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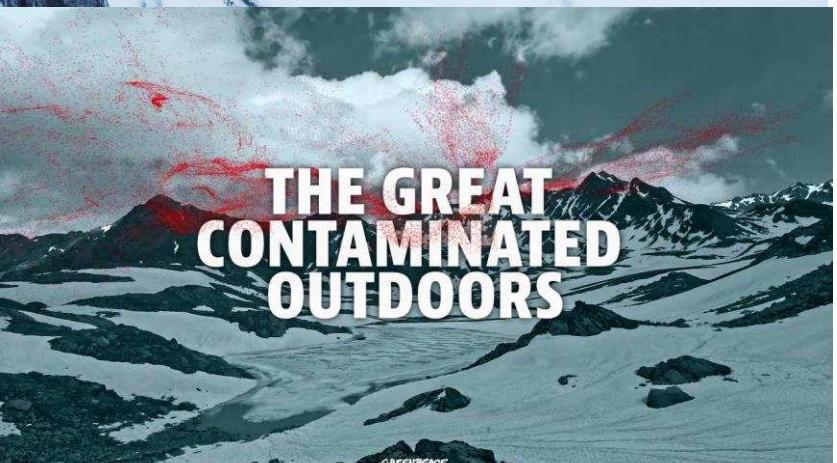
The route to fluorine-free repellent coatings in outdoor apparel: Consumer use, maintenance and physiological comfort



Richard S. Blackburn, Philippa Hill, Mark Taylor, Parik Goswami, University of Leeds, United Kingdom

@RichardBlackb18

Criticism of chemistry use for repellency

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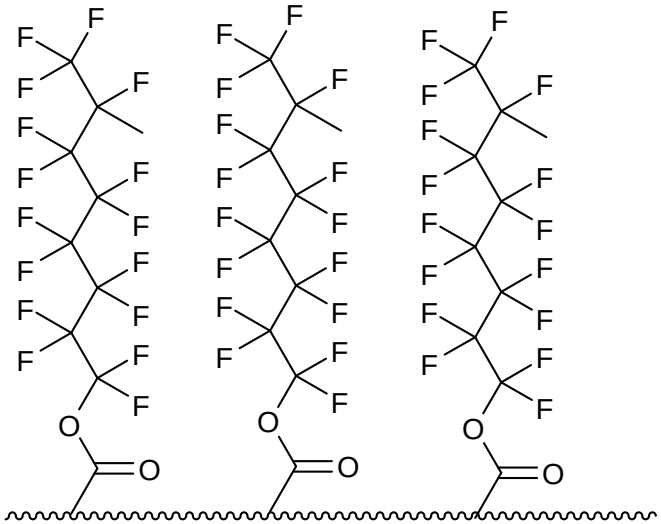
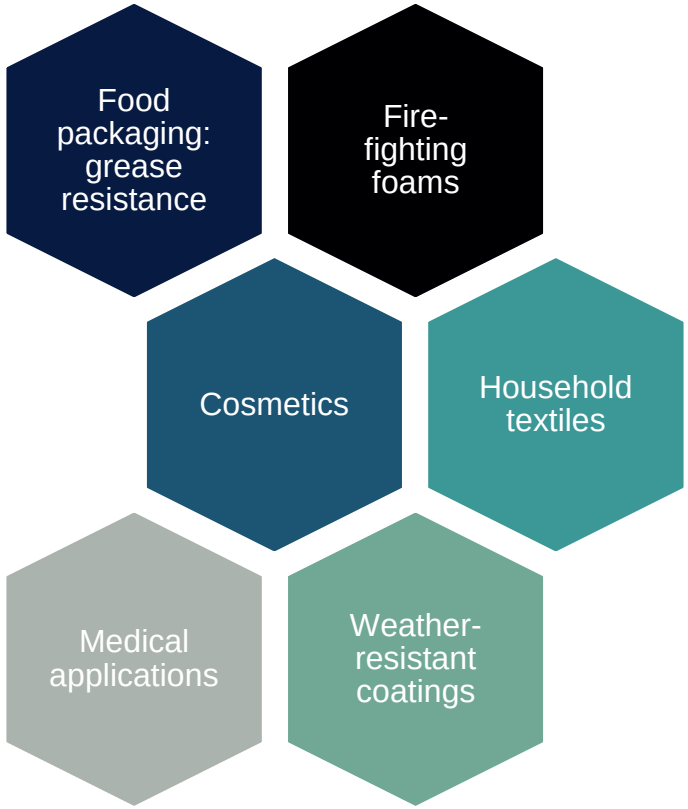
- Durable water repellents (DWR) applied to textiles to impart repellent functionality from water and oil
- For the last 60 years, per- and poly-fluoroalkyl substances (PFASs) used in textile finishing





'...significant adverse effects have **not** been found in the general human population, however, significant adverse effects have been identified in laboratory animals and wildlife' [1]

[1] U.S. Environmental Protection Agency. (2009). *Long-Chain Perfluorinated Chemicals (PFCs) Action Plan*. [Online report]. Available from: https://www.epa.gov/sites/production/files/2016-01/documents/pfcs_action_plan1230_09.pdf [Accessed 08/06/16].

