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Highly fluorinated chemicals in functional textiles can be replaced by re-evaluating liquid repellency and end-user requirements

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ABSTRACT

Ongoing regulation of, and concerns regarding, per- and polyfluoroalkyl substances (also popularly known as “highly fluorinated chemicals”), has driven the textile market to search for sustainable alternative chemistries that can provide similar liquid repellency to per- and polyfluoroalkyl substances in performance textiles. This paper aims to inform the potential substitution of fluorochemicals with more environmentally friendly durable water repellents, taking a case-by-case approach and evaluating protection needs for consumer outdoor clothing and medical protective clothing separately. Recently developed non-fluorinated durable water repellents, some based on green chemistry principles, were evaluated in an in-depth assessment for their functionality against fluorinated short-chain alternatives (with hydro-and oleophobic moieties of carbon chain length of six or less). Repellency towards water and non-polar liquids was evaluated with established standard test methods and by measuring the roll-off angle of liquid droplets with a novel sample holder setup. This improved method allowed an enhanced mechanistic understanding of the droplets' roll-off processes on woven textiles. The best non-fluorinated alternatives demonstrated high water repellency equal to fluorinated side-chain polymers with 'short' fluorinated carbon chains $\leq$6 carbons, and should be considered as suitable substitutes for consumer outdoor clothing. These results are supported by a survey of end-use requirements indicating water repellency and durability were the most important purchasing criteria. For polar liquids, with lower surface tensions, the repellency provided by non-fluorinated alternatives was clearly reduced, although they had a moderate repellency towards liquids with intermediate polarity (e.g. red wine or synthetic blood). Only fluorinated side-chain polymers with 'short' fluorinated carbon chains $\leq$6 carbons were seen to provide sufficient protection to polar liquids with very low surface tension (olive oil or gastric fluid). Since occupational protective clothing (*e.g.* medical clothing) often must provide protection against liquid of a wider range of polarities (*e.g.* in the case of medical clothing, to bodily fluids and protect the wearer from the transmission of diseases), current non-fluorinated DWRs do not provide sufficient liquid repellency. This implies that innovations in textile technology are still needed to substitute PFASs in some types of occupational protective clothing and other end uses where oil and stain repellency is essential.

1. Introduction

Approaches to substitute hazardous chemicals may benefit from a case-by-case evaluation of their functionality in products, since the need for specific material properties can differ widely between different end-user groups (Tickner et al., 2015). The textile and apparel industry is a primary example of this need, especially

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considering that this sector uses 25% of all chemicals produced globally and is a large contributor to environmental pollution (Niinimäki, 2015). Liquid repellency in textile products can range from an optional "nice-to-have" property in leisure rainwear to an essential protection needed in occupational protective clothing. An additional understanding of the relationship between functional chemistries, their properties, and why they are used in specific applications is needed to facilitate a faster, problem-solving process in alternative chemical assessments (Lavoie et al., 2010). Liquid repellent finishes find ubiquitous use in textiles for both consumer products and technical applications (Slade, 1997; Kotthoff et al., 2015). The textile sector often refers to these chemistries as durable water repellents (DWRs), but the leading market technology repels more than just water. Since their introduction in the 1950s (Ahlbrecht et al., 1957), the highest level of repellency for both oil and water resistance has been achieved using polymeric per- and polyfluoroalkyl substances (PFASs), which are also popularly known as "highly fluorinated chemicals".

Repellent properties are essential for protection against harmful liquids, for example within medical textiles and protective clothing in the oil and gas industry; they are also vital for health, safety and comfort of outdoor enthusiasts in inclement weather or extreme environmental conditions (Hill et al., 2017). End-user requirements differ depending on the specific hazards encountered and the environment of use (Fig. 1). Repellency in outdoor apparel is most commonly associated with outer rainwear, offering protection from the rain and outdoor environment, resisting the penetration of rain whilst allowing thermo-regulation of the body (Holme, 1993); a DWR with insufficient water repellent functionality increases the risk of hypothermia (Rengasamy, 2011). In medical textiles, exposure and transfer of blood and bodily fluids between patients and medical personnel during first-response care or within hospitals is of high concern, with the potential for transfer of bacteria and viruses (Virk et al., 2004; Mitchell et al., 2015). Repellency to blood and bodily fluids is essential for occupational protection and a repellent finish is needed for sufficient barrier properties, of which a high level of repellency is currently provided by fluorinated polymers (Midha et al., 2012).

PFASs for repellent textile modifications most commonly comprise non-fluorinated polymeric backbones with polyfluorinated side-chains that branch-off the main chain in comb-shaped structures (Fig. 2) (Fluorocouncil, 2018). Length and degree of fluorination, the chemical nature of the backbone and the flexibility of the spacers units (Wang et al., 2010; Saidi et al., 2005) (non-fluorinated segments) that connect the side chains to the main chain affect the performance characteristics of these side-chain fluorinated polymers (SFPs) (Castelvetro et al., 2002). The most effective liquid repellents are based on SFPs with long perfluoroalkyl side chains (L-SFPs) (with $C_nF_{2n+1}{-}SO_2{-}R$, $\mathbf{n} = 4{-}8$ (Audenaert et al., 1999); $C_nF_{2n+1}{-}C_2H_4{-}R$, $\mathbf{n} = 6{-}14$ (Götz et al., 2011)). The high level of hydrophobicity and oleophobicity provided by SFPs is due to the generation of low surface energy (Nishino et al., 1999) fibre surfaces by the orientation and packing of the terminal $-CF_3$ end groups within the side-chains (Rao and Baker, 1994; Kissa, 1996).

Significant concerns surround loss of PFAS by-products from textiles during production (Heydebreck et al., 2016), use (Gremmel et al., 2016), and end-of-life (Allred et al., 2015). As described in more detail by Holmquist et al. (2016), such PFAS derivatives can be residues from production, substances released by removal (*e.g.* abrasion), or compounds formed through degradation processes (Russell et al., 2008; Rankin et al., 2014). Terminal contaminants released by textiles that contain DWRs based on L-SFPs are long-chain perfluoroalkyl carboxylic acids (PFCAs) ($C_nF_{2n+1}COOH$; $n \geq 7$) and perfluoroalkane sulfonic acids (PFSAs) ($C_nF_{2n+1}SO_3H$; $n \geq 6$) (Knepper et al., 2014). These perfluoroalkyl acids (PFAAs) are criticized as being toxic (Lau, 2015), bioaccumulative (Conder et al., 2008; Ng and Hungerbühler, 2014), and extremely persistent (Sáez et al., 2008) in the environment and have been widely identified within wildlife and humans across the world (Krafft and Riess, 2015). Within the European Union (EU), perfluorooctanesulfonic acid (PFOS) is regulated to detectable levels of 1 $\mu g\, m^{-2}$ in textile fabrics (European Union, 2006). While the limits for PFOA are currently under discussion in the EU, Norway already set their limit to 1 $\mu g\, m^{-2}$ in textile applications (Bureau Veritas, 2014). Bioaccumulation of PFAAs within humans and in the food chain in combination with their toxicity are of primary concern (Hekster et al., 2003; Wang et al., 2013).

