Building knowledge about PFCs in the outdoor industry

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This document presents and makes available a range of opinions by three different, independent experts in scientific or application-oriented fields related to the use of PFCs. The document does not constitute a particular position of the European Outdoor Group (EOG) or any of its members on the issue. Instead, it is the result of a fact finding mission with the primary aim of gathering and making available unbiased, third party, and independent knowledge.

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Introduction

The use of PFC’s (per- and polyflourinated hydrocarbons) in the outdoor industry is high on the agenda. Over the last few years there have been numerous articles in media and reports by organisations regarding the potential impacts of these substances on people’s health and the environment, and some groups are calling for a complete phase out of this group of substances. Among outdoor brands in particular there are ongoing efforts to evaluate and improve the existing use of PFCs as well as available alternatives chemistries.

One big challenge brands as well as suppliers are facing is the nature and complexity of the information on PFCs available: this is sometimes contradictory and/or presented in a way that is confusing and not straight forward to understand, it is hard to differentiate between biased information and hard scientific facts - not only for the product designers but also for the end-consumer.

As a response to this situation, a project group – facilitated by the European Outdoor Group - was formed in September 2015, with the goal to make a concerted and collaborative effort to provide the industry with objective, un-biased information by independent third parties. The goal of the project group is to help build knowledge in the industry, and to enable brands to base their internal decision making processes, and if required also their customer communication, on scientific facts and experts’ insights.

The project followed a four phase process:

1. Creation of a set of questions with the explicit aim that objective and unbiased information is made available to both brands and the public at large.
2. Identification of renowned experts in the field that are recognised for their independence, and who would have no vested interest in the reputation, performance or achievements of the outdoor industry, or the chemical and finishing industries.
3. Request the renowned expert answers to the above mentioned set of questions be delivered within a set time frame of 3 weeks.
4. Make the compiled answers obtained from these experts publically available, unaltered in content and in the complete finalized versions as provided by them.

This document therefore sets out the answers and references provided by the following three experts:

- Philippa Hill, Postgraduate researcher, School of Design, University of Leeds, UK
- Phil Patterson, private consultant, Colour Connections, UK
- Stefan Posner, Senior Researcher, Swerea IVF, Sweden

This document presents the names and affiliation of all experts that responded to the request. The experts have not received any remuneration for the time taken to answer these questions. Where any questions may refer to an area that is not within their field of expertise, respondents were free to leave blank answers. The respondents have agreed to the final texts being presented here in full. A separate document contains the full copy of the letter sent to experts, the original set of blank questions, as well as the full list of experts approached including those that decided not to respond for a range of reasons including: request for remuneration and lack of time.

The project group encourages that this document is shared with as many as possible with the aim of raising awareness and building knowledge on this subject. Please refer to the usage guidelines of this document with regards on how to use the information contained in this document appropriately.

The project group would like to thank the experts for taking the time to provide these answers and hope that many people find them useful.
Contributors’ Profiles

Philippa Hill, Postgraduate Researcher, School of Design, University of Leeds (UK)
- Research focusing on water repellency within outdoor apparel: how it is affected by consumer use and garment maintenance; laboratory test methods; and the effect on physiological comfort.
Philippa is supervised by Dr Richard Blackburn, Dr Mark Taylor and Dr Parik Goswami, School of Design, University of Leeds (UK).
- 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, Associate Professor who heads the Sustainable Materials Research Group 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.

Phil Patterson, private consultant, Colour Connections, (UK)
- Wide ranging expertise in the textile industry gained from a career that has spanned research, manufacturing and retail; fibres, fabrics and garments; legislation, environmental compliance, standardization and innovation.
- Phil was a founder member of the multi-brand AFIRM group, was Chairman of RITE group which aimed to reduce the impact of textiles on the environment.
- Phil consults for many major brands, and international organisations – such as work for the IFC in Bangladesh

Stefan Posner, Senior Researcher, Swerea IVF (Sweden)
- Main focus area: textile and polymer chemistry concerning chemicals in articles and production.
  o their intended uses,
  o environmental and health characteristics and risk profiles from a life cycle perspective with a certain focus on substitution in practice.
- Ongoing research into the substitution of hazardous chemicals with a recent certain focus on highly fluorinated substances and flame-retardants.
- Other groups of hazardous chemicals have been a focus in the past.
Background Questions

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

Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)
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 (Birnbaum & 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 automobiles 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).