Timeline of use and criticism

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1954 DuPont employees express concern on C8 to

1961 Inter

1968 Taves[2] finds organic fluorine in human serum using NMR

1969 ePTFE first created by Gore

1984

2000 U.S. Environmental Protection Agency started review on PFCs; U.S. Environmental Protection Agency imposed ban on PFOS; 3M announces phase out of C8 based chemistry

200

200

POPs

Since the late 1960s, there has been an awareness of potential toxicity issues

Increased research and concerns led to this review which has led to restrictions and legislation

Increasing momentum for cha

2011 Gre Zer (ZD

This was the first report to directly target chemistry use within outdoor apparel.

2012 Greenpeace publish report 'Chemistry for Any Weather'

2014 The Environmental Agency Norway imposes a restriction on PFOA in importing, exporting and sale of consumer goods; Greenpeace ar'

2014/15 l, to the

This report formed the basis for Greenpeace's consumer campaign.

2015 Greenpeace report 'Footprints in the Snow'; Madrid Statement

016 Greenpeace report 'Leaving Traces'; Consumer targeted 'Detox Outdoor' campaign

020 Greenpeace's 'Detox' target; Many brands within the outdoor industry are committing to be PFC free

2020 is the year Greenpeace have set for the industry to be fluorocarbon free. They are urging brands to sign the commitment. Increasingly brands are aiming to phase out fluorocarbon use by 2020.

[2] Taves, D.R. (1968). Evidence that there are two forms of fluoride in human serum. *Nature*, 217 (5133), pp. 1050-1.

Current International and EU regulations

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2000	U.S. Environmental Protection Agency started review on PFCs; U.S. Environmental Protection Agency imposed ban on PFOS.
2006	U. S. Environmental P…ship Program; The EU imposes a re… 2006/122/EC).
2009	Stockholm Conventio… Pollutants POPs; PFOS is added to the…
2014	The Environmental Agency Norway imposes a restriction on PFOA to <1µg/m² in importing, exporting and sale of consumer good. PFOA is identified as a substance of very-hi… legislation.
2014/15	Germany and Norway submit a proposal, to … limit the manufacture and use of PFOA to 2 ppb EU-wide.
2015	The Risk Assessment Committee (RAC) support the German and Norwegian proposal to restrict PFOA and PFOA-related substances at a higher concentration limit (for industrial purposes and enforcement).

Norway became the first country to impose a restriction on PFOA in consumers goods. It highlighted the significance and effect of research studies on potential toxicology.

This is a significant decision in the move away from fluorine-free chemistry and has contributed to the 2020 target.

Holmquist, H., Schellenberger, S., van der Veen, I. Peters, G.M., Leonards, P.E.G., & Cousins, I.T. (2016). Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. *Environment International,* 91, pp. 251-264.
ECHA. (2015). *Annex to RAC's news alert 15 September 2015.* [Online report]. Available at: http://echa.europa.eu/documents/10162/13579/annex_to_rac_news_alert_15_september_2015.pdf [Accessed 07/06/16].

Significant attention into alternative chemistries

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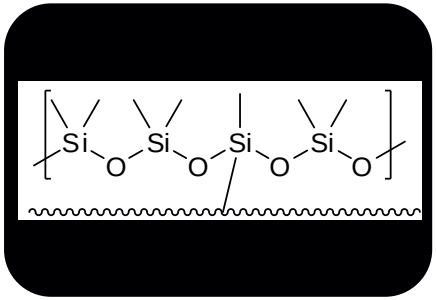
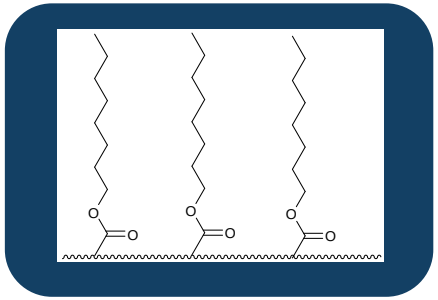
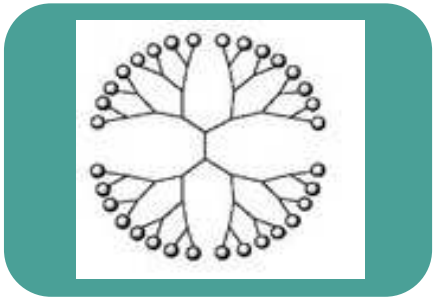