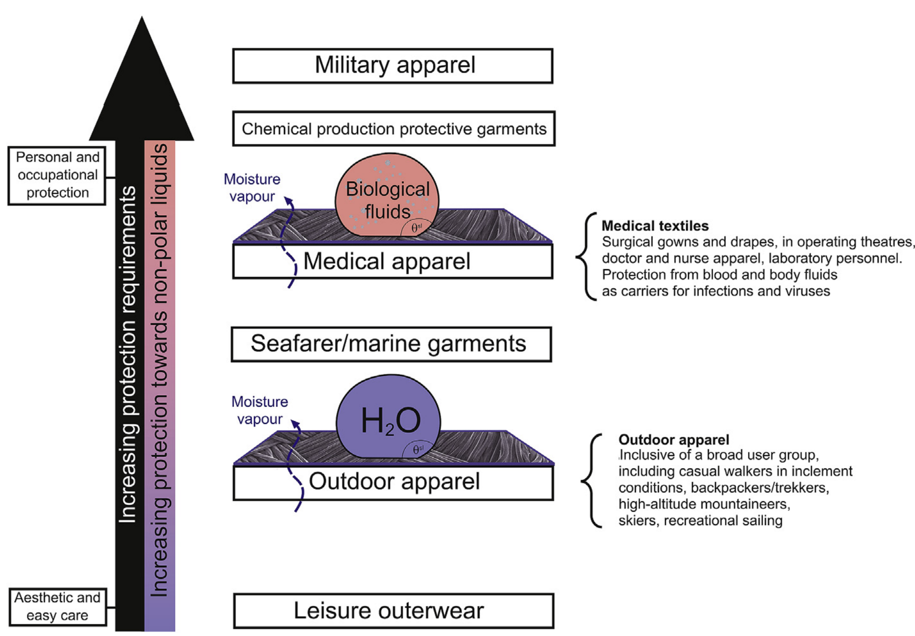

Fig. 1. Repellency performance segmented by requirements by end-use.

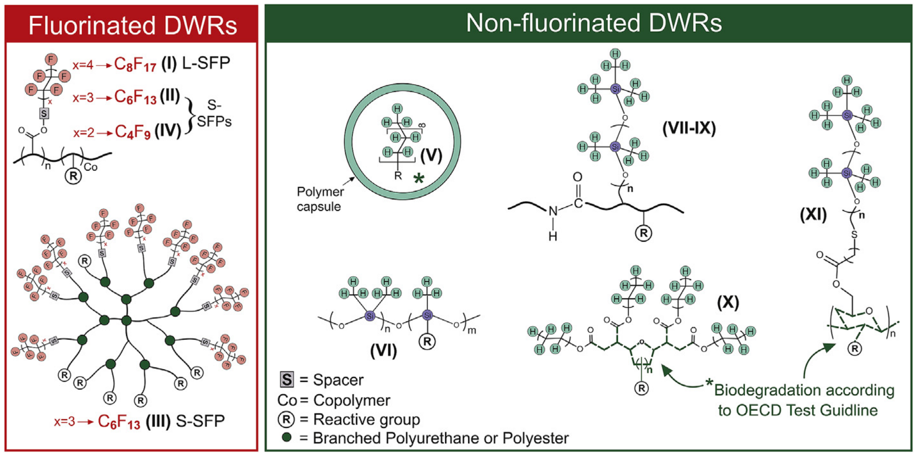

Fig. 2. Simplified structures of fluorinated and non-fluorinated DWRs used in this study. Roman numerals correspond to compounds detailed in Table S1 in the Supplementary Information.

The major challenge is eliminating long-chain PFASs and maintaining the required functionality in repellent textiles. Substitution to 'short-chain' side-chain fluorinated polymers (S-SFPs) with shorter fully fluorinated chain lengths as C6 or C4 analogues (Fig. 2) has occurred, but there is increasing concern on the persistency (Wang et al., 2013; Gomis et al., 2015) and toxicology (Gomis et al., 2018) of these short-chain analogues. The extreme persistency of short-chain PFAAs means that the release of these compounds from textiles (and other sources) could become a 'Planetary Boundary Threat' (Persson et al., 2013) since all future effects are not currently known and their release to *e.g.* ground water is poorly reversible (Cousins et al., 2016). A variety of new non-fluorinated DWR alternatives have been developed to create repellent textile surfaces (Fig. 2) (Holmquist et al., 2016). Non-fluorinated DWRs consist of different polymer architecture including linear polyurethanes (Williams, 2017), hyper-branched polymers (Hu et al., 2008) and nanoparticles (Namligoz et al., 2009). The functional moieties in terms of liquid repellency consist of either saturated alkyl chains or polydimethylsiloxane (PDMS) chemistry.

Some manufacturers have developed and are now producing non-fluorinated, biodegradable DWRs as greener alternatives to persistent PFAS chemistry (Achroma, 2014; Chemours, 2015; OrganoClick, 2018). These biodegradable DWRs are beginning to find application in commercial apparel, and compounds **X** and **XI** (Fig. 2) evaluated herein are examples of such technology. However, it should not be assumed that just because a DWR is biodegradable that the compounds formed as a result of that biodegradation do themselves not pose an environmental and/or toxicity issue. Each biodegradable DWR should be investigated in this regard to ascertain if biodegradation results in products of the lowest possible impact. As exemplified herein, **X** is a fatty acid-modified saccharide, hence, its biodegradation products would be fatty acids and simple sugars, which are likely to be relatively innocuous; **XI** is a silicone-modified saccharide, hence, its biodegradation products would include Si-containing moieties (as well as be fatty acids and simple sugars), which although are not inherently hazardous should still be thoroughly evaluated.

