



PROJECT MIDWOR Deliverable A2.1

Report on the state of the art technical and environmental data of the selected conventional and alternative DWOR

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1. Introduction

In this action, a pre-screening of the technical performance and environmental impact of the selected DWOR repellents and their alternatives (Action A1) has been done, according to the available information of the products, on databases or provided directly by the manufacturer.

Action A1 provided an estimation of the chemical composition of the selected products, which has been used in this action to assess the technical performance of the materials. Both conventional DWOR and alternative products have been compared and classified according to their oleophobic and hydrophobic properties.

Regarding the environmental pre-screening, a theoretical analysis of the environmental impact of the selected materials has been performed, with the information available in scientific reviews and articles, on Internet, and also from the suppliers. Moreover, a comparison of the selected repellent finishing is done from an environmental view.

This pre-screening will help to prepare the next implementation actions, and to compare the available and current data with the results obtained in the implementation actions (Action B1 and B3). It also gives an idea of the main restriction the alternative products and conventional DWOR are submitted to.

The main problem with the pre-screening is the lack of comparative or studies results, which turn into a lack of some important data. This could provide different results as the ones expected, since the interaction between fabrics, products and process conditions is not completely known. In order to collect more data, some estimated values from manufacturers or finishers have been adopted. It is of great importance, that in Action B1 these results are previously checked, and the application is optimized depending on the fibres composition and process conditions, established by the final user.

2. Products selected

During Action A1 following conventional DWOR and alternative products were selected:

TABLE 1. PRODUCT SELECTION

Ref.	Category	Chemistry	Comments
C8_A	CONVENTIONAL	Long-chain fluorocarbon (C-8)	-
C8_B	CONVENTIONAL	Long-chain fluorocarbon (C-8)	-
C6_A	ALTERNATIVE	Short-chain fluorocarbon (C-6)	PFOA-free
C6_B	ALTERNATIVE	Short-chain fluorocarbon (C-6)	PFOA-free. Nano-dispersion of fluoropolymer
C6_C	ALTERNATIVE	Short-chain fluorocarbon (C-6)	PFOA-free dendrimer and 3D hyperbranched polymer
C6_D	ALTERNATIVE	Short-chain fluorocarbon (C-6)	PFOA-free
Sol-gel	ALTERNATIVE	Sol-gel	Sol-gel without fluorine. PFOA-Free
PFSi	ALTERNATIVE	Perfluorosilicone	Structured coating: C6 + silicone
Si	ALTERNATIVE	Silicone	Completely Fluor-free

After performing Action A1, a “sol-gel” product was selected. However, after some research it was clear that it was not a sol-gel based product, and a research is being performed in order to find a commercially available substitute which accomplishes this condition.

3. State of the art of technical data

A review has been done in order to collect the technical performance of the materials. In Table 3 the collected data is presented, including:

- Application method suitable for each material
- Conditions of the application (concentration, drying and curing products, and other products generally added to the emulsion)
- Oil repellency, following AATCC 118, before and after the washing.
- Water repellency, following AATCC 22, before and after the washing.
- Fabric substrates suitable for the product application.

As it has been said, the standards followed to characterize the different product performance are AATCC ones:

AATCC 118: Oil repellency – Hydrocarbon Resistance Test

The AATCC Oil Repellency Grade is the numerical value of the highest-numbered test liquid which will not wet the fabric within a period of 30 sec. A grade of 0 is assigned when the fabric fails the Kaydol test liquid.

AATCC Oil Repellency Grade Number	Composition
0	None (Fails Kaydol)
1	Kaydol
2	65:35 Kaydol: n-hexadecane by volume
3	n-hexadecane
4	n-tetradecane
5	n-codecane
6	n- cecane
7	n-octane
8	n-heptane

TABLE 2. STANDARD TEST LIQUIDS – AATCC 118

In Figure 1 can be seen an example of the rating criteria:

- A: Passes – clear, well-rounded drop
- B: Borderline pass – rounding drop with partial darkening
- C: Fails – wicking apparent and/or complete wetting
- D: Fails – complete wetting

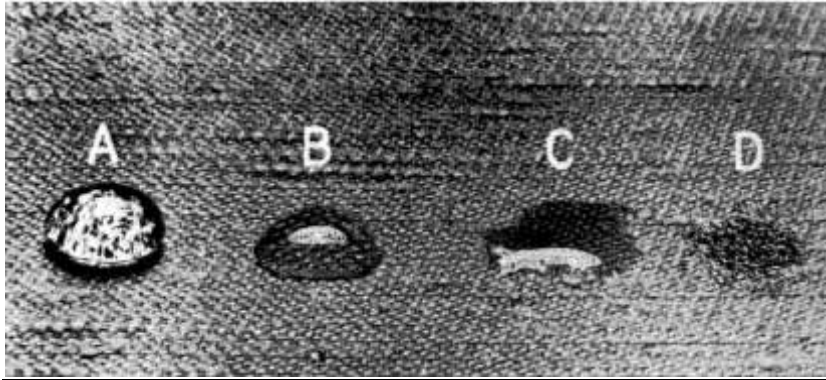


FIGURE 1. AATCC 118 GRADING EXAMPLE

AATCC 22: Water repellency – Spray test

This standard measures the resistance of fabrics to wetting by water or the water repellency of fibres. In Figure 2 are presented the Spray Test Ratings:

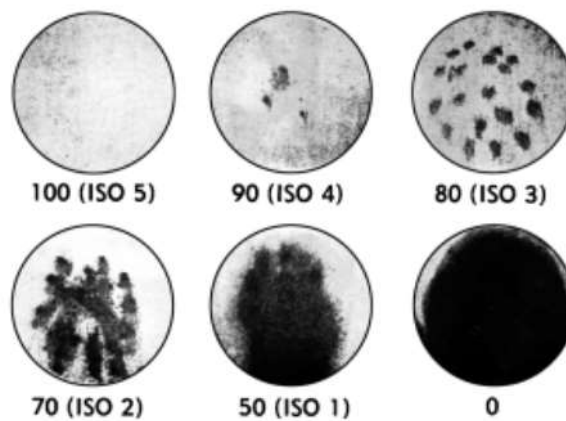


FIGURE 2. STANDARD SPRAY TEST RATINGS

- 100 (ISO 5): No wetting of the specimen face
- 90 (ISO 4): Slight random wetting of the specimen face
- 80 (ISO 3): Wetting of specimen face at spray points
- 70 (ISO 2): Partial wetting of the specimen face beyond the spray points
- 50 (ISO 1): Complete wetting of the entire specimen face beyond the spray points
- 0: Complete wetting of the entire face of the specimen

In Table 3, the collected data is presented for each product. A comparison is done between oleophobic and hydrophobic properties before and after washing process. It is also of importance, the fabric substrates onto which the product can be applied, as well as, the process conditions.



Ref.	Application	Conditions	Oil repellency (AATCC)		Water repellency (AATCC)		Fabric substrates
			B ³	A ⁴	B	A	
C8_A	Padding	40 g/L Drying: 130°C / 4 min Polymerization: 160°C / 1.5 min	8	8	90	90	All
C8_B	Spraying Foaming Padding	20-30 g/L Drying: 120°C Polymerization: 170°C / 1 min	8	8	100	100	Cotton PES
	Coating	30-60 g/L Drying: 120°C Polymerization: 150°C / 3 min	8	8	100	100	
C6_A	Padding	30-80 g/L	5	>3	90	>80	All
C6_B	Padding	30 g/L Polymerization: 165°C / 1 min	6	>4	100	>80	
C6_C	Padding	20-50 g/L	5	2 (3 cycles)	100	100 (3 cycles)	All
C6_D	Spraying Foaming Padding Coating	30-100 g/L Drying: 110°C Polymerization: 150°C / 3 min	OK		100	70 (5 cycles)	Cellulosic, polyester, polyamide, wool and aramide fibres
Sol-gel	Spraying Padding Coating						

³ Before washing

⁴ After washing



PFSi	Padding	20-80 g/L <i>Drying: 110°C / 1-2 min</i> <i>Polymerization: 170°C / 1-3min</i>	6	100		Cotton
Si	Padding	50-75 g/L <i>(with catalyst: half quantity of silicone)</i> <i>Drying: 110°C / 2 min</i> <i>Polymerization: 150°C / 1.5 min</i>	No oleoproof effect	100	90 (5 cycles)	PES Cotton

TABLE 3. TECHNICAL PERFORMANCE OF THE MATERIALS

3.1. Conventional DWORs based on long-chain fluorocarbon (C8)

C8_A product is an ecological optimized agent, water, oil and soil-repellent finish, which gives very good resistance to washing and dry cleaning. It is free of perfluorooctanoic acid (PFOA) and Alkyl phenol ethoxylates (APEO).

The product C8_B is a permanent water, oil and stain repellent finishing, specially recommended for synthetic fibres. It is approved by Bluesign, GOTS and Öko Tex.

3.2. Alternative DWOR products

The product C6_A is a high abrasion oil and water repellent for upholstery and automotive fabrics. It is durable through extended use and has no impact on fogging or light fastness. It is compliant with all four classes of Öko Tex standard 100 and Bluesign approved

C6_B product is a “PFOA free” water repellent solution C6-based finishing product for durable water and oil repellent and/or soil and stain finishing of textiles, made of synthetic and cellulosic fibres. It meets Bluesign criteria.

The product C6_C is a durable, breathable, water, oil and soil-repellent for padding all types of fibres. It is approved by Bluesign and Öko Tex.

C6_D product is a permanent water, oil and stain repellent finishing for cellulosic, polyester, polyamide, wool and aramide fibres and their blends. It is suitable for many applications, being very versatile for the following company selection in action B1.2. It is approved by Bluesign, GOTS and Öko Tex.

The product categorised as “sol-gel” based offers stain protection, and hydro- and oleophobic properties. It can be applied by spraying, rolling or foulard, being a versatile product for the posterior company selection for the implementation actions (Action B1.2). This product is used for dirt-repellent textiles and leather finishing.

However, after some research it was clear that is not a sol-gel based product, and a research is being performed in order to find commercially available alternative products, which can be industrial applicable.

The perfluorosilicone-based product provides excellent water and oil repellency to all types of fabric substrates. It is not based on C-8 fluoroalkyl compounds, resulting in a PFOA-free product. Its performance is durable through extended home laundering.