Phil Patterson, private consultant, Colour Connections, (UK)
Multiple uses as they are also in polymerized form – used as surfactants, as refrigerants, repellent/non-stick surfaces. The most high profile uses are those such as non-stick and DWR’s that carry common brand names e.g. Teflon or Gore-tex.

Stefan Posner, Senior Researcher, Swerea IVF (Sweden)
PFAS is a very large group of substances with many different uses and applications. In a study conducted by the Swedish Chemicals Agency in 2015 “Occurrence and use of PFAS and alternatives”, identified a wide range of commercial uses where some of these are listed below:
- Synthesis Chemicals
- Electronics Products
- Printing Products
- Cosmetic Products
- Textile / leather impregnation
- Pharmaceuticals

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- Plant protection
- Biocides
- Paints
- Adhesive raw materials
- Paper impregnation
- Foam-based fire extinguishing agents

Some conclusions from this study:

- Information on how the substance is used (about 3000 substances in total) is unknown for about half of the substances.
- The market information found for most PFAS was often short.
- Information on functionality such as "surfactant" could be linked to 20% of the PFAS substances.
- PFAS that were called "surfactants" had a wide range of applications often briefly described.
- For a third of all the substances that were identified (approximately 1000 PFAS), a bit more detailed market information was available.

One major conclusion of this study is that there are likely more uses of PFAS for which we still don’t have comprehensive market information, often due to company trade secrets.

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

**Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)**

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).

**Phil Patterson, private consultant, Colour Connections, (UK)**

There are multiple studies using many different methods and approaches.

**Stefan Posner, Senior Researcher, Swerea IVF (Sweden)**

This question requires answers from different groups of expertise of which I only can provide short answers. In short the following characteristics described below are measured and quantified according to certain protocols. However to my knowledge there are still data gaps for many PFAS still to be filled so I leave this to be better answered in detail by colleagues in their particular fields of expertise.

**Persistence (P):** Substances that are persistent are highly stable and resist the natural processes of degradation.

Persistence for all PFAS: The fluoro - carbon bond is very strong, meaning that all perfluorinated substances are extremely persistent. They do not occur in nature and therefore no natural system that have the ability to degrade the fluoro – carbon bond of these substances.

**Bioaccumulation (B).** Substances that bioaccumulate are readily absorbed in fatty tissue and can accumulate in the body fat of living organisms. These substances become more concentrated as they move up the food chain, especially into larger longer-living organisms.
Bioaccumulation for PFAS: PFAS are hydrophobic and oleophobic meaning that these substances do not really bioaccumulate in the same way as other organic substances. Some PFAS have a high biomagnification potential meaning that these substances are in a higher concentration in an organism than the background concentration of these substances in the organisms diet.

Long-Range Transport (LRT): Substances that are released in one part of the world and have the ability to can travel far from their original source via wind, water, and, to a lesser extent migratory species LRT of PFAS: There are several studies where PFAS have been detected in rural and uninhabited areas on our planet, especially the terminal degradation products of PFAS namely the perfluorinated carboxylic and sulfonic acids.

Toxicity (T): Substances that are toxic chemicals that laboratory, field, and health studies have linked to certain adverse (chronic and acute) health effects in people and wildlife. 

Toxicity of PFAS: There are several recent studies that indicate chronic toxic effects of both long and short-chain PFAS to both humans and environment.

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

Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)

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, 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.