Hill et al. (2017) and Schellenberger et al. (2018) evaluated the properties of non-fluorinated DWR alternatives and demonstrated suitable water repellency and durability, but low oil repellency. This lack of oleophobicity makes the broad end-use application of non-fluorinated DWRs in textiles still unclear. One resolution to the environmental issues of SFP DWRs is to re-evaluate the requirements of repellent textiles for different end-user groups and their protection needs. Segmenting the textile sectors in terms of liquid repellency, this paper sets out to outline the different requirements for outdoor consumers and that of occupational medical apparel. This evaluation of the liquid repellency function based on end-user application provides clearer indications on the use of non-fluorinated DWRs and sectors in which substitution of PFASs is possible.

2. Experimental

2.1. Materials

An investigation was undertaken to evaluate repellency provided by current fluorinated short-chain and non-fluorinated alternative DWR polymers. These different DWRs and their general structures are shown in Fig. 2. Detailed information about formulations of these DWRs and their curing conditions can be found in Table S1 in the Supplementary Information. In previous literature, non-fluorinated DWRs have been observed to have inadequate oil repellency for textiles (Namligoz et al., 2009; Hill et al., 2017) so the research herein focused on new DWRs specified to be repellent towards liquid stains (as stated on technical data sheets provided by suppliers). Black 100% polyethylene terephthalate (PET) fabric, $120 \pm 5\ g\ m^{-2}$ (threads per cm: warp 60 ± 2; weft 38 ± 1) was provided by FOV AB (Sweden) as a representative fabric used within performance outdoor clothing and medical protective clothing. Different liquids with a range of polarities and surface tensions (γ_{LG}) applicable to the end-use user groups were chosen for simulating 'stains'. Whilst staining covers a broad category of soils, from polar to non-polar liquids, this work specifically concentrated on liquids with low viscosity since they have the highest potential of penetration through textile fabrics. The surface tensions of different liquids were measured first (Fig. S1 in the Supplementary Information) and some liquids that showed a range of different γ_{LG}s were chosen for the further experimental work. For consumer outdoor apparel end-use: laboratory grade distilled water ($\gamma_{LG} = 73.2 \pm 0.3\ mN\ m^{-1}$); 100% fruit orange juice ($\gamma_{LG} = 50.5 \pm 0.7\ mN\ m^{-1}$) was supplied by Bravo; 13% ABV red wine ($\gamma_{LG} = 48.1 \pm 0.7\ mN\ m^{-1}$) was supplied by Prime Wine Sweden AB; and olive oil ($\gamma_{LG} = 34.6 \pm 0.1\ mN\ m^{-1}$) was supplied by Zeta. For medical apparel end-use: synthetic blood ($\gamma_{LG} = 50.2 \pm 0.1\ mN\ m^{-1}$) was supplied by Tritech; Noscapine cough medicine suspension ($\gamma_{LG} = 38.1 \pm 0.4\ mN\ m^{-1}$) was supplied by McNeil Consumer Healthcare; and fasted state simulating gastric fluid ($\gamma_{LG} = 28.8 \pm 0.9\,mN\,m^{-1}$) was formulated according to literature, comprising HCl (0.05 N), SLS (8.67 mM) and NaCl (0.2%) in aqueous solution (Aburub et al., 2008). All general chemicals were supplied by Millipore-Sigma.

2.2. Application of DWR formulations to fabrics

1 L of each DWR formulation was stirred in a 2 L glass beaker for 5 min at 400 rpm prior to application to ensure good homogeneity. Stability of the formulations was assessed by visual inspection prior to application. Water-based DWR formulations were applied in a laboratory non-continuous padding process (dip coating). Fabric samples (35 cm × 40 cm) were immersed in a 2 L glass beaker, containing 1 L of DWR formulation, for 30 s with continuous stirring. Excess liquid was removed using a non-continuous finishing foulard between two rollers (BVHP, Roaches, England) with two runs at 2.9 rpm and a nip pressure of 3.7 bar. The fabrics were dried followed by curing in an oven (Discontinuous Labdryer; type LTE; Mathis, Switzerland) to promote the crosslinking reaction of the DWR-polymer. Both fluorinated and non-fluorinated DWR emulsions were applied with curing temperatures specific to formulation, as recommended by suppliers (Table S1 in the Supplementary Information).

2.3. Determination of water repellency

Surface wetting of the coated fabrics by water was evaluated using two standard test methods, the ISO 4920:2012 spray test (International Standards Organisation, 2012), and the ISO 9865:1991 Bundesmann rain-shower test (International Standards Organisation, 2016); both tests evaluate resistance of the fabrics to surface wetting by simulating a rain shower. The spray test evaluates fabrics ($180\,mm^2$) held at a 45° angle in an embroidery hoop (155 mm) under a specified spray head (water volume of 250 mL) for 25–30 s; the sample fabric was tapped smartly twice before assessment. The Bundesmann method tests the fabric under a rain shower head (300 nozzles; 140 mm in diameter) at a drop height of 1500 mm, with the shower dropping onto four cups with rotating elements beneath the fabrics, for 10 min; this experimental setup simulates fabrics being rubbed (*e.g.* body motion); the sample fabric was centrifuged (700 rpm, 15 s) before assessment. Water absorption (A) was calculated, relative to fabric mass, according to equation (1):

$$A(\%) = \frac{m_2 - m_1}{m_1} 100 \tag{1}$$

Where m_1 is the mass of the sample before the water repellency test and m_2 is the mass after testing. Mean (ISO 4920:2012, n = 3; ISO 9865:1991, n = 4) values of A (%) was calculated for each fabric type. In the ISO 9865:1991 Bundesmann rain-shower test, water penetrating through the fabric samples was collected within cups below the sample and the volume measured.

2.4. Evaluation of static stain repellency and transmission

The repellency of DWR treated fabrics to non-polar liquids was first evaluated using ISO 14419 :2010 (International Standards Organisation, 2010) at 20 ± 2 °C and 65 ± 2% Relative humidity (RH). 30 μL of each of eight standard hydrocarbon-based liquids with a range of surface tensions (white mineral oil, $31.5\,mN \cdot m^{-1}$; 65:35 white mineral oil:*n*-hexadecane, $29.6\,mN \cdot m^{-1}$; *n*-hexadecane, $27.3\,mN \cdot m^{-1}$; *n*-tetradecane, $26.4\,mN \cdot m^{-1}$; *n*-dodecane, $24.7\,mN \cdot m^{-1}$; *n*-decane, $23.5\,mN \cdot m^{-1}$; *n*-octane, $21.4\,mN \cdot m^{-1}$; *n*-heptane, $19.8\,mN \cdot m^{-1}$) were individually placed as droplets onto the fabrics and the wetting behaviour visually judged after 30 ± 2 s. Fabrics were not tilted and remained static without movement during testing. Wetting behaviour was categorised according to different cases (Fig. S6a in the Supplementary Information), ranging from optimal drop shape with high contact angle (Case 1) to complete wetting of the fabric surface (wet-out) (Case 4). Oil droplets pass when they show a clear droplet shape (Case 1 and 2) and fail when liquid penetration into the fabrics occurs (Case 3 and 4). Any liquid penetration through the fabric was judged visually by inspection of the backside of the fabric sample. The static repellency of selected stains relevant to consumer outdoor and medical textiles were evaluated using the same method and visual rating scale used in ISO 14419:2010 (International Standards Organisation, 2010).

