Building knowledge about PFCs in the outdoor industry

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- Main focus area: textile and polymer chemistry concerning chemicals in articles and production.
 - o their intended uses,
 - environmental and health characteristics and risk profiles from a life cycle perspective with a certain focus on substitution in practice.
- Ongoing research into substitute hazardous chemicals with a recent certain focus on highly fluorinated substances and flameretardants.
- Other groups of hazardous chemicals have been in focus in the past.



Background Questions:

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

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" they identified a wide range of commercial uses and some of these are listed below:

- Synthesis Chemicals
- Electronics Products
- Printing Products
- Cosmetic Products
- Textile / leather impregnation
- Pharmaceuticals
- 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 very limited.
 - 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.

Only for a third of all the substances that were identified (approximately 1000 PFAS) was slightly more detailed market information 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?

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 there is no natural system that has 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 hydrofobic and oleofobic 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 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 are 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'?

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)
 - The most well-known example is PFOA that contain 7 perfluorinated carbons 0
- 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 0
 - Precursors that can degrade to the above compounds
 - Such precursors are mostly alcohols and acrylates 0

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?

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

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?

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 be 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 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 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 items that involve the degradation of highly fluorinated side chain polymers.

Category	Subcategory	Some applications	Emissions	
Salts	K+, Li+, NH ₄ +	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		
	Amines	Mist suppressant for metal plating baths	ingredients/processing aids	
	Ammonium Salts	Mist suppressant for metal plating baths		
	Amphoterics	Water/solvent repellence for leather/paper. Oil recovery		
Polymers	Carboxylates	Antistatic agent in photographic paper. Optical elements	Direct emissions as transformation/ degradation products	
	Amides	Pesticide active ingredient		
	Oxazolidinones	Waterproofing casts		
Polymers		Soil/water repellence for carpet, fabric/upholstery, apparel, leather, metal/glass	Indirect emissions as transformation/ degradation products	

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

Category	Subcategory		Some applications	Emissions
	Copolymers, esters	phosphate	fabric/unholstery apparel leather metal/glass	

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?

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 of 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 that they 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?

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 since the terminal degradation products of PFAS, namely the perfluorinated carboxylic and sulfonic acids, are extremely persistent, it becomes a question of when adverse health and environmental effects will occur beside those that have 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'?

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.,?

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?

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 <u>surfactants</u> with extremely low surface tension or <u>side chain fluorinated polymers</u> with extremely low surface energy.

Schematic figure of a PFAS molecule:

Perfluorinated tail	Spacer	Hydrophilic group
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PFAS are <u>not fluoropolymers e.g.</u> 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 being 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?

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 <u>not</u> 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 that will act as active components¹. 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 (www.supfes.eu).

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 to be less harmful to the environment and humans than the current PFAS chemistry. These efforts are still emerging and not in any way close to either pilot or 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?

There are a number of recent scientific and governmental studies that describe the hazard characteristics of 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?

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 of 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 indoor 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?

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 / is 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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Have a look at the full report: "Building knowledge about PFCs in the outdoor industry"