Building knowledge about PFCs in the outdoor industry

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- Research focus is how water repellency is affected by use and garment maintenance, including relevant laboratory test methods.
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- Dr. Taylor, Research Fellow. Research focus is the comfort and protection of clothing systems for extreme and hostile environments and the role of textiles in protection in falls from height or from falling objects.
- Dr.. Blackburn, senior lecturer working within the area of Green Chemistry and Sustainability within the coloration and textiles industries. Current research interests include; 'green' coloration and finishing technology for all textile fibres and replacements for hazardous and non-eco-friendly chemicals used in coloration and textile operations.
- Dr. Goswami heads the Fibre and Fabric Functionalisation Research Group at the University of Leeds. Research areas include product development using flexible materials and application of chemistry for functionalising textiles.

Background Questions:

PFCs are a large group of chemicals. For what type of applications are these chemicals used, and where?

Fluorochemistry is extensively used worldwide in the manufacture of technical and consumer goods. Since the 1950s the large chemical classification group of per- and polyfluoroalkyl substances (PFASs) have been used as precursors to surfactants due to their highly favourable properties (Birnbuam & Grandjean, 2015). Surfactants are referred to as 'surface active agents' and are substances which interact with the surface changing its properties such as lowering the surface energy (or tension) (Rosen & Kunjappu, 2012). Surface energy refers to the ability of the surface to resist a liquid; it is dependent on the molecular interaction and the interface energy of the surface (Holme, 2003).

PFASs refers to the complete classification of per- and polyfluoroalkyl substances, including fluoropolymers and perfluorinated compounds (PFCs), this comprises an undefined number of derivatives (OECD, 2013; Buck et al., 2011). PFASs are used for a wide variety of end uses with each fluorochemical being individually designed for its end purpose (Bowman, 2015). This employs the desired functionality but means that thousands of fluorochemical compound derivatives are being utilised in manufacturing and processing. Fluorochemicals are organic compounds produced synthetically and do not occur naturally (Audenaert et al., 1999).

PFASs impart reliable functionality which is currently unrivalled by alternative fluorine-free chemistries. The highly stable carbon-fluorine bonding provides high thermal and chemical stability, strength and unrivalled durability (OECD, 2013). A fluorochemical surfactant imparts low surface energy presenting a highly repellent surface to water, oil and stains.

Due to this wide range of reliable properties, fluorochemistry, or PFASs, are used in most aspects of daily life as protective surfactants (Bowman, 2015; Birnbaum & Grandjean, 2015). These chemicals are used as surfactants in automotives for seals and fuel-delivery; as coatings in constructions for weather-resistance, on, for example, concrete and tiles; as additives in paint; as PTFE (polytetrafluoroethylene) in wiring for communication allowing high speed data transfer due to dielectric properties; as cosmetics in shampoo and denture cleaning; as insulative linings for tubing and pipes; within fire-fighting foams; in household cleaning products; and in medical applications such as some surgery items and in surgical clothing (OECD,2013; Bowman, 2015).

Most notably recognised is the use of fluorochemistry in food packaging and within textiles. PTFE, most commonly known under the brand name 'Teflon', is commonly used in non-stick cookware, common within households, whilst fluorine-based coatings are used on food packaging to prevent the spread of moisture, fats or oil from food contact, such as takeaway containers or microwave popcorn bags (Begley et al., 2005). Within textiles, fluorochemistry is used to impart liquid,, oil, water and stain repellency to both technical and consumer items. Most commonly this functionality is associated with protective rain outerwear such as mountaineering jackets, but is also imparted to daily apparel for stain resistance, household carpets and upholstery (OECD, 2013).

How are per- and polyfluorinated chemicals (PFCs) assessed for potential hazard for human health and the environment?

Due to the numerous derivatives of PFASs it is difficult to fully assess the hazard that this large classification of chemicals poses to human health and the environment. Research has shown a positive association with the use of PFASs and the degradation product perfluorooctanoic acid (PFOA), although there are many potential sources from which it can originate (Birnbaum & Grandjean, 2015; Buck & Schubert, 2009).

Analytical assessment methods of PFASs are still evolving. The first analytical studies of textiles were carried out in 2006 by Berger and Herzke (Knepper et al., 2014). Analytical assessment is carried out by extraction methods and liquid chromatography spectrometry (LC-MS and HPLC) (Farré et al., 2012).

Research studies have focused on localised population samples. The chemical class of PFASs contains an undefined number of derivatives and the movement of these chemicals within the environment are beyond the scope of current research (Lindstrom et al., 2011; Buck & Schubert, 2009; Buck et al., 2011; Webster, G., 2010). Localised data can only indicate suggested effects to the population. As even Greenpeace acknowledge, further research is needed to further determine exposure to these chemicals and potential hazards to health (Greenpeace, 2013).

What is known about the issues associated with 'long-chain PFCs' and 'short-chain PFCs'?

Long-chain PFASs, commonly referred to as C8, have eight carbon atoms in the fluorinated backbone chain length of each molecule; a short-chain has a fluorinated chain length of six, or less, carbon atoms (Andrews & Walker, 2015).