2.5. Liquid surface tensions

Liquid surface tensions (γ_{LG}) were measured by drop shape analysis (DSA-30, Kruss GmbH, Germany) of pendant droplets using the Young-Laplace equation (Equation (2)), which relates the Laplace pressure (pressure difference between the inside and the outside of a curved surface) across an interface with the curvature of the interface and the the interfacial tension. The equation (2) describes a normal stress balance for static fluids meeting at an interface, where the interface is treated as a surface (zero thickness):

$$\Delta p = \gamma_{LG}\left(\frac{1}{R_2} + \frac{1}{R_1}\right) \tag{2}$$

and where Δp is the pressure difference across the fluid interface and R_1 and R_2 are the principal radii of curvature of the pendant droplet (Fig. S1 in Supplementary Information).

2.6. Roll-off angle

The roll-off angle of water droplets (30 μL; manual dosage with Eppendorf pipette) was measured using optical drop-shape analysis (DSA-30, Kruss GmbH, Germany) and a tilting table device combined with a novel fabric holder construction (Fig. S2 in Supplementary Information). The fabric holder consisted of three aluminum elements creating a ~15 mm wide plateau onto which the fabric specimen is clamped, resulting in a ratio of drop-baseline: fabric-plateau ~1:5. The construction of this narrow platform allowed the fabric to be fixed flat and horizontal for droplet placement. With this experimental setup, precise analysis of the liquid roll-off behaviour could be observed with minimal background interference of the fabric surface structure. Video files (n = 10) of the droplet roll-off (with tilting speed of 60° min^{-1} and tilting angles of $\alpha_{tilt} = 0°–90°$) were recorded. The recorded video files were analysed with manual baseline detection using a polynomial fitting method (tangent 2) for asymmetrical droplet shapes. The roll-off angle was calculated by observing the movement of the receding contact point (CP_{rec}) of the liquid droplet. The position of the CP_{rec} was plotted against the tilt resulting in two functions that can be described with linear regressions with: Function 1 where change in CP_{rec} (ΔCP_{rec}) ~0 (no movement; changes in ΔCP is caused by the movement of the fabric holder through the image); and Function 2 where ΔCP_{rec} = high (fast movement of the droplet) (Fig. S3 in Supplementary Information). The intersection of these two functions was calculated as the roll-off angle estimate. Selected liquids relevant to consumer outdoor and medical textiles were also evaluated using the same experimental set up. Due to high adhesion, liquid interaction was assessed qualitatively.

2.7. Determining end-user requirements

To establish the requirements of outdoor apparel consumers, a thirteen-question online survey was conducted (Bristol surveys in affiliation with the University of Leeds), between 5th and 22nd July 2014, with a total of 300 respondents. The questions included demographic descriptors, indicators of the respondents' participation in outdoor activities, inquiry on the preferences in purchasing decisions and questions aimed to understand the consumer awareness of current industry criticism. The research aimed to define the consumer requirement for outdoor apparel, and therefore whether DWR alternatives are sufficient. It was believed that the group of consumers targeted would have some knowledge of the criticism through brand marketing, retailers or Greenpeace literature. The survey was initially promoted to two Facebook pages concerned with outdoor activities, with 547 members and 10,752 members respectively. Following this, 50 randomly selected Ramblers' groups were contacted by email and asked to circulate the survey to their members. Nine email responses were received from these groups confirming circulation. The survey was also posted within popular outdoor focused Internet forums. Each age range had at least 15 respondents, with most female respondents in the range 61–65 years and most male respondents in the range 21–25 years; the majority of respondents were male (70%). Respondents gained access to the survey through a URL address. Completion was voluntary and respondents could withdraw at any time. A detailed report about healthcare for protection against microorganisms in blood and body fluids provided by the Centers for Disease Control and Prevention (2014) was considered as a basis for repellency needs in occupational medical textiles. Full details of the questions asked in the consumer survey are given in Supplementary Information (section S1.4).

3. Results and discussion

3.1. Determination of water repellency

Fig. 3 summarises all water repellency measurements that were conducted for the PET fabrics modified with different DWR chemistries; full details of experimental results can be seen in Table S2 in Supplementary Information. By using two industrial test methods to simulate a rain shower (Spray test and Bundesmann), and by measuring the roll-off angle, differences were observed between the water repellency provided by fluorinated and non-fluorinated DWR chemistries. Roll-off angle of single water drops provided valuable data to compare DWRs, and strong correlation between water absorption and roll-off angle measurements was observed (Bundesmann $R^2 = 0.93$; Spray test $R^2 = 0.86$; Fig. S4 in Supplementary Information).

Comparing all DWR chemistries tested, fluorinated long-chain, C8 SFPs (**I**) had the lowest water absorption (~1% wt. increase) and roll-off angles ($\alpha_{roll\text{-}off}$ ~11°); this explains their extensive use in textile applications prior to the phase-out. This $\alpha_{roll\text{-}off}$ is close to the superhydrophobic state (<10°) (Lafuma and Quere, 2003; Deng et al., 2012) where droplets have a very low adhesion and are effectively repelled; the low 'stickiness' is likely to be a result of a low contact area between water droplets and the textile weave, which is referred to as the "Cassie-Baxter state" (Cassie and Baxter, 1944). Fabrics treated with short-chain C6 (**II** and **III**) and C4 (**IV**) SFPs also had low water roll-off angles and low water absorption, albeit slightly higher than long chain SFPs ($\alpha_{roll\text{-}off} = 16.8°$(C6) and ~17.4°(C4)). Studies have shown that shorter perfluoroalkyl chains (S-SFPs) result in non-optimal surface orientation of the repellent moieties on fibre surfaces (Honda et al., 2005; Wang et al., 2010), which accounts for this slightly decreased repellency. There were no signs of water penetration through any SFP fabrics, indicating that water remains on the outer surface without overcoming the DWR and wetting the fabric bulk.