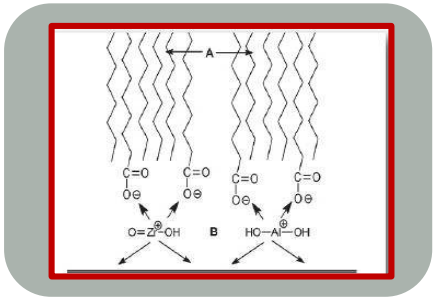
Silicones



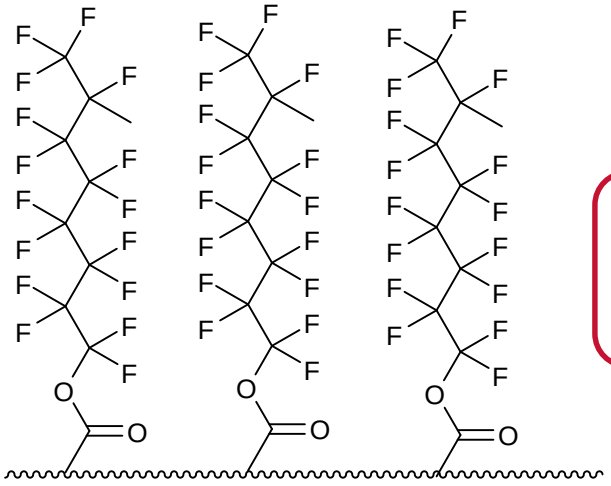
Hydrocarbons



Dendritic/hyper-branched chemistry



Wax-based repellents



Suitable for requirements?

Surface terminal groups	Critical surface tension γ_c (mN/m) at 20°C
$-CF_3$	6
$-CF_2$	18
$-CH_3$	22
$-CH_2$	31

3,4

[3] Holmquist, H., Schellenberger, S., van der Veen, I. Peters, G.M., Leonards, P.E.G., & Cousins, I.T. (2016). Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing. Environment International, 91, pp. 251-264.

[4] Holme, I. (2003). Water-repellency and waterproofing. In: Heywood, D. ed. Textile Finishing, Society of Dyers and Colourists; England, p. 141.

Repellency requirements

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Increasing repellency

Harmful liquids	Military clothing Chemical protection Surgical clothing First response	Life protection
Increased staining	Fishermen protective clothing Oil rig workers	
	Outdoor apparel	
Stain + water	Jeans Household textiles	
Water	Skiwear Leisure outerwear	Wearer comfort

Increasing protection required

- Mixed opinions on requirements for outdoor apparel
- Encompasses a wide range of activities, varying environmental conditions, and demands on the wearer
- 'Wetting' of the fabric can cause detrimental cooling of the wearer – 'life protection'
- **Re-evaluation of requirements and consumer needs.**

Focus on outdoor apparel

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59.3 % of the UK adult population participate in an outdoor recreation

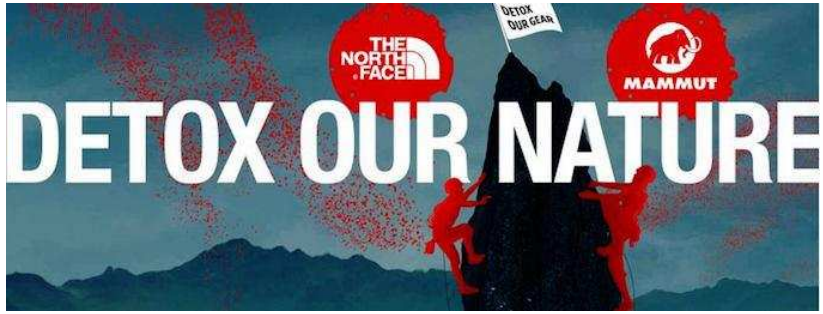
250,600 people climbing or hill-walking at least once a month

UK £20bn outdoor economy

Specifically targeted

- Highly visible apparel industry to consumers: marketing images and end-use environment.

- The outdoor apparel industry has been directly targeted by Greenpeace
- The industry's PFAS use has been discussed in three reports since 2012
- 'Detox Outdoor' public campaign



However, ratio of PFAS use in the outdoor apparel industry compared to whole textile industry unknown