Finally, the silicone-based product is a permanent to washing and dry cleaning reactive silicone emulsion gives durable waterproof finish and softening properties to both cellulosic and polyester fabrics and their blends. On cellulosic fibres, it is generally used with thermosetting resins. It is both formaldehyde and fluorocarbon free and complies with the Öko Tex Standard 100.

4. State of the art of environmental data

According with the results from the previous Preparatory Action (A1), nine DWOR finishing products have been selected for evaluation in MIDWOR Life project (Table 1). As the environmental impact of these products it is mostly related by its chemical composition, this environmental pre-screening has been addressed by sorting the 9 DWOR products in 5 groups, according to its characteristics:

- Conventional DWORs based on long-chain fluorocarbon (C8)
- Alternative DWORs based on short-chain fluorocarbon (C6)
- Alternative DWORs based on perfluorosilicones (C6 analogues)
- Alternative DWORS non-based on fluorinated chemistry
 - SOL-GEL DWORS
 - Silicones

4.1 Conventional DWORs based on long-chain fluorocarbon (C8)

Two conventional finishing products have been selected from the survey carried out in the textile sector (Action A1. Both products base its oil and water repellent capacity on long chain fluorocarbon products.

According to supplier, one of the products is produced by monomers from telomerisation process. Thus, no Perfluorooctane sulfonic acid (PFOS) arises or accumulates as by-product. However, the product may contain smalls amounts of Perfluorooctanoic acid (PFOA) as by-product of the polymerisation process, and also detectible amounts of PFOA (ppb range) might be found in finished textiles when recommended quantities are used⁵. The other product is also composed by a perfluoroalkyl acrylic copolymer produced by telomerisation.

4.1.1. Main characteristics of C8 DWOR products

Long chain fluorinated polymers ($C_n > 7$) have been employed in many industries since 1950's (cookware, clothing, food packing, firefighting foams, paint, electronics, etc.), due to their non-stick and water repellent properties. In the textile sector, side-chain fluorinated polymers have been widely used to provide fabrics with repellency to water, oil, and stains.

C8-based DWORS have a comb-like structure with a linear bone made of C8 perfluoroalkyl chains and additional side chains responsible of conferring other properties to the polymer such film formation, linking with the fabric surface, etc. (Figure 3).

⁵ «Information on PFOS and PFOA - Rudolf GmbH».

Perfluoroalkanesulfonyl fluoride or fluorotelomer based polymers have been the base fluorinated polymers of these compounds, which were usually applied as an aqueous emulsion on the fabric to achieve a non-polar fibre modification that gives the water and oil repellent capacity to the garment⁶.

From the environmental perspective, **the main concern** raised by these DWORs is that its **fluorinated chains may be severed** from the polymeric backbone, **releasing perfluoroalkyl substances (PFAs)**. Later these PFAs will **degrade to form highly persistent perfluoroalkyl acids (PFAAs)**, such perfluoroalkane sulfonic acids and perfluoroalkyl carboxylic acids of different chain lengths⁶.

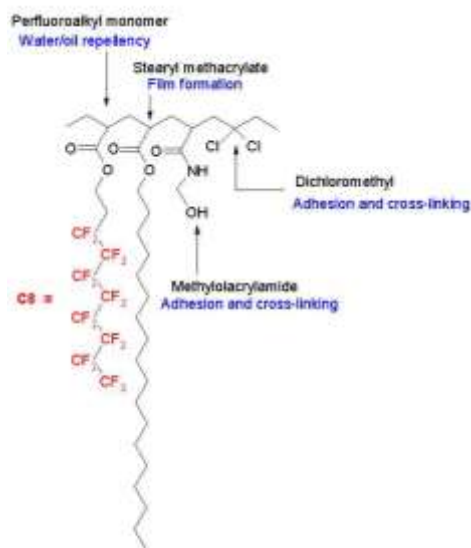


FIGURE 3. EXAMPLE OF A PERFLUOROCARBON REPELLENT POLYMER.

Among these perfluorocarbon substances (PFCs), **two groups of compounds have raised a great concern** in the past years, as consequence of their widespread presence in the environment, humans and wildlife; **perfluorinated carboxylates (PFCAs) and sulfonates (PFSAs)**. From these two families, the two most widely known PFCs are perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA)⁷.

PFOS, its salts and related compounds have been included under the Annex B of the *Stockholm convention on Persistent Organic Pollutants*, as one of the substances that countries must restrict. Also UE have limited the presence of PFOS in consumer products (<1 µg/m² in coated products).

PFOA has been classified as Substance of Very High Concern (SCHV) by the European Chemical Agency (ECHA) due to its toxicity for reproduction, persistence and bioaccumulation. This implies the need of authorisation procedure to ensure that this type of substances are properly controlled and progressively replaced by suitable alternatives as they become technical and economically available. Due to its similarity to PFOS substances, Germany and Norway proposed the inclusion of PFOA substances in the restriction list, limiting its manufacture and use in concentrations equal or greater than 2 ppb. The Risk Assessment Committee (RAC) supported on September 2015 that proposal and currently PFOA restriction is pending on the final decision by the ECHA⁸. In addition, PFOA, its salts and related compounds have been proposed for its inclusion in persistent pollutants under the Stockholm convention⁹.