Phil Patterson, private consultant, Colour Connections, (UK)

Such a broad question is in danger of eliciting an answer that treats all PFCs as having the same risk factors. PFCs are a large group of chemicals and each individual chemical will have a different profile. The perceived wisdom is that long chain PFCs are more problematic than short chain PFCs, but that is largely down to long chain PFCs being less biodegradable and more bioaccumulative. However, if you consider the dose/exposure of long chain PFCs relative to NOAEL’s in certain end uses there may be a case to say they could be less harmful than exposure to the breakdown products of short chain PFCs – typically short chain PFCs have to be used in higher quantities than long chain PFCs to get the same effects on certain end uses.

There has to be a sensible discussion on whether certain reactions can (theoretically) happen or do (actually) happen when looking at degradation of certain less harmful PFCs to certain more harmful PFCs.

Stefan Posner, Senior Researcher, Swerea IVF (Sweden)

First a short explanation of the terminology of so called long and short chain PFAS as below: Every PFAS substance contains a perfluorinated tail meaning that all hydrogens on these carbons are replaced with fluorine. By definition long chain PFAS can be described as follows below:

Long chain PFAS – the fluorinated “tail” contains:
- More than or equal to 7 perfluorinated carbons if a perfluorinated carboxylic acids (PFCA)
  o The most well-known example is PFOA that contain 7 perfluorinated carbons
- More than or equal to 5 perfluorinated carbons if a perfluorinated sulfonic acid (PFSA)
  - The most well-known example is PFOS that contain 7 perfluorinated carbons
- Precursors that can degrade to the above compounds
  - Such precursors are mostly alcohols and acrylates

PFAS with shorter fluorinated “tails” than above are called short chain.

There are differences in some human and environmental characteristics between short and long chain PFAS, but I leave this to be better answered in detail by colleagues in their particular fields of expertise.

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?

Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)
Due to unknown accuracy of statistics on the total production of textiles and PFAS on imported articles, the proportion of PFAS 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).

Phil Patterson, private consultant, Colour Connections, (UK)
The answer to this should be elicited from the PFC manufacturers who have reliable data on sales. The information in reports with an agenda to stop the use of PFCs in certain end uses cannot be trusted.

Stefan Posner, Senior Researcher, Swerea IVF (Sweden)
As mentioned in the first question above, the major conclusion from the Swedish Chemicals Agency study in 2015 “Occurrence and use of PFAS and alternatives” is that there are likely more uses of PFAS of which we still don’t have comprehensive market information, often due to company trade secrets.
Therefore it is not possible to provide specific and exact answers to quantities of certain uses of PFAS on the global market.

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?

Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)
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.

Phil Patterson, private consultant, Colour Connections, (UK)
The concept of release/exposure and NOAEL’s should be used at all stages from manufacture to end of life and low biodegradation and bioaccumulation must be factored in. It is likely that science will suggest there are some end uses where it is wise to use alternatives and others where ongoing use can continue. For example, the use of PFCs to impart non-stick performance to food contact items would logically be a higher priority for substitution than end use where exposure is less likely.
Stefan Posner, Senior Researcher, Swerea IVF (Sweden)
There are guidelines for Best Available Technology (BAT) and Best Environmental Practice (BEP) issued by UNEP/Stockholm Convention, (2012 updated in 2014 and ongoing) for PFOS and related substances and alternatives that is applicable for other PFAS and their alternatives. These guidelines are based on best current knowledge and practice that is continuously developed as soon as new knowledge is available. Important foundations for these guidelines are an increasingly strict international legislation on the phasing out of certain long chain classes of PFAS.

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

Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)
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 PFAS. 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).

Phil Patterson, private consultant, Colour Connections, (UK)
Air, water [manufacture/application/consumer use and laundry]. Disposal/landfill/incineration of products incorporating PFCs. This is not well profiled and fully understood and there are ongoing studies. There are ways to minimize PFC emissions but is the level low enough? E.g. DWR Formulations with ‘loose’ by-products can be purified by manufacturers to prevent losses during application. Using the most effective type of PFC from a performance end/use perspective means less is manufactured, used and put into the environment compared to using less effective PFCs – again the need to consider specific chemical species and dose/exposure is important.
With respect to DWR’s there needs to be consideration of what is worse…..a very small amount of stable PFOA associated with C8 or larger amounts of less stable/more biodegradable PFHA associated with C6?