Balancing requirements and knowledge

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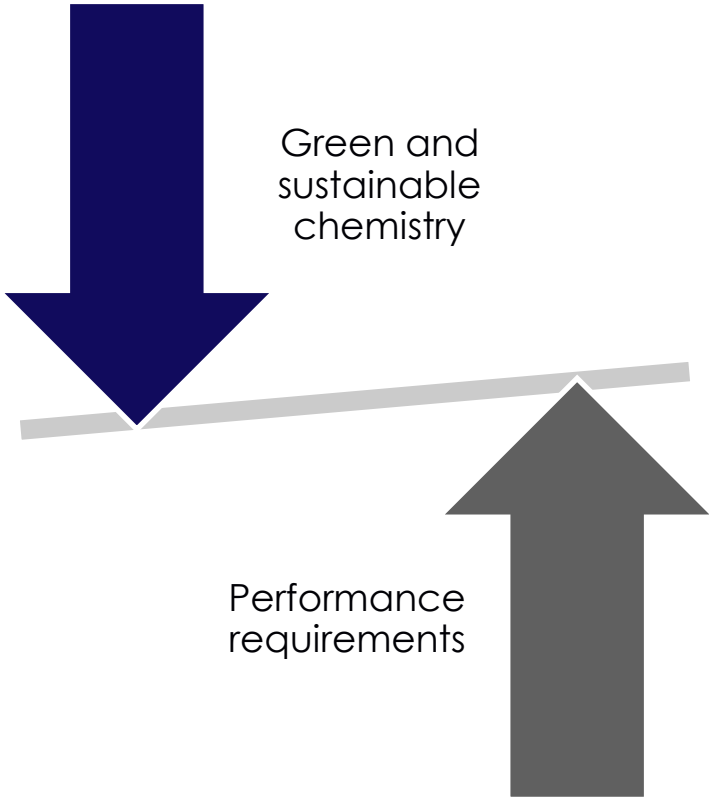

Gaps in knowledge

- Lack of market information on PFAS use
  - Many derivative compounds
  - Global market use
- PFAS used in a wide range of industries
- Not been publically highlighted
- Many potential sources of origin

- Evolving analytical assessment methods
- Research studies have focused on localised population samples
- Greenpeace acknowledge that further research to determine exposure and potential hazards to health needs to be carried out[5]
- Potential health implication of alternative chemistries?
- Sustainable product-life?

[5] Greenpeace. (2013). *Chemistry for Any Weather Part II: Executive Summary- Outdoor Report 2013.* [Online report]. Available at: http://www.greenpeace.org/russia/Global/russia/report/toxics/ExecSummary_Greenpeace%20Outdoor%20Report%202013_1.pdf [Accessed 07/06/2016].

Considerations of this research

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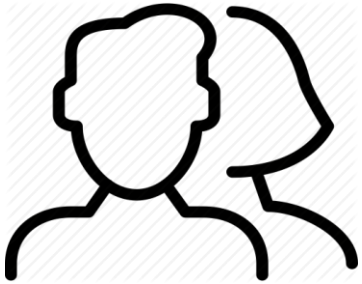
Information



Consumers

Performance expectations

End-use environment

Care and maintenance

Re-evaluation of consumer requirements
Sustainable product-life

<u>Independent research – no direction from external companies or brands</u>

Consumer requirements and understanding

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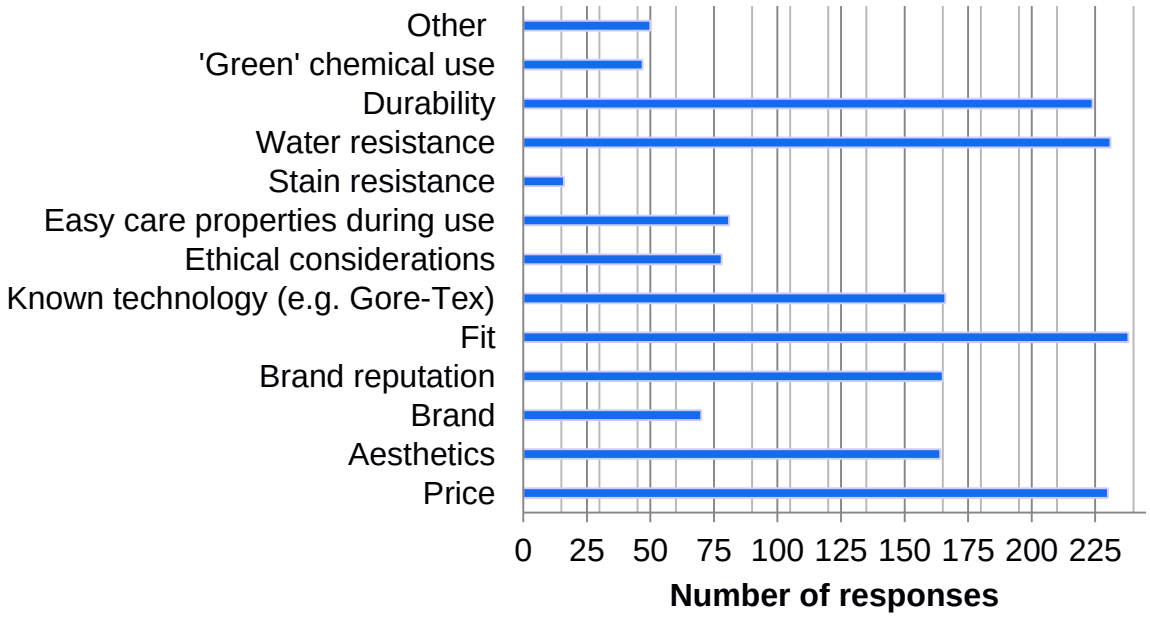
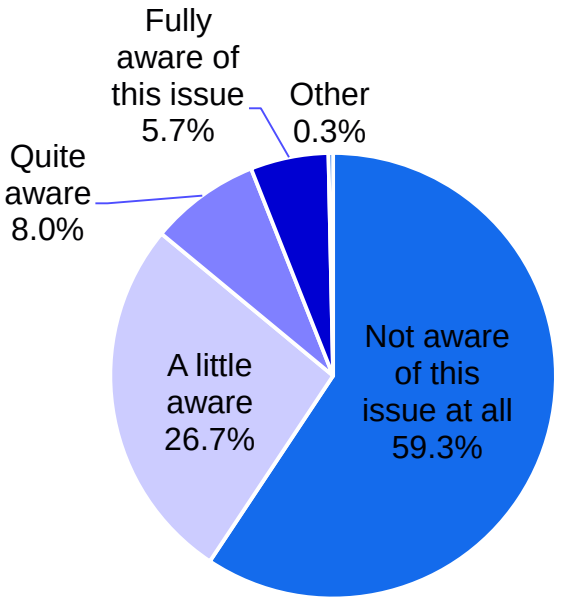
- Preliminary survey of 300 outdoor apparel users (2014)
- Consumers did not see additional benefits of oil and soil repellence
- Qualitative data revealed that water repellency was stressed to be highly important for physiological comfort
- Few respondents were aware of the criticism on the industry's chemical use
- Only 15% were aware of the Greenpeace reports