⁶ Holmquist et al., «Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing».

⁷ Butt et al., «Levels and trends of poly- and perfluorinated compounds in the arctic environment».

⁸ «News - ECHA: RAC concludes on PFOA restriction».

⁹ «Chemicals proposed for listing under the Convention».

4.1.2. Environmental footprint of C8-based DWORs

Release of PFCs derivatives to the environment may occur during the whole life of the textile products, from the production of the DWORs itself to the final disposal of the garment at the end of its life.

The great stability of the C-F bond gives perfluorinated compounds the properties needed for its wide industrial applications. This stability is responsible of the **bioaccumulation of PFCs along the food chain** and its global distribution. Long range transportation and oxidation mechanisms has been wide analysed in the past to determine the potential transport pathways of these compounds, its transformations and the risk to both human health and wildlife animals (Figure 4).

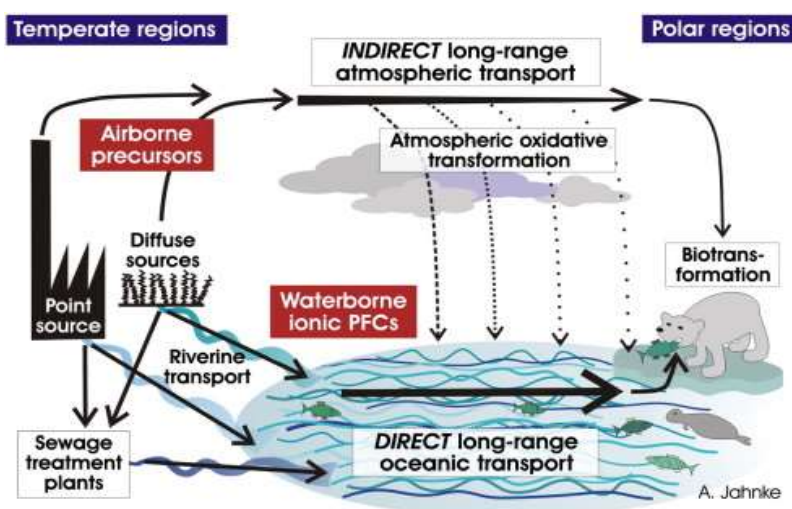


FIGURE 4. MAJOR TRANSPORT PATHWAYS OF PFCs TO THE ARCTIC¹⁰

PFCs have been reported in places such distant from the emission sources such the Arctic region. Unlike other persistent pollutants monitored in the environment, PFCs used in commercial products are not what are detected in the environment (PFCAs, PFSA, etc.). In example, PFCAs and PFSA are degradation compounds from commercial products (i.e. fluorinated phosphate surfactants) or from compounds used in the manufacture of commercial products (i.e. fluorinated alcohols and acrylates). PFOS and PFOA are the only compounds observed in the environment which has been manufactured in large quantities¹⁰.

4.1.2.1 Main sources of PFCs release to the environment

Two main emission sources can be identified as consequence of the manufacture and use of C8 based DWORs; production of the C8-fluorochemical used in the DWOR, and the emissions linked to DWOR application and garment use. Both are described and quantified below:

¹⁰ Butt et al., «Levels and trends of poly- and perfluorinated compounds in the arctic environment».

A) Emissions linked to manufacturing process

Manufacturing of PFCs has been considered the main source of PFOA and PFOS release to the environment¹¹, with an especially high impact in the regions next to the chemical factories¹². Two large-scale manufacturing techniques have been used in the fluorochemical industrial production: Electrochemical Fluorination (ECF) and Telomerisation process

- Electrochemical Fluorination (ECF)** is the oldest process. Developed by 3M in the early 50s, it has been the main source of perfluorooctane sulfonyl fluoride (POSF) and PFOA production (80-90%) until 2002. ECF involves organic hydrocarbon compounds being fluorinated with anhydrous hydrogen fluoride in an electrochemical cell¹³. ECF process is also used to manufacture perfluorooctanoyl fluoride (C₇F₁₅COF), which is further reacted to make PFOA and its salts¹⁴.
 The production of undesired branched perfluorinated C chains is one of the drawbacks of this process, which might account for over 30% of the total PFOS and PFOA production¹³.
- Telomerisation** is the other main process for perfluorinated compounds. This involves the reaction of perfluoroethylene (CF₂=CF₂) and perfluoroethyl iodide (CF₃-CF₂I) to produce straight chain perfluorinated iodides with even carbon atoms. These perfluorinated iodides are further used in the synthesis of several perfluorinated compounds without the branched or cyclic materials characteristics of the ECF process¹⁵. Currently, telomerisation is the main industrial PFC production process¹⁶.

3M was the major global producer of PFOS worldwide until 2003, when 3M voluntarily phased out its production of PFOS towards different compounds, in order to make its water and oil repellent Scotchguard® more environmental friendly. The global production of PFOS by 3M until the production ceased is estimated to have been 13.670 metric tonnes (1985 to 2002), with the largest production volume in 2000 (3.700 t)¹³. The main applications of these compounds were surface treatments for different textile products (48%), followed of paper protection (33%), performance chemicals (15%) and fire fighting foams (3%). 3M was also the world's first PFOA producer, as raw matter compound for DuPont's fluoropolymer manufacturing.