Stefan Posner, Senior Researcher, Swerea IVF (Sweden)
There are a few scientific studies that have tried to get a view of distribution ways, both historical and current pathways for various PFAS, but our knowledge is far from complete in this matter.
The table below superficially illustrates how various PFAS possibly distribute and emits to the environment but there are still pieces, some unknown, in this complex puzzle that need to added to get a better understanding in this complex matter.
The table below illustrates that PFAS can be emitted through so called direct and indirect sources where the direct sources have their origin in from production sites and other similar installations e.g. firefighting foam installations. Indirect sources have their origin from degradation of applied highly fluorinated side chain polymers and impurities from consumer products such as textiles and leather items. In volume the direct sources dominates of the indirect sources of emissions of PFAS. A number of studies indicate that around 90% of all emissions have their origin from direct sources of emissions of PFAS and less than 10% from consumer products such as textiles and leather products. However it is not fully clear of the mechanisms that involve the degradation of highly fluorinated side chain polymers.

Table 1: Various categories and sub categories of PFAS, their uses and possible emissions to the environment.

<table>
<thead>
<tr>
<th>Category</th>
<th>Subcategory</th>
<th>Some applications</th>
<th>Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salts</td>
<td>K⁺, Li⁺, NH₄⁺</td>
<td>Surfactant in fire-fighting foam, surfactant for alkaline cleaners, emulsifier in floor polish mist, suppressant for metal plating baths, surfactant for etching acids for circuit boards, inks. Photoresist</td>
<td>Direct emissions as ingredients/processing aids</td>
</tr>
<tr>
<td>Category</td>
<td>Subcategory</td>
<td>Some applications</td>
<td>Emissions</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td>-------------------------------------------------------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>Polymers</td>
<td>Carboxylates</td>
<td>Antistatic agent in photographic paper. Optical elements</td>
<td>Direct emissions as transformation/ degradation products</td>
</tr>
<tr>
<td>Polymers</td>
<td>Amides</td>
<td>Pesticide active ingredient</td>
<td></td>
</tr>
<tr>
<td>Polymers</td>
<td>Oxazolidinones</td>
<td>Waterproofing casts</td>
<td></td>
</tr>
<tr>
<td>Polymers</td>
<td>Alcohols, silanes, alkoxylates, fatty acid esters, adipates, urethanes, polyesters, acrylates</td>
<td>Soil/water repellence for carpet, fabric/upholstery, apparel, leather, metal/glass</td>
<td>Indirect emissions as transformation/ degradation products and impurities/ residual products</td>
</tr>
<tr>
<td>Polymers</td>
<td>Copolymers, phosphate esters</td>
<td>Soil/water repellence for carpet, fabric/upholstery, apparel, leather, metal/glass. Oil/water repellence for plates, food containers, bags, wraps, folding cartons, containers, carbonless forms, masking papers</td>
<td>Indirect emissions as transformation/ degradation products and impurities/ residual products</td>
</tr>
</tbody>
</table>

Those PFAS relevant for textiles and leather are highly fluorinated polymers that are addressed as polymers in table 1. Their distribution into the environment probably occurs through degradation and transformation of highly fluorinated side chain structures finally into their respective perfluorinated acids.

**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?**

**Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)**

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.

**Phil Patterson, private consultant, Colour Connections, (UK)**

The whole testing debate is coloured by the almost universal use of the wrong terminology – the phrase ‘limit of detection’ is routinely [wrongly] applied to the ‘limit of quantification’.

We have to consider limits of detection (the limit above which someone can say a specific chemical is definitely there) and limits of quantification (the amount above which someone can say a specific chemical is definitely there at a specific concentration)

For legal judgments then you have to work to the limit of quantification.

For detection of manmade chemicals in areas of the world where no such chemicals have ever been deliberately used the anything above the limit of detection is potentially significant in terms of highlighting mobility of chemicals.

Statistical analysis of samples and blanks is critical because test methods are now so sensitive they can detect ppq (parts per quadrillion) of some chemicals. At these levels contamination from laboratory staff, equipment and reference samples can be significant.