Purchasing factors rated as important by respondents



Respondents awareness of the criticism



Consumer requirements and understanding

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Survey launched May 2015
Publicised through social media and UK magazines

- Weather and environment conditions
- Frequency of use
- Consumer expectations
- Purchasing factors and decisions
- Maintenance and re-proofing
- Marketing and sources of information

- **Received new 556 respondents, 92% UK**

EUROPEAN OUTDOOR GROUP

leeds.onlinesurveys.ac.uk/outdoorclothingsurvey

Consumer requirements and understanding

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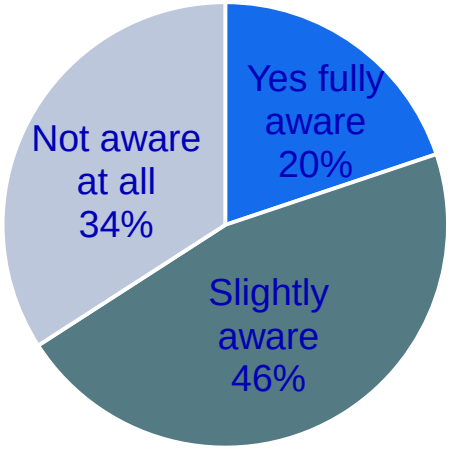
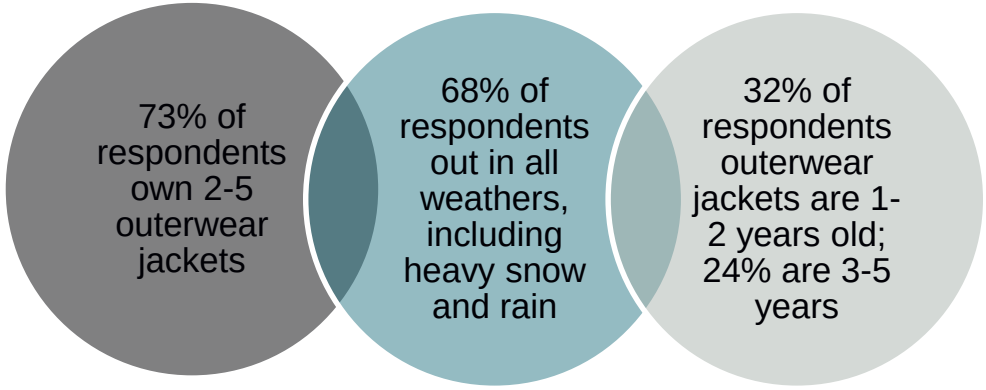
Most important factors for an environmentally friendly outerwear jacket

- Functionality to not be lessened 16 %
- Ethically sourced 13 %
- Repairable product 13 %
- Non-toxic chemicals 12 %

Respondents awareness environmental issues and criticism concerning outdoor clothing production





Consumer survey
leeds.onlinesurveys.ac.uk/outdoorclothingsurvey

Move to fluorine-free: sufficient functionality?