The non-fluorinated treatments (**V**) and (**X**) demonstrated comparable water repellency to short-chain SPFs, both having low water absorption and low roll-off angle ($\alpha_{roll\text{-}off} = 23°$(**V**) and 22°(**X**)); neither fabric showed water penetration during testing. However, all other non-fluorinated DWRs demonstrated lower water repellency. Samples **VII** to **IX**, based on silicon modified polyurethanes, had very high water absorption values (12–24 wt%) and high (33–70°) or no roll-off angle, and also showed greater penetration of water through the fabrics, wetting through the fabric bulk. This has the potential to cause significant cooling to the wearer by wetting through the clothing system and inhibiting thermal insulation. Observing roll-off behaviour of single water droplets provides a further explanation on water repellency and the differences between DWR formulations. Fig. 4 provides a demonstration of the change in droplet movement when the textile surface is tilted.

All water droplets first undergo a period with no movement (ΔCP_{rec} is low and just caused by the relative movement of the fabric holder through the picture) followed by sudden roll-off of water droplets with increasing surface tilt. At this point, the drops

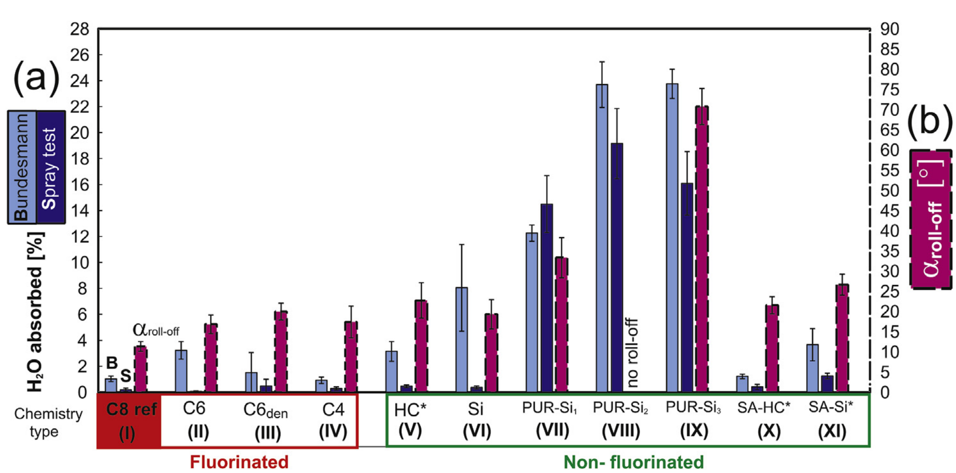

Fig. 3. Water repellency of PET fabrics treated fluorinated and non-fluorinated DWRs: (a) water absorption with the ISO 9865:1991 Bundesmann rain-shower test and the ISO 4920:2012 spray test; (b) water roll-off angle.

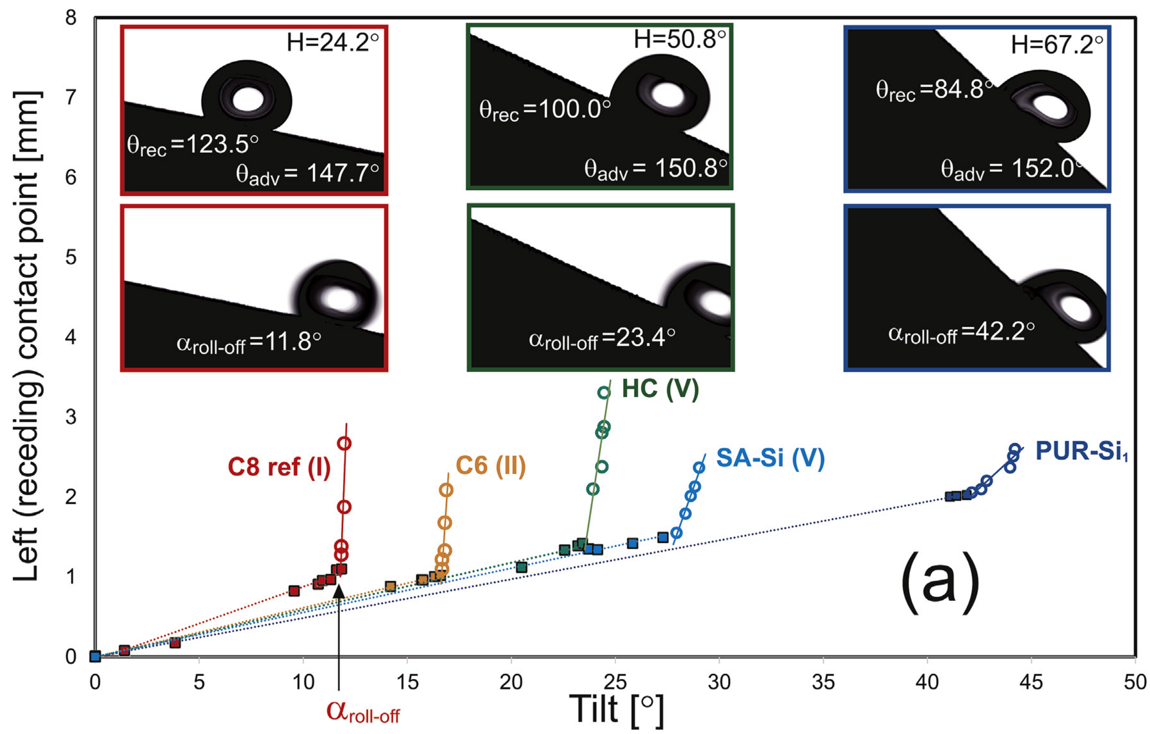

Fig. 4. Schematic representation of a single water drop on a tilted textile surface and examples of roll-off angle estimation for PET fabrics with different DWR chemistries.

overcome the fabric's 'stickiness' and move down the fabric due to their weight (~0.03 g for 30 μL drops). This process transports the liquids across the fabric surface; a process that aids understanding of surface mechanisms for liquid repellency in textiles. For the best DWR formulation, droplet roll off occurred at low tilting angles (C8-SFP in Fig. 3 with $\alpha_{roll-off} = 11°$) while other DWRs modifications had much higher roll-off angles (PUR-Si$_1$ in Fig. 3 with $\alpha_{roll-off} = 33°$). For formulation **VII** (PUR-Si$_1$) the water droplets remained on the fabric surface after tilting the fabric into a vertical orientation ($\alpha = 90°$). DWRs with higher roll-off angles also had a lower roll-off velocity (lower slope of the regressions after roll-off). All observations showed that several non-fluorinated DWR formulations increase the fabric's 'stickiness'.