Another critical issue here is what happens to laboratory waste – we could reach a situation where the deliberate use of PFOA and other PFCs in laboratories as reference samples exceeds the unintentional use of the PFOA present in trace amounts in certain products.
Stefan Posner, Senior Researcher, Swerea IVF (Sweden)
First of all detection limits (LOD) are laboratory specific depending on their in house performance concerning sample preparation, laboratory equipment, reference standard availability and quality etc. This means that no general answer can be provided that is independent and valid for every laboratory worldwide. Reporting limits are decided by each and every laboratory in agreement with their customer and/or their policy how to present and report analytical results. Conclusively it is up to each customer to have a dialogue with the laboratory they want to use to assure good quality of these laboratories. Since international standards are still lacking both in performance and validity it is then especially important for the customer to assure good analytical performance from the laboratory to use.

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?

Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)
Declined to answer as not within expertise of research group.

Phil Patterson, private consultant, Colour Connections, (UK)
This is a question for experts in the field.
The most recent report by Greenpeace indicated that PFCs were present but at very low levels – for the first time Greenpeace acknowledged the presence of multiple sources of PFCs rather than just the use of DWR’s on textiles.
How hazardous are such quantities?…?? We need to be very careful to talk in terms of hazard, dose/expose and risk. The reported levels pose almost no risk but it makes good sense to monitor levels to ensure they are not increasing. It is also important to consider bioaccumulation and degradation of PFCs when judging harmfulness of any species.

Stefan Posner, Senior Researcher, Swerea IVF (Sweden)
Currently there are numerous monitoring studies that indicate various levels of PFAS in the environment. It is however hard to draw certain conclusions on hazards but since the terminal degradation products of PFAS namely the perfluorinated carboxylic and sulfonic acids are extremely persistent so it is only a question of when adverse health and environmental effects will occur beside those that already happened over the decades.
As mentioned above I leave to colleagues that are experts in this field to give more comprehensive answers to this question.

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’?

Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)
Declined to answer as not within expertise of research group.

Phil Patterson, private consultant, Colour Connections, (UK)
The concept of dose/exposure is rarely applied. There is also very little attention paid to the units – any number above zero is used to create alarm by some reporters. It is worth considering that 1 ppm is 1 second in 11 days, 1 ppb is 1 second in 32 years and 1 ppt is 1 second in 32,000 years.
It would appear that workers exposed to high levels of some PFCs have suffered significant health issues and it appears that historically manufacturing facilities have not managed leakages and discharges as well as we may have expected so neighbours could have also been affected… but that should not necessarily be extrapolated to assume that anyone exposed to tiny quantities of PFCs are at risk. Workers exposed to high levels of
radiation typically get radiation sickness and cancers but everyone on earth is exposed to radiation on an ongoing basis – largely without harm. Formaldehyde is classified as a carcinogen and it also present, naturally, in every living cell. The amount of PFCs in environmental surveys is very much in the ‘not very much at all’ category but there is a good argument to say it should not be there and it would be better if it wasn’t there.

**Stefan Posner, Senior Researcher, Swerea IVF (Sweden)**
This a rather complex question that I leave to colleagues that are experts in this field to give more comprehensive answers to this question

*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.?*

**Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)**
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.

**Phil Patterson, private consultant, Colour Connections, (UK)**
This is one for the PFC experts and it needs a degree of honesty regarding by-products present at the point of manufacture and also an honest appraisal of PFCs degradation and what is actually formed from what.

**Stefan Posner, Senior Researcher, Swerea IVF (Sweden)**
There are a number of recent scientific studies that tries to correlate environmental PFAS observations to possible sources of PFAS production and/or use. However there are still considerable data gaps to get a comprehensive view of these correlations.
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?*

Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)

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.

Phil Patterson, private consultant, Colour Connections, (UK)

The use of PFOA in the manufacture of PTFE and releases of PFOA from manufacturing facilities was the catalyst for the focus on PFCs. PTFE itself is generally regarded as inert and safe but it can contain minute traces of PFOA. PTFE can degrade with extreme heat generating species that are lethal to birds.