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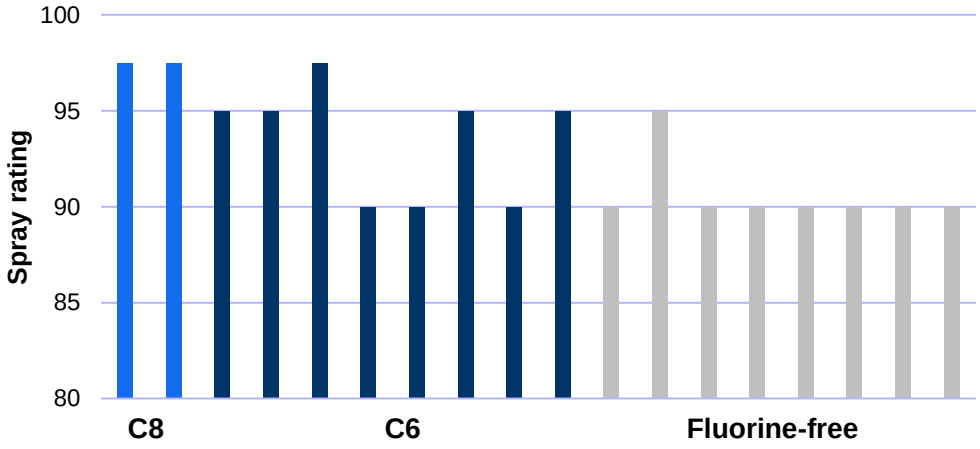
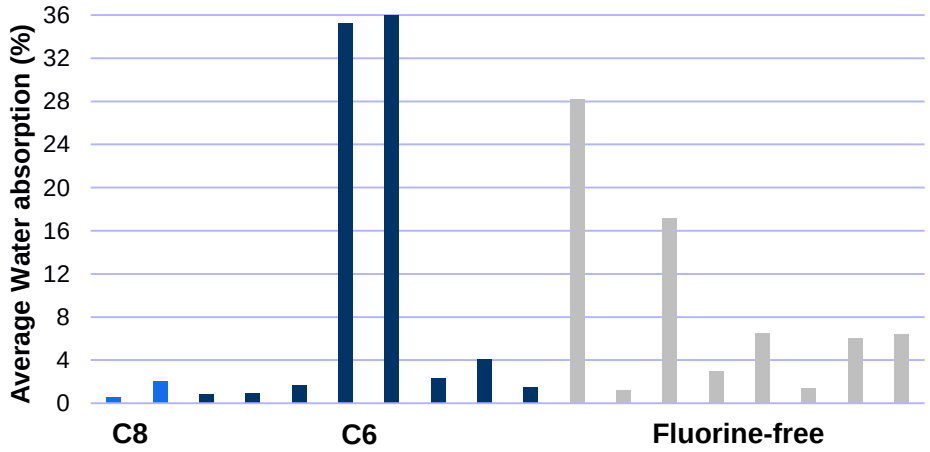
Characterisation of repellent fabrics currently in use/garment development from a number of brands





Spray test BS EN ISO 4920

Industry standard for testing resistance to surface wetting

Move to fluorine-free: sufficient functionality?

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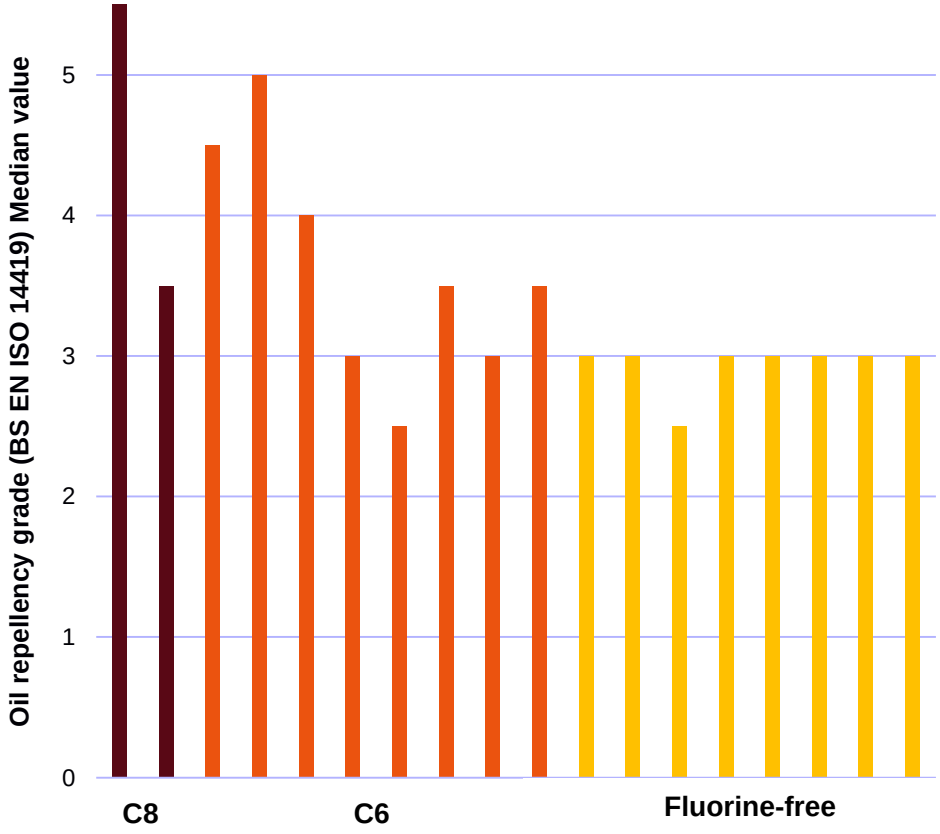