3.2. Evaluation of stain repellency

Liquids with lower polarities and consequently lower surface tensions have in general higher droplet-surface interaction and it is therefore more difficult to make textiles stain repellent. The increased adhesion of stain droplets (Fig. 5b1) caused changes in the drop shape, in comparison with the fast roll-off behaviour observed with water droplets (Fig. 5a2). It was noted that even for the C8-SFP (**I**), the reference material, the roll-off mobility decreased for liquid stains with low surface tensions and droplets were observed to roll slowly along the textile surface. This greater adhesion is due to the lower surface tensions of these stain liquids compared to water. Due to the higher proportion of non-polar molecules in the liquid (Slade, 1997), the surface tension is reduced as a result of lower attractions of molecules within stain droplets (Fig. 5 a1 compared to 5 b1) (Fowkes, 1964). The lower surface tension of liquid stains causes: (i) a higher affinity of the liquids to the hydrophobic fibre surface, and (ii) increases the tendency for liquids to migrate into the interstices of the fabric structure (a more detailed characterization of the surface topography of weave is provided in Fig. S5 in the Supplementary Information).

Table 1 shows the roll-off behaviour of different stains that were observed for fabrics with fluorinated DWRs and the best performing non-fluorinated DWR (**X**). By observing the change of drop shape during tilting, the roll-off behaviour of stains could be categorised into four specific scenarios (Fig. 6). Depending on the DWR, some stains showed a fast water-like roll-off (scenario A), while others showed a slower “slip-off” and left residue liquid in form of small drops (scenario B), or liquid films (scenario C) behind; this happened when the droplets deformed into an elongated shape due to the greater adhesion and droplets showed strong decrease in thickness towards the receding contact angle. This resulted in liquid residue remaining on the surface when the adhesion between the liquid and the surface was greater that the downhill force dragging the droplets down the tilted fabric (acting forces on tilted liquid droplets are illustrated in Fig. S5b in the Supplementary Information). Several stains with intermediate surface tensions (*e.g.* red wine and cough medicine with intermediate surface tensions) did not demonstrate roll-off at a vertical tilt of 90° (scenario D). Where no droplet movement was seen, there was increased ahesion between the liquid-weave interface and the surface tension hindered the droplets to get dragged down by their weight. This was enhanced when the liquid had a high viscosity (e.g. for example cough medicine).

It was found that only fabrics with a fluorinated DWR demonstrated a fast roll-off (scenario A; Fig. 6) for any stains, and this was observed for liquids with high and intermediate surface tensions, while low polarity liquids demonstrated greater adhesion (scenarios B-D; Fig. 6). The roll-off mobility also decreased for shorter chain length of perfluoroalkyl side chains ($C_8F_{17} > C_6F_{13} > C_4F_9$), and the C_4F_9 based SFP had a clearly reduced dynamic stain repellency. None of the stains showed a roll-off behaviour similar to water. The non-fluorinated DWR (**X**) had high water repellency, but lower stain repellency when roll-off behaviour was observed with respect to the fluorinated DWRs, however, it did present evidence of slower

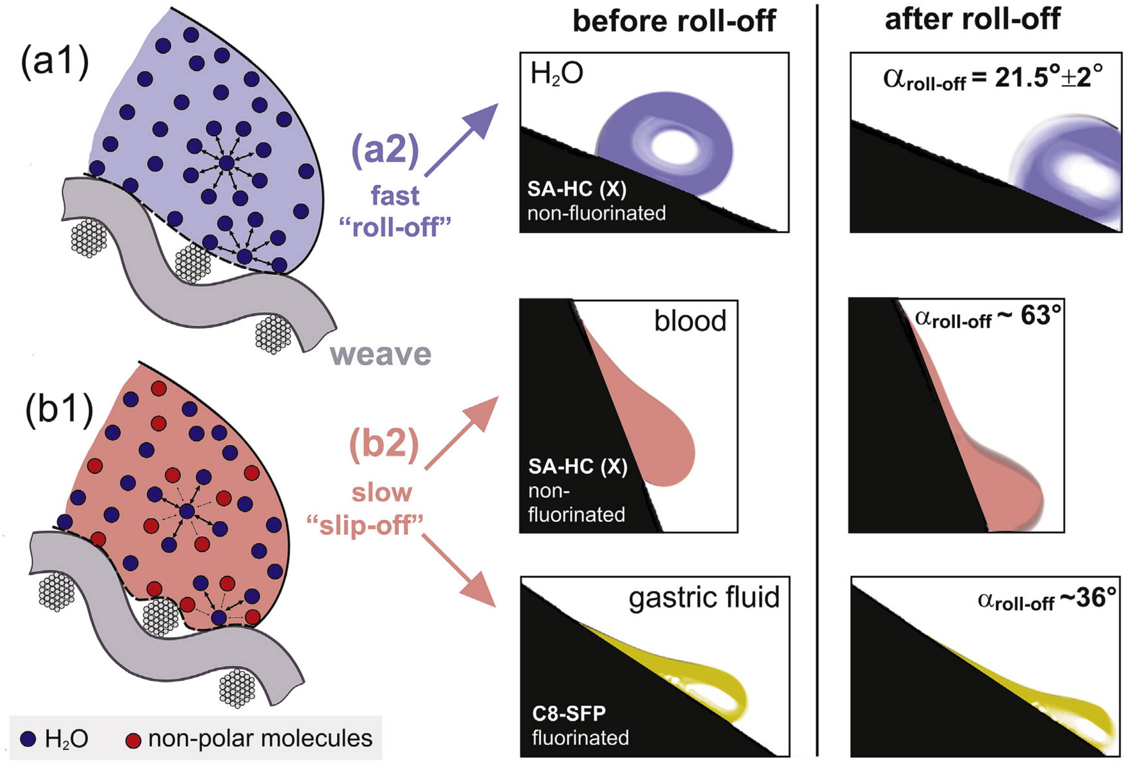

Fig. 5. Examples of different droplet roll-off behaviours on DWR treated textile: (a1) schematic representation of liquid with high surface tension and low droplet-surface interactions resulting in (a2) a fast droplet roll-off; (b1) schematic representation of liquid with reduced surface tension that increases droplet-surface interaction and results in (b2) a reduced droplet mobility and slow roll-off.