As replacements to long-chain C8 fluorochemical structures chemical companies have switched to using short-chain compounds but there are an undefined number of varieties. To date there is no conclusive information on the safety of these chemical compounds and the quantity of these which have already been used on products. The Helsingør Statement (2014) expressed concern on shorter-chain PFASs, and their likeness - in chemical structure, ubiquitous nature and hazardous potential to the environment and human health - to long-chain structures (Birnbaum & Grandjean, 2015). Similarly, the Madrid Statement on Per- and Polyfluoroalkyl substances (PFASs) questioned, and expressed concern, on the use of the entire classification (Blum et al., 2015). It called on a collaborative effort to limit the use of PFASs, of all chemical chain lengths, and develop fluorine-free alternatives (Blum et al., 2015).

It has been found that fluorinated chemical structures based on six carbon atoms exhibit similar degradation to long-chain structures into short-chained carboxylic acids (such as PFOA) and sulfonic acids (PFBS, PFBA, PFHxA and PFHxS) (Wang et al., 2013). Contamination can also occur within the supply chain and has raised concerns on short-chain alternatives.

What is the proportion of PFCs used in textiles relative to the quantity of PFCs used globally across all industries (including electronics, plastics etc.)? Is it known what fraction of that is used specifically in the outdoor industry?

Due to unknown accuracy of statistics on the total production of textiles and PFAS on imported articles, the proportion of PFASs used in textiles, compared across all industries, cannot be conclusively defined. Production of PFOA within Europe has ceased. But the EU imports of PFOA, and its salts, is estimated to be 20 tons per year in the form of substances, 10 tons per year in the form of mixtures, and 10 tons per year as articles (UNEP, 2015; ECHA, 2014). It has been estimated that textile imports into the EU contains between 1000-10000 tons PFOA-related substances per year (UNEP, 2015; ECHA, 2014).

For the outdoor industry, the value share of outerwear apparel can be used as an indication to the use of PFASs in the outdoor industry. Few confirmed statistics are publically available but it was recently said that goods, materials and equipment, treated with PFASs and used within the outdoor industry, are globally worth 27 million US dollars annually (Shiwanov, 2015).

Given that there exists such a huge variety and quantity of PFCs in different industrial applications, does science suggest a 'safe' way of using PFCs

The public exposure to PFASs has been reducing since the start of phase-out in 2002 (Andrews & Walker, 2015). Nevertheless an environmental legacy, from previous use of PFASs, still remains (D'eon et al., 2006).

Increasingly, legislation will be the domineering factor in the use of PFASs. For textile uses, a reassessment of needs and requirements of the end-use of the product should be carried out to assess the level or repellency and functionality necessary, and therefore whether an alternative chemistry would be adequate.

In what ways do PFCs get into the environment and are distributed? Are there effective measures to minimize PFC emissions?

Perfluorinated compounds enter the environment during synthetic production of the chemistry through breakdown and degradation products. It is also thought that they are released during the lifespan of the treated product during transport, use and disposal (OECD, 2013; ECHA, 2014).

Toxicology research studies suggest many ways in which humans and the environment have been exposed to PFASs. It is understood that main sources of exposure for humans are through food and water, in dust through release into air, waste water during processing on food packaging, and contact with treated products (Webster, 2010; ECHA, 2014). However, human exposure is not fully understood and the main pathways of exposure remain unclear (Andrews & Walker, 2015).

What is the detection and reporting limit for PFCs and similar substances in commercial laboratory tests of products? What about water, snow and other types of samples? Are there reliable tests for all known, resp. relevant, substances?

Analytical studies, to date, are difficult to compare due to the differences in analytical methods and the different products which have been investigated (Knepper et al., 2014). ZDHC (2015) sets limits for PFOS and PFOA at 2 ppm based on concentration in chemical formulations used in the textile supply chain for fabric finishing. VF Corporation (2015) sets the same formulation limits as "Allowed" at 0.05-0.50 ppm, and "Preferred" at <0.05 ppm. Bluesign (2015) sets limits for PFOS at 0.02 ppm and PFOA at 0.01 ppm based on extractable concentration in finished garments.

What concentration of PFCs and related substances can we habitually find in the environment these days? How hazardous are such quantities from a scientific point of view?

Declined to answer as not within expertise of research group.

PFC concentration, air and water pollution are typically measured in milligrams or nanograms. Can you illustrate how the PFC amounts measured in environmental samples compare to what we know these days about the order of magnitude of e.g. air pollution? How big is 'big' in this context, and what means 'just a little bit'?

Declined to answer as not within expertise of research group.

Is there a way to ascertain where the PFC traces found in the environment originally come from? Can we e.g. trace them back to a specific industry, such as electronics, textiles etc.?

There are an undefined number of PFASs derivatives, used by a number of industries, and the degradation.products and impurities cannot be traced back to their original source. With localised population samples, within research studies geographically close to a production plant using fluorinated compounds the original source can be ascertained (Barry et al. 2013; Vieira et al., 2013).
However, evidence of perfluorinated compounds found in remote locations cannot be associated with a specific industry. It cannot be concluded from which items the PFC traces originated from. Additionally, in results and evidence of these particular studies, the high likelihood of cross-contamination from testing equipment or clothing worn by those collecting samples should be significantly considered. The amount of fluorinated compounds found within control samples should be given as an important comparison, with the use, and storage, of control samples highly regulated.