Stefan Posner, Senior Researcher, Swerea IVF (Sweden)

Before I provide any direct answer to this question I need to emphasise that PTFE is a fluoropolymer that represent another chemistry than PFAS as illustrated below:

PFAS are surfactants with extremely low surface tension or side chain fluorinated polymers with extremely low surface energy.

Schematic figure of a PFAS molecule:

| Perfluorinated tail | Spacer | Hydrophilic group |

PFAS are not fluoropolymers e.g. PTFE that represents another chemistry than PFAS. Fluoropolymers contain an extremely long perfluorinated carbon chain with no other atoms included than carbon and fluorine.

Schematic figure of a fluoropolymer:

| Perfluorinated polymer chain (extremely long chains) |

However PFOA has been or possibly still is used as a processing agent (emulsifier) for the production of fluoropolymers such as PTFE. This means that traces of PFOA may be found in the so called microporous membranes that are made of PTFE.

*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?*

Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)

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 equaling 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 (Assarakul, 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.

Phil Patterson, private consultant, Colour Connections, (UK)
The best repellent finish for textiles is based on a C8 fluorotelomer. It provides a lower surface energy than short chain alternatives and therefore repels oil, solvents and water. Short chain alternatives only really repel water. There is a sort of insurance buffer with C8’s in that if they become contaminated with anything like detergent residues (anything that is washed or cleaned is guaranteed to pick up residues) they will still repel water. Short chain alternatives need more chemical to be applied to get comparable water repellency to C8 and then the performance drops off relatively quickly and water-repellency is lost – this generally results in the purchase of a new product and all the attendant environmental damage caused during its manufacture.

Fluorocarbon free alternatives are even worse than short chain FC’s in terms of repellency. The challenge is that the repellency is a function of the electronegativity of Fluorine and the strength of F-C bonds which are the second strongest bond in chemistry after Si-F. Looking for alternatives as good as C8 is a bit like looking for light that’s a bit slower.

People often cite the lotus leaf for inspiration but have you ever seen a lotus leaf that’s been through 50 wash cycles? There may be some merit in nano-technology but the risks of nano-technology are arguably greater than the risks of PFCs.

Stefan Posner, Senior Researcher, Swerea IVF (Sweden)
Highly fluorinated side chain polymers have unique oleophobic and hydrophobic properties, which provide extremely low surface tension and consequently oil repellent properties. This cannot be achieved with other groups of chemicals. If so called non fluorinated alternative polymers are used, they may achieve water repellent properties but not oil repellent properties due to their higher surface energy.

Some of the main alternative DWR chemistries are siloxane-based or hydrocarbon-based polymers. There are also hyperbranched hydrophobic polymers (dendritic, i.e., highly branched polymers) and specifically adjusted comb polymers as active components. Less common are fluorinated siloxane structures of which we know almost nothing. There is also research on plasma technology that may be an alternative to modify textiles surfaces to DWR properties.

Conclusively the only way forward from a scientific perspective to maintain oil repellent properties are to invent and apply new structures of fluoro chemistry, that can provide the same oil repellent performance as the current PFAS chemistry and that these new structures are scientifically shown less harmful to the environment and humans than the current PFAS chemistry. These efforts are still emerging and not in any way close to neither pilot nor full scale production as far as recent studies in these matters are concerned.

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?
**Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)**

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.

**Phil Patterson, private consultant, Colour Connections, (UK)**

The manufacturers will have to have such data to place them on the market – they will promote the benefits over FC’s.

As yet there hasn’t been a persistent campaign against the PFC-free alternatives but if studied to the extent that PFDA has been then it is likely that a by-product present at trace levels could be targeted based on the effects of the chemical at higher doses. There is some concern over certain siloxanes which are used in silicones products (most textile finishes are polymers and the concern is over the presence of unreacted monomers). Another popular FC-free approach has been the use of dendrimers – these are highly branched polymers and to date I don’t think they have been assessed with the same rigour as PFCs. They can be made of different materials and the risks of the dendrimer species, catalysts, residual starting materials, by-products and contaminants would need to be judged.