Oil repellency BS EN ISO 14419

Composition	Oil rating grade	Surface tension at 25 ℃ mN/m
White mineral oil	1	31.5
65:35 hexadecane	2	29.6
Hexadecane	3	27.3
Tetradecane	4	26.4
Dodecane	5	24.7
Decane	6	23.5
Octane	7	21.4
Heptane	8	19.8

Decreasing repellency

Post-purchase: deterioration

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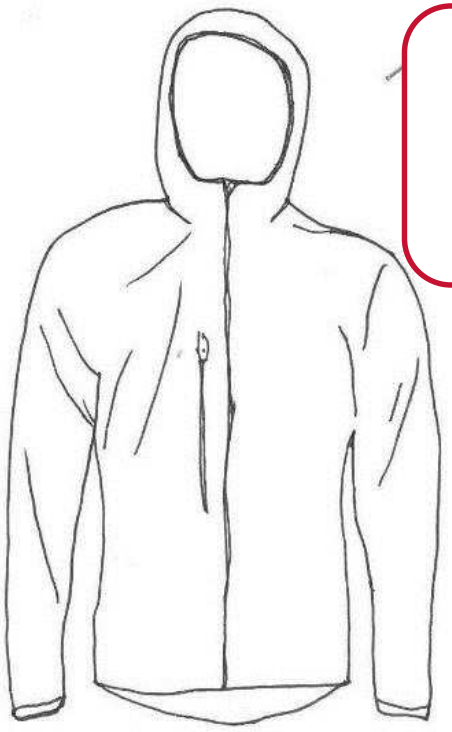
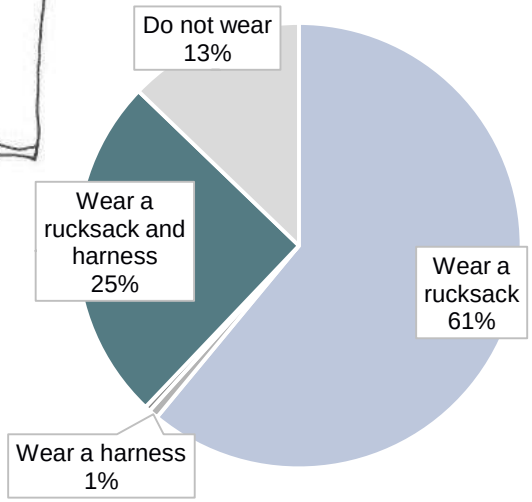


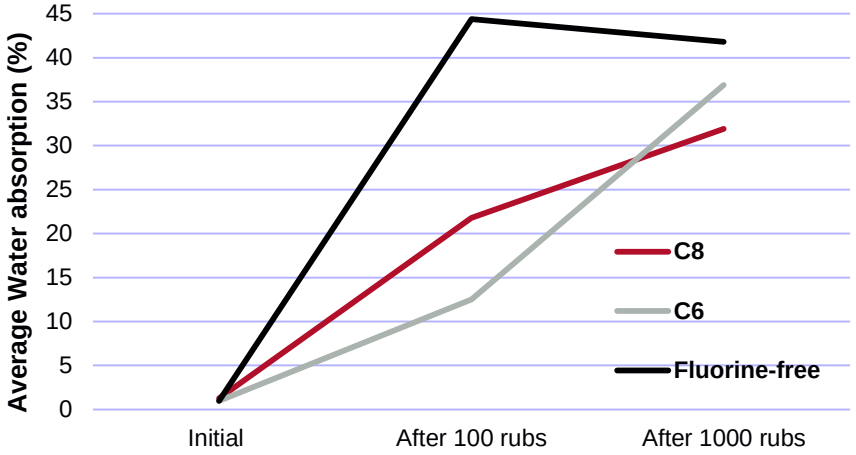
Release of chemicals? Deterioration of repellency?