Outdoor / textile related Questions:

PFCs (spec. a substance called PTFE) are also used in fabric membranes of outdoor products. How ‘hazardous’ are the PFCs if they are inherent in membranes?

PTFE (polytetrafluoroethylene) is a significantly used fluoropolymer in a range of industries and accounts for approximately 60 % of the fluoropolymer market (UNEP, 2015; ECHA, 2014).It is common for protective weather outdoor apparel to include multi-layered fabrics, including a membrane or laminate layer.
PTFE can be processed by using PFOA (perfluorooctanoic acid) as an ‘ingredient’. In this case PTFE, in use, will therefore contain PFOA as a production residue (ECHA, 2014). PFOA as a production residue, on PTFE, will contribute to the overall emission of PFOA found within the environment.

PFC-free alternatives are supposedly performing less good than PFC-containing DWR finishes. What are the issues, and what are the reasons? Where is research at with regards to solving these challenges?

The industry is seeking alternative chemistries which give equivalent properties and functionality to fluorine containing DWR finishes. Fluorinated chemistry use has grown exponentially since the 1950s due to its unrivalled properties. Fluorine-free alternatives are said to not ‘perform’ as well due to their functionality not equalling that given by fluorochemistry, in particular repellency and durability.
Repellency is dependent on the wettability of the surface and the surface structure’s resistance to the penetration of the liquid, in further detail referenced as the ‘surface energy’ and determined by the molecular interaction and arrangement (Holme, 2003). The repellency, given by fluorine-based repellent chemistries enables the surface to repel a wide range of liquids, from oils to water.
High repellency is a unique feature of this classification of chemical compounds (Bryce, 1964). The chemical structure, specifically the chain length, of the fluorinated compound has been shown to directly affect the repellent functionality (Assakul, 1972; Holme, 2003). With decreasing chain length, from 8 carbon atoms to 6, for example, the repellency has been shown to reduce, particularly repellency to oil-based liquids (Holme, 2003).
Research is continuing to seek an alternative chemistry to give suitable equivalent functionality to fluorochemistry. There has been recent experimentation with the way in which the chemicals are applied to the surface, changing the chemical structure of fluorine-free repellent chemistries (for example hyperbranched or dendritic structures) and developing surface roughness, on a nano-scale, to enhance the repellent properties of the subsequent treatment of repellent chemistry.

Does any scientific data exist how PFC-free alternative DWR finishes compare to those containing PFCs with regard to their hazardousness for human health and the environment?

Before fluorine chemistry was used for repellency, previous repellent chemical treatments utilised silicone chemistry and wax-based emulsions (Moilliet, 1963). Currently, there are many combinations of chemical compounds being researched, and therefore there is little consistent information available on the hazardousness nature.

Do PFC-treated jackets pose a risk to the wearer?

Perfluorinated compounds are ubiquitous in everyday products and emissions are already present within the environment. They are unavoidable in our daily lives.

Outdoor jackets have been frequently tested for concentrations of PFASs. However, it is difficult to compare these studies due to differences in analytical methods used, and the different products being investigated (Knepper et al., 2014). A recent study found that although compounds of PFASs were found on the garments tested, the majority (6 out of 10) had concentrations of PFOA below the restrictive limit set of 1 $\mu g/m^2$ (Hanssen & Herzke, 2014).

These studies have quantified concentrations of a variety of PFASs on garments during a singular phase of their life-cycle. Further research assessing the release of PFASs during the entire lifespan of the garment would determine the release of PFASs, taking into account possible cross-contamination during transport, during production and use (Knepper et al., 2014). It has been researched that during laundering, PFASs are released into the waste water during washing (Knepper et al., 2014).

Do DWR treatments on a garment last ‘forever’? I.e. do they ever ‘fall off’ the fabric? Why? What can be done about it?

The use, care and maintenance of a garment differs greatly between end-users. The durability of the repellent finish depends on the frequency of use and consumer laundering behaviours. The repellent finishes will diminish, depending on initial processing application, due to abrasion and/or laundering (Knepper et al., 2014).

Impregnation is said to be necessary to restore the repellent finish, although this may not re-establish the initial level exhibited (Knepper et al., 2014). However, impregnation products, either spray or wash-in applications, have been shown to contain PFASs (Knepper et al., 2014). Isolated incidents of respiratory illnesses have been reported since the 1980s (Division of Chemical Products, 2008). Silicone-based impregnation treatments are available and, as research continues to seek an alternative chemistry, research to alternative formulations for impregnation sprays continues alongside these alternative chemistries..

As alternative chemistries are used on textile products, the durability and functionality during the products life-cycle is unknown. The compatibility between impregnation sprays and the variety of alternative repellent finishes has not been assessed – Will commercial treatments restore the repellent finish? Research at the University of Leeds is currently investigating how consumer use, maintenance and laundering will affect the functionality of alternative repellent chemistries.

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