The US Environmental Protection Agency (EPA) compiled a list of **20 non-US companies** which are believed to **supply PFOS-related substances to the global market**. Of these (and excluding the plant of 3M in Belgium), six plants are located in

¹¹ 3M, «Sulfonated Perfluorochemicals in the Environment: Sources, Dispersion, Fate and Effects».

¹² UNEP, «Report of the Persistent Organic Pollutants Review Committee on the work of its second meeting. Risk Profile on perfluorooctane sulfonate».

¹³ Audenaert et al., «Fluorochemical Textile Repellents—Synthesis and Applications».

¹⁴ Buck et al., «Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment».

¹⁵ Lindstrom, Strynar, y Libelo, «Polyfluorinated Compounds».

¹⁶ Vierke et al., «Perfluorooctanoic acid (PFOA)—main concerns and regulatory developments in Europe from an environmental point of view».

Europe (4 in UE member states), six are located in Asia (of which four are in Japan) and one in Latin America¹⁷. The **total historical worldwide production of PFOS** was estimated to be **96.000 t** (or 122.500 t, including unusable wastes) between 1970-2002. with an estimated **global release of 45.250 t to air and water in that period** from and indirect sources¹⁷.

The Organisation for Economic Co-operation and Development (OECD) also compiled a list of the main PFCs producers worldwide in 2002, identifying **26 factories** (Table 4).

PFOS-compounds Producers	
Miteni S.p.A (Italy)	EniChem Synthesis S.p.A (Italy)
BNFL Fluorochemicals Ltd. (United Kingdom)	Fluorochem Ltd. (United Kingdom)
Dianippon Ink & Chemicals, Inc. (Japan)	Milenia Agro Ciencias S.A. (Brazil)
Midori Kaguka Co., Ltd. (Japan)	Changjiang Chemical Plant (China)
Tohkem Products Corporation (Japan)	Indofine Chemical Company, Inc. (India)
Tokyo Kasei Kogyo Company, Ltd. (Japan)	Fluka Chemical Co, Ltd. (Switzerland) Scientific Industrial Ass
PFOA producers	
3M Company (United States) – production ceased	Hoechst Aktiengesellschaft (Germany)
DuPont (United States)	EniChem Synthesis S.p.A. (Italy)
Exflour Research Corporation (United States)	Miteni S.p.A (Italy)
PCR Inc. (United States)	Asahi Glass (Japan)
Ciba Speciality Chemicals (Germany)	Daikin (Japan)
Clariant (Germany)	Dainippon Ink & Chemicals, Inc. (Japan)
Dyneon (Germany)	Tohkem Products Corporation (Japan)

TABLE 4. MAIN WOLDWIDE PFOS AND PFOA PRODUCERS

China is nowadays the first PFOS producer and consumer of these PFOS substances (Figure 5), and its annual production of POSF increased significantly after 3M production phased out¹⁸. Unlike trends observed in Europe and USA, PFOS concentrations has increase dramatically in some regions of the Country, while PFOA has remained relatively low¹⁹.

Germany and Japan were the leading producers and users of PFOS among developed countries in the period of 2003-2008. Metal plating along with the photographic and the semiconductor industries largely account for the high production

¹⁷ Paul, Jones, y Sweetman, «A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate».

¹⁸ Lim et al., «Emission Inventory for PFOS in China».

¹⁹ Chen et al., «A review of spatial and temporal assessment of PFOS and PFOA contamination in China».

and use of PFOS in these countries. Brazil is a rather large consumer of PFOS, mainly due to the large use of sulfuramid, an insecticide which includes PFOS in its formulation.

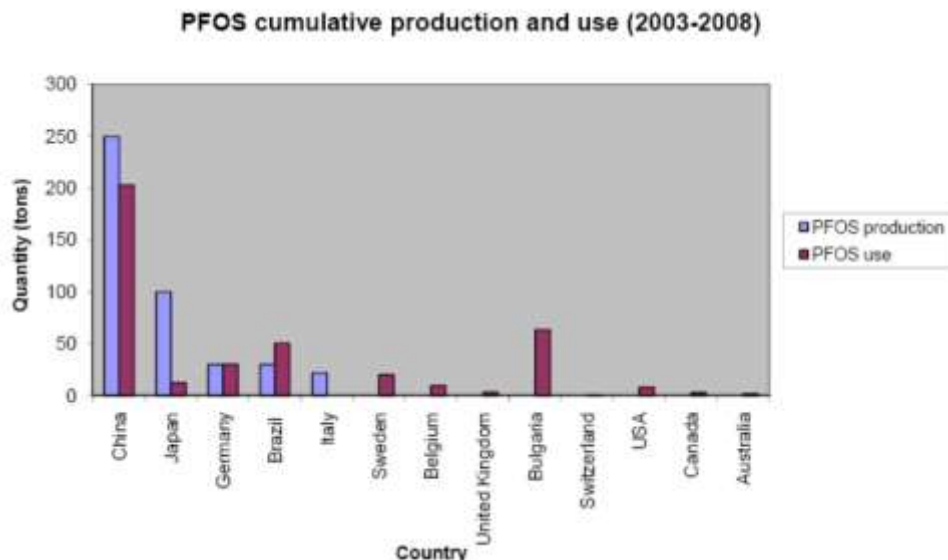


FIGURE 5. PFOS CUMULATIVE PRODUCTION AND USE (2003-2008)²⁰

High concentrations of PFCs nearby production sites are widely reported in literature. In example high levels of PFOS have been reported in wood mice collected in the immediate vicinity to 3M's fluorochemical plant in Antwerp, Belgium²¹ Also high concentrations of PFOS were found in liver and blood samples from fish collected in the Mississippi River nearby of another 3M fluorochemical plant at Cottage Grove, Minnesota²², Wuhan region (China), Tokyo Bay (Japan), and several Asian industrialized areas²³.