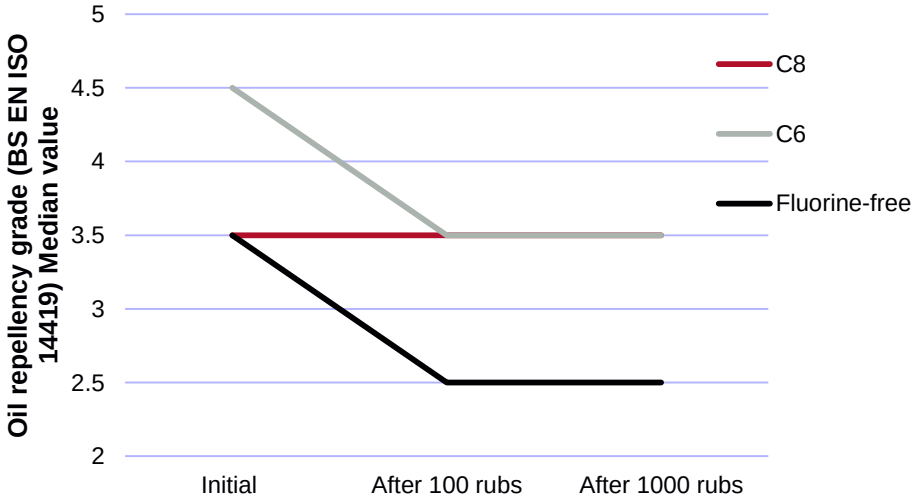
Abrasion by rock
Abrasion by other apparel: rucksack, harness



481 survey respondents wear a rucksack and/or harness with their jacket

Simulated wear using the Martindale





Post-purchase: emission pathways

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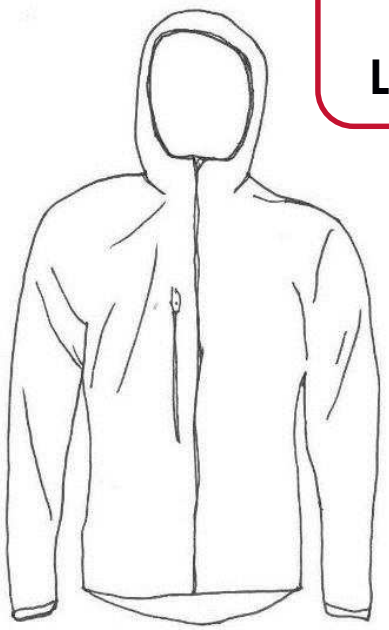
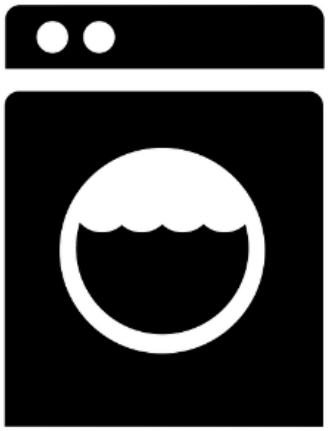
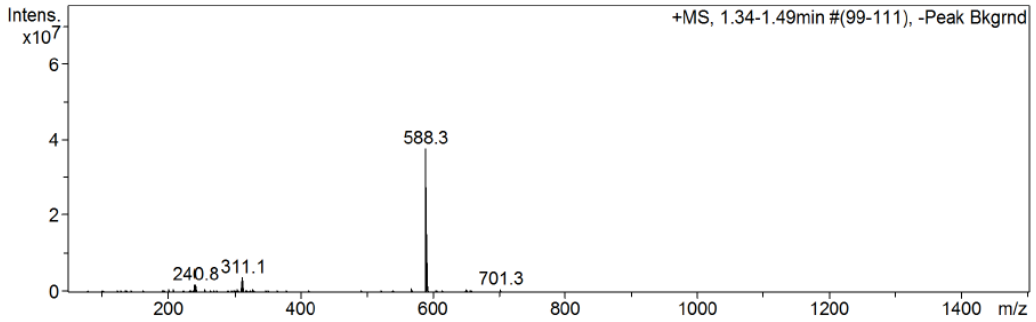
Release of chemicals into wastewater? Loss of functionality?





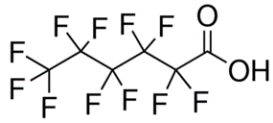
Analysis of washing wastewater by LC-MS/MS (no detergents)

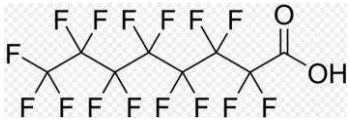


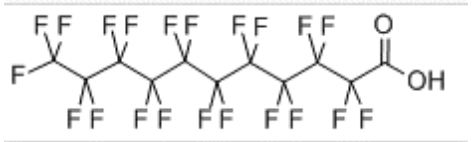
C8, 40° - wastewater LC-MS/MS analysis, C18 column

<u>Possible compounds detected</u>

PFUnDA
PFOA
PFHxA
4:2 Fluorotelomer alcohol







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How Green is your rain jacket?

Further work

- Validation of analytical detection – washing effluent
- Test method development
- The use of aftercare products: wash-in or spray formulations for 're-impregnation'

Open to collaborations with other academic groups/industry

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