Table 1
Roll-off behaviour for liquid stains relevant for consumer outdoor clothing and medical textiles for different DWR treatments of the PET woven fabric. Roll-off angles are shown numerically; corresponding roll-off scenario is given in parentheses (see Fig. 6).

DWR treatment	Consumer liquids (γ_{LG}, mN m^{-1})			Medical liquids (γ_{LG}, mN m^{-1})		
	Orange juice (50.5 ± 0.7)	Red wine (48.1 ± 0.7)	Olive oil (34.6 ± 0.1)	Synthetic blood (50.2 ± 0.7)	Cough medicine (38.1 ± 0.4)	Gastric fluid (28.8 ± 0.9)
C8 (**I**)	22° (A)	45° (A)	41° (C)	36° (A)	39° (B)	36° (C)
C6 (**II**)	23° (A)	55° (B)	46° (C)	41° (A)	41° (B)	38° (C)
C4 (**IV**)	43° (A)	None (D)	53° (C)	63° (B)	44° (C)	32° (C)
SA-HC (**X**)	60° (B)	None (D)	48° (C)	63° (B)	None (D)	40° (C)

"slip-off" (scenarios B and C) for many stains evaluated. This suggests that the DWR could provide some stain repellency, albeit not as efficiently as fluorinated DWRs.

3.3. Static oil and stain repellency and transmission

It was observed that only fabrics with fluorinated DWRs demonstrated significant oil repellency (Table 2), in agreement with previous studies (Namligoz et al., 2009; Hill et al., 2017); on fabrics with non-fluorinated DWRs oils penetrated through to the fabric bulk. Evaluation of static stain repellency demonstrated similar observations for 'stains' with low surface tensions. The visual judgement of the border cases (Fig. S6a in Supplementary Information) showed that none of the non-fluorinated DWRs provided sufficient resistance towards non-polar liquids, for example olive oil and gastric fluid, with the liquids wetting the fabric surface. Only the fluorinated S-SFPs demonstrated repellency to stains with low polarities. Although non-fluorinated DWRs showed no repellency towards stains with very low polarity, they were sufficient in the static repellency of stains with high and intermediate surface tension, such as orange juice, red wine or synthetic blood. These liquids formed droplets with high contact angles and did not penetrate through the fabric bulk (Fig. S6b and Table S3 in Supplementary Information).

3.4. Survey data

Data from the consumer survey of outdoor apparel users highlighted the particular needs of this end-use market; 84% of the respondents participated in outdoor pursuits at least once a week, mostly hill walking and climbing, and 15% of respondents at least once or more a month. From the consumer perspective, fit, price, water resistance and durability were the most important factors when purchasing a new outerwear garment; stain resistance was ranked least important (Fig. 7). Only 67% of the respondents who participated daily or more than three times a week in activities thought it was necessary for clothing to be fully waterproof. Respondents stated that their clothing needs to be resistant to water, but 57% of respondents did not consider repellency to oil, soil or dirt essential to the garment. Many respondents reasoned that they were more concerned with performance than appearance. One response commented that stain repellency is "not crucial to

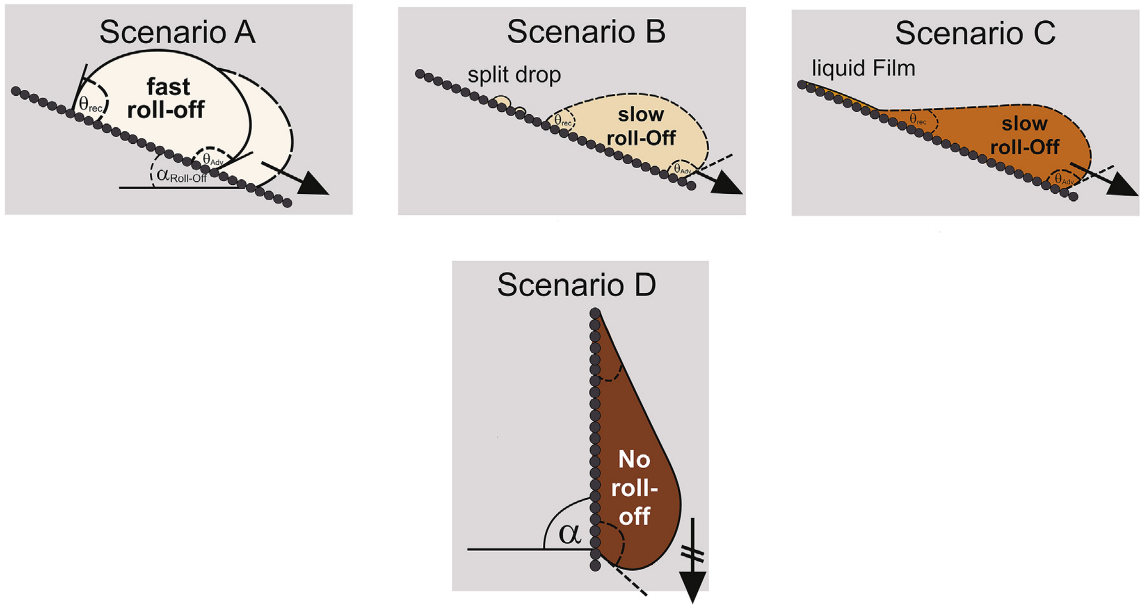

Fig. 6. A schematic representation of different roll-off scenarios that were for liquid stains relevant for consumer outdoor clothing and medical textiles.

Table 2
Static oil repellency of PET-fabrics with different DWR formulations tested according to ISO 14419:2010.

No.	Ref Code	Oil repellency rating
I	C8-ref	5.5 ± 0.5
II	C6	3.8 ± 0.5
III	$C6_{den}$	3.5 ± 0.5
IV	C4	2.5 ± 0.5
V	HC	0
VI	Si	0
VII	PUR-Si_1	0
VIII	PUR-Si_2	0
IX	PUR-Si_3	0
X	SA-HC	0
XI	SA-Si	0

preventing hypothermia on the mountains", highlighting primary consumer requirements. Overall, respondents stated they had either not considered repellency to oil, soil or dirt or did not expect to be exposed to these substances: "I don't get oily when walking". The ability to wash off oil, soil and dirt was commonly reasoned as why repellency to these substances was not necessary. Respondents to the research survey did not consider repellency to oils as essential. However, water repellency was highlighted as being very important for physiological comfort; keeping dry was stressed to be important. In the survey only 5.7% of respondents were fully aware of the criticism concerning PFASs use, while 59.3% of respondents were completely unaware of the criticism. 33% of the respondents who had an awareness stated that their knowledge had come from press articles, blogs, magazines and online forums. 61.6% of respondents strongly agreed or agreed that there was a lack of transparency on the chemicals that brands use and the issues affecting the chemical use.