Due to the characteristics of the compounds and its solubility, **wastewater is the main source of PFCs pollution linked to manufacturing process**. PFCs are not fully degraded in conventional wastewater treatment plants, and its discharge to water courses and sludge are two main paths of PFC emissions. The most illustrative case of PFC emission linked to manufacturing process, and its impact on the environment was reported at Decatur (Alabama, US), where two main fluorochemical companies (3M and Daikin) are located²⁴.

In this area, both EPA and FDA (Food and Drug Administration) reported high levels of PFOA and PFOS in sewage sludge (up to 2,531 ppm), soil samples (317-408 ppb) and even at the public drinking water system of cities downstream from the 3M facility in the

²⁰ Carloni, «Perfluorooctane Sulfonate (PFOS) Production and Use: Past and Current Evidence».

²¹ Hoff et al., «Biochemical Effect Evaluation of Perfluorooctane Sulfonic Acid-Contaminated Wood Mice (*Apodemus Sylvaticus*)».

²² MPCA, «Investigation of perfluorochemical contamination in Minnesota: Phase one Report to Senate Environment Committee».

²³ Zhao, Wong, y Wong, «Environmental contamination, human exposure and body loadings of perfluorooctane sulfonate (PFOS), focusing on Asian countries».

²⁴ Renner, «EPA Finds Record PFOS, PFOA Levels in Alabama Grazing Fields».

Tennessee River²⁵. Also traces of these compounds were found in blood and tissues from selected cows/steers, and milk from farms where Decatur WWTP sludge was land applied in the past²⁵. The final cause of these high PFCs levels in the area was the use of a common wastewater treatment plant for both domestic and industrial wastewater from the industry, and the use of this sludge as fertiliser in grazing fields.

In addition to the environmental impact linked to the fluorochemical industry, **also DWOR production will lead to the release of PFCs into the environment**. DWORs are composed by a suspension of a fluorochemical compound (35-40%vol) in different chemical solvents²⁶. Production process produces waste and wastewater streams which might be an additional source of PFCs release to the environment if they are not properly managed. However comparing with the global production volumes of the fluorochemical industry, DWOR manufacturing impact might be less significant.

B) Emissions linked to DWOR application in the textile industry and treated garments.

In addition to the production of DWORs and the fluorochemicals in which are based, **textile sector** can be also considered as a source of long-chain PFC release to the environment. **Two sources** can be identified; the **finishing process where DWOR is applied** to garments, and the **loss of DWOR coating during the use of the garment**.

Most common process to provide water and oil repellency to a fabric requires the immersion of the fabric in a bath with the repellent. Then the impregnated fabric is transported to a drying senter where the product is fixed into the fabric. The use of different products, cleaning of the equipment, etc may lead to the presence of small amounts of DWORs in the wastewater produced.

PFC based DWORs have a **high toxicity for fishes**, (10-100 mg/L), **low biodegradability** and contribute with a **significant amount of organic matter** to the wastewater effluent (DBO: 400-800 mg O₂/g) due to both the fluorochemical polymers and the solvents used in its composition (isopropanol, ethanol, butanol, etc.). Thus, industrial application might have a significant impact if discharged into a water course, besides the previously discussed effects of the PFOA/PFOS emissions. PFOA and PFOS have been measured in wastewater from textile companies, despite the presence of wastewater treatment plant systems²⁷.

Another source of DWOR emission is the re-impregnation of garments with DWORs, in order to recover its initial performance. This process, limited at industrial scale to work-wear, is more common at domestic scale using DWORs which are added into the washing process or as an aerosol spray. When re-impregnation is performed at domestic scale, garments treated are expected to lose 73% of their treatment during cleaning over

²⁵ Environmental Protection Agency, «Q&A's - Soil Contamination in Decatur, AL Prepared by U.S. Environmental Protection Agency».

²⁶ «Textiles | Repel and Release Finishes | Capstone™ Fluorosurfactants».

²⁷ Choudhury, «Environmental Impacts of the Textile Industry and Its Assessment Through Life Cycle Assessment».

a 2 year life span. A loss of 34% to air can be expected from spray products during its use, while up to 12.5% may remain in the can at the time of disposal²⁸.

Most of DWOR finished garments will undergo a reduction in repellency during its life, as result of the loss of the DWOR chemical. Several mechanisms can lead to the loss of the DWOR compounds and its release to the environment (Figure 6). Rough surfaces, such cotton fabric might have a greater tendency for abrasion than synthetic fibres, leading to the loss of DWOR compound by wearing. Also the characteristics of the DWOR agent, its linkage with fibre surface, and other factors determine its loss along the use phase²⁹.

