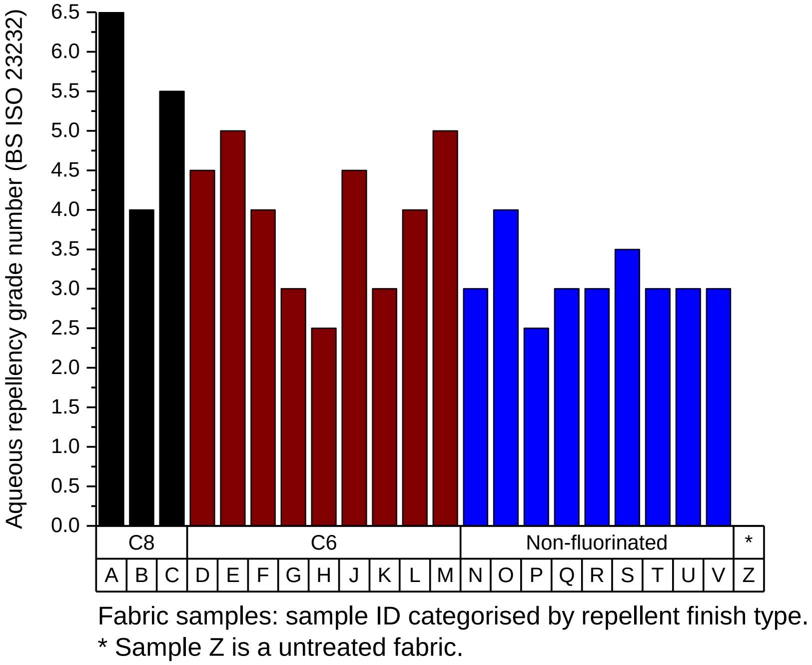


Figure 4. Repellency to aqueous liquids of the repellent outerwear fabric samples, according to BS ISO 23232:2009.[64] Higher grades signify a greater level of repellency. The samples are categorized by repellent chemistry type.

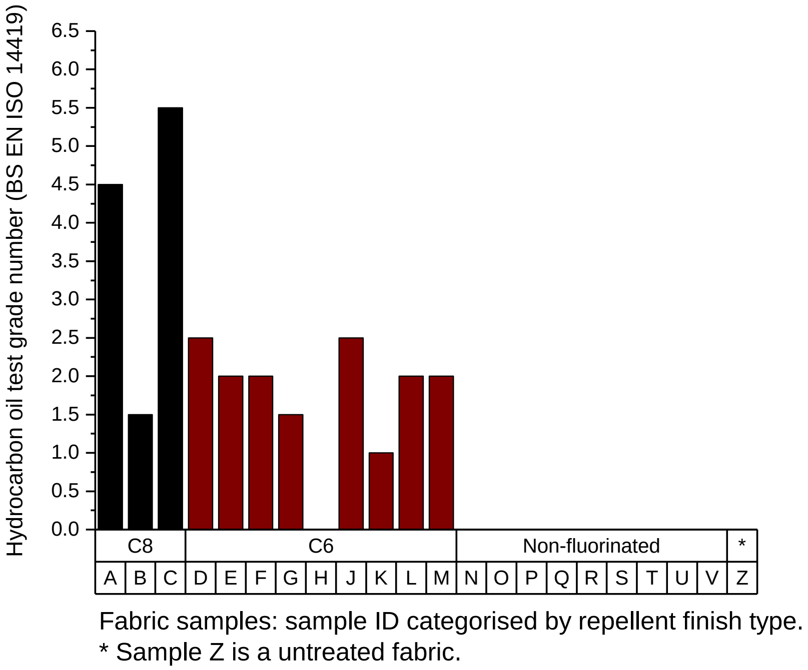


Figure 5. Repellency to hydrocarbons (oil repellency) of the repellent outerwear fabric samples, according to BS EN ISO 14419:2010.[65] Higher grades signify a greater level of repellency. The samples are categorized by repellent chemistry type.

4. Conclusions

This is the first study to report functionality specifically for repellent outerwear used by the outdoor apparel industry and a direct comparison of commercially available long-chain (C8) PFAS, shorter-chain (C6) PFAS and non-fluorinated repellent finishes. It was demonstrated that a DWR finishing treatment is required to provide a level of water repellency to woven apparel fabrics, exemplified by the untreated fabric showing no resistance to surface wetting by water, with associated high water adherence and absorption. EDX was employed as a semi-quantitative method to assess the type of repellent finish; analysis detected fluorine content in several of the long-chain (C8) and shorter-chain (C6) PFAS repellent fabric samples, potentially showing presence of PFASs. EDX analysis has vividly shown difference in elemental content between fluorinated and non-fluorinated repellent fabric samples, and demonstrated that all non-fluorinated repellent samples to be based on hydrocarbon chemistry. Information supplied with seven of the non-fluorinated finishes stated a hyper-branched hydrocarbon polymer surface chemistry, which is typical of dendrimer technology, wherein multiple hyper-branched (tree-like) alkyl end-groups provide the function of aqueous repellency, but have a lower repellence to oil staining (hydrocarbon test liquids) that have lower surface tension values than the critical surface tension provided by the finish. Fluorine was not detected on any non-fluorinated samples, highlighting sustainable substitution chemistries that may be adopted. Limits of detection, however, meant that definite connections between elemental composition and functionality could not be made.