4. Conclusions

This study of repellent textile functionality combined with end-user requirements has highlighted the opportunities and limitations for substitution of PFASs in performance textiles. For outdoor apparel, water repellency and durability of the textiles were rated by consumers as more important than stain repellency; keeping the wearer dry and warm is a textile function that is directly related to water absorption and penetration through the fabric.

In-depth assessment of water repellency showed that some non-fluorinated, biodegradable DWRs give comparable performance to C6- and C4-SFPs, and only slightly lower performance compared to long-chain C8-SFPs. Consumers indicated that stain repellency was not a priority in outdoor apparel, however, non-fluorinated DWRs were found to have some resistance towards stains with high and intermediate surface tensions (e.g. orange juice and red wine). Non-fluorinated DWRs demonstrated no repellency to stains with low surface tensions (such as olive oil) from the stains selected to be relevant to the outdoor and medical sectors.

Comparable trends were observed in the liquid repellency requirements for medical protective clothing. Non-fluorinated DWRs showed some resistance to synthetic blood (high surface tension) and cough medicine (medium surface tension), but none for gastric fluid (low surface tension). Short-chain C4- and C6-SFPs did demonstrate sufficient repellency to "medical" stains with low surface tensions. Decreasing stain repellency was observed with decreasing chain length of the fluorinated chains in side-chain fluorinated DWRs indicating that an increased concentration of the DWRs based on 'short-chain' SPFs might need to be applied to fulfil protection requirements. Repellency to bodily fluids is an essential requirement to avoid the transmission of diseases, but non-fluorinated DWRs evaluated within this study did not show sufficient functionality to be used in this end-user sector. Decreasing stain repellency was observed with decreasing chain length of the fluorinated chains in side-chain fluorinated DWR indicating that an increased concentration of the DWRs based on 'short-chain' SFPs might need to be applied to fulfil protection requirements.

Decreased liquid repellency of non-fluorinated DWRs is more of an issue for occupational protective clothing (medical protective clothing, military uniforms, firefighting garments, protective clothing used in the oil and gas industry, *etc.*), which need repellency towards non-polar stains as part of hazard management. Therefore, substitution of PFAS-based DWRs cannot be considered as an option at this time; these occupational textiles need to be

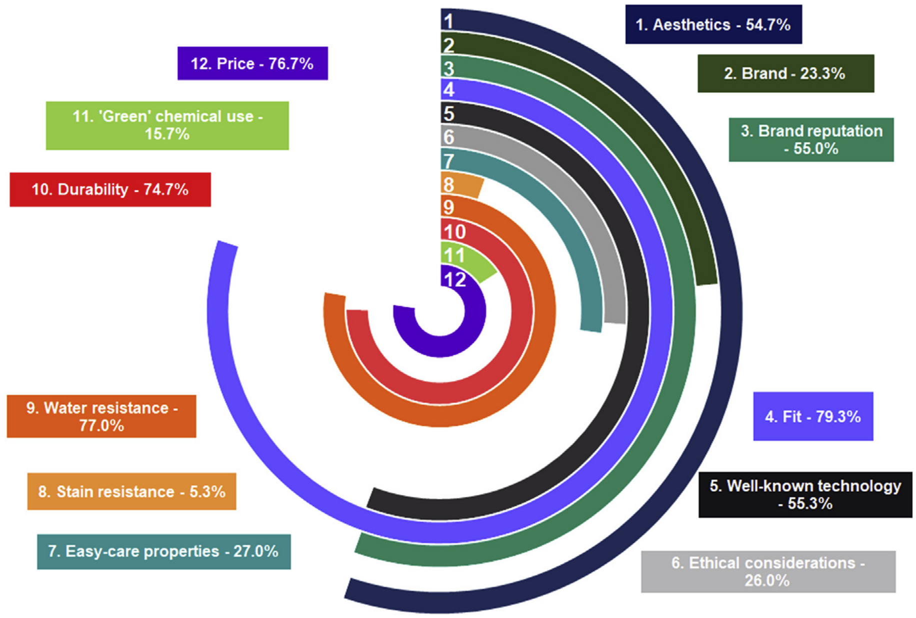

Fig. 7. Important purchasing factors to consumers of outdoor apparel (n = 300).

rethought in terms of product design to make non-fluorinated alternatives viable in these use categories.Decreasing stain repellency was observed with decreasing chain length of the fluorinated chains in side-chain fluorinated DWR indicating that an increased concentration of the DWRsbased on ‘short-chain’ SFPs might need to be applied to fulfil protection requirements.

By comparing the findings of end-user repellency function for outdoor and medical apparel to other textile applications, this study gives an indication of the substitution potential for PFASs in other textile segments. When considering the application of repellent textiles by their end-use, substitution of fluorinated DWRs is possible. Many brands in the outdoor industry moved actively away from long-chain C8-SFPs in an attempt to disassociate their clothing from the controversy of toxicology and environmental reports that highlight significant concern. However, the industry has switched to 'short-chain' C6- and C4-SFPs based on an assumption that 'short-chain' SFPs are safer. These assumptions are based on a lack of research, and recent literature has demonstrated that the environmental threat of C6 and C4 analogues is of concern (Persson et al., 2013; Wang et al., 2013; Gomis et al., 2015; Cousins et al., 2016). Brands are reluctant to utilise available non-fluorinated DWRs, citing a lack of stain and oil repellency as insufficient for user requirements.

The research herein has demonstrated that certain non-fluorinated, biodegradable DWRs are likely to be sustainable alternatives for water repellency (and certain stain repellency) meeting consumer requirements and expectations for most outdoor apparel. Green chemistry solutions are therefore available, but are being resisted by some manufacturers and retailers. The reasons for this are unclear, but is most probably a lack of information and appropriate technical research that demonstrates the appropriate functionality of non-fluorinated DWRs, and a lack of engagement with a wide consumer base. This study, together with our previous research Hill et al. (2017) and Schellenberger et al. (2018), demonstrates that non-fluorinated alternatives are a viable option in all cases where stain repellency is not an essential textile function. Non-fluorinated alternatives provide excellent rain protection and their lack of stain protection should be balanced with the long-term ecological benefits of phasing out PFASs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2019.01.160.

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