This loss of DWOR is considered as a diffuse emission source of long-chain fluorocarbons. Paul et al³⁰ estimated the diffuse emission of **PFOS in between 450-2700 t of PFOS**, primarily released into water streams through losses from stain repellent treated carpets, waterproof clothes, and aqueous fire fighting foams.

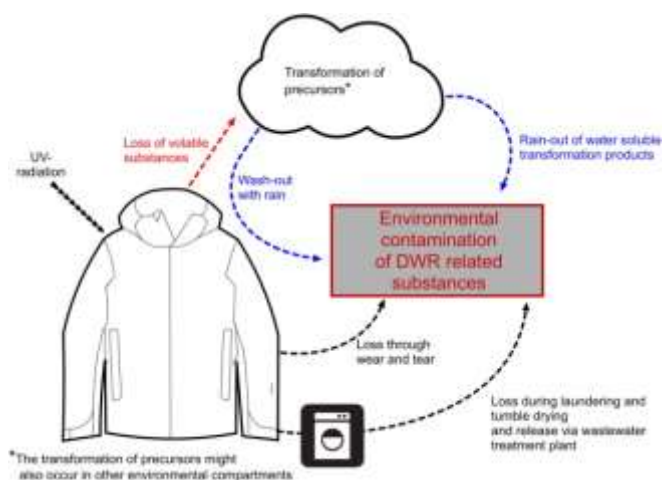


FIGURE 6. SIMPLIFIED MECHANISM OF DWOR LOSSES DURING USE PHASE²⁹

4.1.2.2 Persistence and long-range transport potential

Although there are examples of microbial catalyzed defluorination reactions³¹, neither PFOS nor PFOA are degradable under aerobic or anaerobic conditions. Some functional groups may undergo some degree of degradation, but the perfluorinated **side chain of DWORs** remains intact and it is **highly persistent**. This behaviour has been widely reported on long-chain PFCs and it may also be extrapolated to short PFCs as well³².

Long-chain PFCs does not undergo hydrolysis or other physicochemical degradation process under environmental conditions^{33,34}. Hydrolysis tests performed on PFOS

²⁸ Audenaert et al., «Fluorochemical Textile Repellents—Synthesis and Applications».

²⁹ Holmquist et al., «Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing».

³⁰ Paul, Jones, y Sweetman, «A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate».

³¹ Sha, Xing, y Jiang, «Strategies for synthesizing non-bioaccumulable alternatives to PFOA and PFOS».

³² Wang et al., «Hazard assessment of fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors».

³³ OECD, «Hazard Assessment of perfluorooctane sulfonate (PFOS) and its salts, Co-operation on existing chemicals».

³⁴ ECHA, «Member State Committee support document for identification of pentadecafluorooctanoic acid (PFOA) as a substance of very high concern because of its CMR and PBT properties».

indicated a half-life greater than 41 years for water hydrolysis and 3.7 years for indirect photocatalysis. The only known mechanism where PFOS is fully degraded is by high temperature incineration³⁵.

Persistence of PFCs is caused by the stability of the C-F bond and it is one of the key characteristics of these substances. Also it is responsible of its persistence after conventional wastewater treatment processes, which leads to its discharge in water courses, and boost its long-range transportation.

Degradation of **fluorotelomer-based acrylate polymers** have been also widely studied in different environments³⁶. Russel et al.³⁷, suggested a **half-life period** (amount of time needed for reduce its initial concentration by half) for these compounds in the range **hundreds and even thousands of years** for those with high molecular weights. In this line, PFOA hydrolytic degradation tests performed by 3M reported a hydrolytic half-life at 25°C over 92 years. Over the different condition tested, **the most likely value** for PFOA half-life degradation in the environment is estimated in **235 years**³⁴.

The perfluoroalkyl chain is one of the most hydrophobic molecular fragments known and, similarly, the anionic/acid functional groups are some of the most hydrophilic functional groups known. Thus, these acids are likely to be transported substantially in the environment by water surfaces, while the less soluble, more volatile fluorotelomer alcohols (FTOHs) are more likely to be transported via air³⁸

Due to its vapour pressure and low air-water partition coefficient, PFOS does not volatilise significantly. Therefore is assumed that its transportation in the atmosphere is bound to particles because of its surface-active properties, rather than in gaseous state. However, some PFOS precursors, such N-EtFOSE alcohol, N-MeFOSE alcohol, N-MeFOSA and N-EtFOSA are more volatile and can be widely transported through air³⁵. This compounds might eventually condense on particles present in the atmosphere or be washed out by rain³⁹.

As result of this persistence, and its chemical characteristics, PFCs are long-range transported and can be found in remote areas far from the emission sources. PFOS has been detected in rainwater, water and sediment samples collected from interior rivers to deep sea oceans, as well as in snow water from both highly developed urban areas and insulated.

Long-range transportation mechanisms are still not completely understood. It has been hypothesized that **PFOS must be globally transported via volatile precursors** which are further degraded to yield free acids. Due to its characteristics, once released to the

³⁵ UNEP, «Report of the Persistent Organic Pollutants Review Committee on the work of its second meeting. Risk Profile on perfluorooctane sulfonate».