One of the biggest issues with a move away from C8’s is the unintended consequences of doing so. Alternatives are not as good and need replacing more frequently – what are the impacts of manufacturing replacements? How many dioxins, PAH’s and so on go up the chimneys of coal fired power stations? How much global warming? How much water pollution from the dyers/finishers who make them?

From the very outset of the PFC debate it has been clear that moving to less good alternatives – as were doing – will have negative environmental effects. Do those outweigh the removal of small quantities of PFCs? I don’t know the answer to that but in my opinion the strict control of PFC emissions would have been preferable to de-facto bans whilst the environmental issues of poor performance and durability were considered.

**Stefan Posner, Senior Researcher, Swerea IVF (Sweden)**

There are a number of recent scientific and governmental studies that describe hazard characteristics on both fluorinated and non-fluorinated DWR chemistries. Though there is scarce hazard data for some of these alternatives there is no way possible to conclude that non fluorinated alternatives are “better” than highly fluorinated DWR chemicals in a general way. As always these matters have to be assessed on every individual DWR chemistry and their specific precursors.

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

**Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)**

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 µg/m² (Hanssen & Herzke, 2014).

These studies have quantified concentrations of a variety of PFASs on garments during a singular phase of their lifecycle. 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).

**Phil Patterson, private consultant, Colour Connections, (UK)**

No.
Stefan Posner, Senior Researcher, Swerea IVF (Sweden)

Before I answer this question there is a need to define the terms hazard and risk. The term hazard means the intrinsic characteristics of each specific substance as illustrated by the answer to the second question in this fact sheet. The term risk is a combination how a particular substance is exposed and emitted under normal foreseeable use and its hazard characteristics. This means that a very hazardous substance may be used under normal very controlled conditions and pose a very low or negligible risk. This does not mean that any accidental use may create unacceptable high risk scenarios for this particular very hazardous substance given in this example. Concerning PFAS the answer to this question is far more complex than a simple no or yes. With our current knowledge we need to define a range of criteria to answer this question in a comprehensive way. These criteria may include

- What is the actual content of PFAS in readymade textiles and what are the characteristics for these PFAS?
- How we are exposed to these PFAS during actual use?
- Washing conditions and consequently PFAS emissions to environment and PFAS exposure through in door dust and debris.
- Most likely different risk scenarios concerning PFAS exposure and emissions for various textile products depending on their various normal uses and compositions.

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

Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)

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 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.

Phil Patterson, private consultant, Colour Connections, (UK)

See also answer to this section’s Question 2, above.

PFCs do require an occasional ‘pep-up’ via the use of heat to refresh performance. This isn’t widely known or advertised but many garments will be discarded because water fails to fully bead up. A quick treatment in a tumble dry will normally restore performance. The time taken for a short chain FC to require a pep-up is much shorter than for a C8.

The best C8 DWR’s are referred to a ‘durable’ rather than permanent and they will slowly wear off or wash off the surface of a fabric over 50 or so washes to a point where repellency is compromised. FC-free alternatives can be based on silicones, PU’s or oils/waxes – these will have similar levels of actual durability (i.e. they will wash off slowly), however they will fail to be repellent long before a C8 DWR.

Stefan Posner, Senior Researcher, Swerea IVF (Sweden)

There is no easy way to answer this question since durability depends on a number of conditions such as

- Processing conditions e.g. machinery, physical and chemical parameters etc.
- Type and structure of textile materials applied
- Type of DWR chemistry and recipe combinations.
• Use patterns e.g. differences in washing instructions if the garment is washable or not
• Etc
In order to reply to this question in a proper way then comparable conditions as mentioned above are essential to fully understand which DWR treatment has possibly better durability than another DWR treatment even within the same chemical group of DWRs e.g. polysiloxane based DWR treatments.
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Philippa Hill, Postgraduate researcher, School of Design, University of Leeds (UK)


**Stefan Posner, Senior Researcher, Swerea IVF (Sweden)**

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