Water repellency ratings were similar across the range of fabrics tested (excluding the untreated fabric); all demonstrating a high level of resistance to wetting, with only random sticking or minor wetting of the fabric face observed. Measurements showed that several non-fluorinated repellent fabric samples provide similar water repellency to long-chain (C8) or shorter-chain (C6) PFAS finished fabrics. Using standard test method BS ISO 23232, some resistance to aqueous-based staining by non-fluorinated repellent fabrics was observed, surface tension of each non-fluorinated fabric ranging between 46.0-33.0 dyn cm^{-1}; this can be associated with repellence of commonplace polar liquids such as wine, coffee and fruit juice. Standard test method BS EN ISO 14419 was used to evaluate the fabric's resistance to oil-based liquids corresponding to non-polar liquids used within daily life such as cooking oil, butter, petrol, and sun cream. Non-fluorinated repellent finished fabrics demonstrated no oil repellency, therefore no resistance to these commonplace liquids; and were clearly inferior in this property to long-chain (C8) PFAS finished fabrics, two of which demonstrated good oil-resistance (standard test method BS EN ISO 144419; sample ***A*** grade 4.5; sample ***C*** grade 5.5). Further investigation into the effect of laundering, abrasion and ageing of these fabrics would provide further insight into the durability of the water repellency, and whether oil repellency is necessary in practice for longevity of performance, and the authors are currently conducting research into this.

For a majority sector of outdoor apparel consumers, non-fluorinated chemistry can currently meet repellency requirements. As shown within the consumer survey study, the primary repellency function required in outdoor apparel is water repellency, and we would propose that the use of PFAS chemistry for such garments is therefore over-engineering, providing oil repellency that is in excess of consumer requirements. Consumers ranked stain resistance and dirt and oil repellency to be of lesser importance; evidencing that oil repellency is in excess of consumer requirements. Performance functionality was of greater concern than appearance; however staining may compromise repellent functionality and requires further investigation. From the consumer study, it can also be reasoned that outdoor consumers have an interest in environmental and social impact. Accordingly, significant environmental and toxicological benefits could be achieved by switching outdoor apparel to non-fluorinated DWR chemistry, such as hydrocarbon chemistry, and our further research into the effect of laundering, abrasion and ageing will help in confirming this.

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Supporting Information.

Table S.1. Characterization of repellent outerwear fabrics supplied to the study; PA, polyamide; PET, polyester.

Sample	Alleged repellent finish type	Weight (g m^{-2})	Thickness (mm)*	Fabric face structure	Fibre type	No of layers	Membrane or laminate
A	Long-chain PFAS (C8)	239.5	0.70	Plain weave	100% PA	2	-
B	Long-chain PFAS (C8)	146.8	0.31	Twill weave	100% PA	3	Membrane
C	Long-chain PFAS (C8)	165.4	0.22	Plain weave	100% PET	2	Laminate
D	Shorter-chain PFAS (C6)	135.9	0.22	Plain weave	100% PA	2	PU coating
E	Shorter-chain PFAS (C6)	133.6	0.35	Plain weave	PA/elastane	1	-
F	Shorter-chain PFAS (C6)	47.1	0.09	Plain weave	100% PA	1	Wax coating
G	Shorter-chain PFAS (C6)	53.4	0.05	Plain weave	100% PA	1	Acrylic coating
H	Shorter-chain PFAS (C6)	50.2	0.04	Plain weave	100% PA	1	Coating
J	Shorter-chain PFAS (C6)	77.2	0.12	Plain weave	100% PA	2	Laminate
K	Shorter-chain PFAS (C6)	121.8	0.26	Plain weave	100% PA	3	Membrane
L	Shorter-chain PFAS (C6)	193.3	0.38	Plain weave	96% PA/ 4% elastane	3	Laminate
M	Shorter-chain PFAS (C6)	167.4	0.24	Plain weave	100% PET	2	Laminate
N	Non-fluorinated (fat-modified resin)	136.9	0.21	Plain weave	100% PA	2	PU coating
O	Non-fluorinated (specifics unknown)	139.5	0.37	Plain weave	PA/elastane	1	-

P	Non-F (dendrimers with PU backbone)	54.6	0.09	Plain weave	100% PA	1	-
Q	Non-F (dendrimers with PU backbone)	121.5	0.25	Twill weave	100% PET	2	PU laminate
R	Non-F (dendrimers with PU backbone)	138.5	0.19	Plain weave	65% PA/ 35% PET	2	PU coating
S	Non-F (dendrimers with PU backbone)	198.0	0.63	Plain weave	100% PET	3	Laminate
T	Non-F (dendrimers with PU backbone)	222.5	0.54	Plain weave	100 % PA	3	Laminate
U	Non-F (dendrimers with PU backbone)	138.5	0.33	Plain weave	85% PA/ 15% elastane	1	
V	Non-F (dendrimers)	165.1	0.20	Plain weave	100% PET	2	Laminate
Z	Untreated	114.6	0.18	Plain weave	100% PA	1	-

*Thickness measured using a FAST-1 Compression Tester at two fixed loads: 2 g cm^{-2} and 100 g cm^{-2} over a 10 cm^2 area of the fabric.

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Table of Contents Graphic and Synopsis

PFAS chemistry for outdoor apparel is over-engineering; significant environmental and toxicological benefits can be achieved by switching to non-fluorinated finishes without significant reduction in water-repellency performance.