³⁶ Holmquist et al., «Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing».

³⁷ M.H. Russell, «Aerobic degradation of fluorotelomer-based acrylic polymers».

³⁸ Jesper Kjølholt, Allan Astrup Jensen, y Marlies Warming, «Short-chain Polyfluoroalkyl Substances (PFAS)».

³⁹ 3M, «Sulfonated Perfluorochemicals in the Environment: Sources, Dispersion, Fate and Effects».

aquatic environment, PFOS will stay in the water compartment and sediment while **soil seems the main sink** for releases to air and soil⁴⁰.

Three pathways have been suggested for **PFOA transportation**; oceanic transport of the anion, atmospheric transport of primary emitted PFOA, and transport of volatile precursors which are further degraded to PFOA in the environment.

Figure 7 reflects the documented presence of several PFCs in the Arctic region, by taking air samples and from tissues from upper trophic-level animals. Most of the temporal trend studied from Northern American Arctic and Greenland shows increasing levels of PFCS from 1970, with a recent decline in PFOS levels in Canadian Arctic. In contrast, upper trophic-level animals such as seals and polar bears continue to show increasing PFOS concentrations. This inconsistency may reflect differences in emissions from source regions⁴¹.

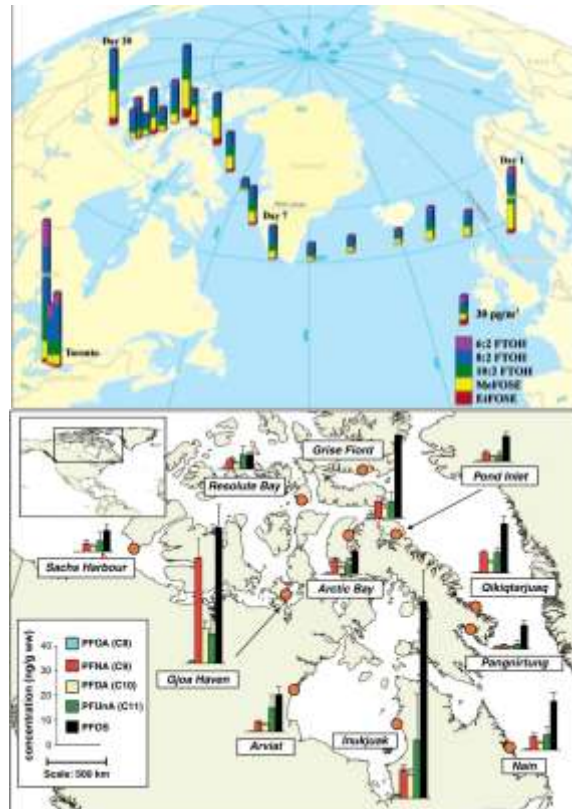


FIGURE 7. PRESENCE OF DIFFERENT PFCS IN AIR (IZQ.) AND RINGED SEAL LIVER FROM ARCTIC REGION (DCH.)⁴¹.

Based on the different characteristics of PFOA produced by ECF and Telomerisation (% of branched polymers), and the different periods where these technologies were predominant, Benskin et al.⁴² studied the origin of PFOA present in the Arctic region. The authors concluded that PFOA found in Norwegian Sea and Atlantic region was mainly “old PFOA” from 3M process, while PFOA found in Eastern US coast and Canadian Archipelago was contemporary sources, attributed mainly to PFOA emissions currently produced in Asia or the atmospheric transport and oxidation of contemporary PFOA-precursors⁴².

⁴⁰ Lassen et al., «Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances».

⁴¹ Butt et al., «Levels and trends of poly- and perfluorinated compounds in the arctic environment».

⁴² Benskin et al., «Manufacturing Origin of Perfluorooctanoate (PFOA) in Atlantic and Canadian Arctic Seawater».

4.1.2.3 Impact over water sources

Given its water solubility and negligible vapour pressure, water **and sediments are considered as the final sinks of PFCs in the environment**. In addition, it is known that oceans and rivers play a key role in the long-range transportation of PFCs around the world⁴³.

Wastewater from both industrial and domestic sources has been suggested as the main source of PFAS to aquatic ecosystems, as it is globally accepted that PFOA and PFOS are not degraded in conventional wastewater treatment processes. Also **landfills** have also been pointed as a significant source of PFCs to water bodies, as well as the **application of sewage sludge** as fertiliser in agricultural soils⁴⁴.

Assessments performed by different Public Health organisms shows that PFOA exhibits **moderate to low toxicity in traditional acute studies with aquatic species** such as fish (LC₅₀ ranging from 70-2470 mg/L) and in general PFOS appears to be about **10 times more toxic to aquatic organisms than PFOA**⁴⁵. Experimental evidence shows a higher bioaccumulation of PFOA in aquatic mammals, suggesting that gills might provide an additional mode of elimination of PFOA than air-breathing organism does not have. However, studies with other aquatic organisms such as freshwater male tilapia, marine mussels and Baikal seals showed **negative effects over water biodiversity**, such estrogenic effects, hepatotoxicity, inflammation, and chemosensitivity⁴⁶. Also **fish** has been pointed out as **one of the main sources of human exposition to PFCs through the food chain**.

⁴³ UNEP, «Report of the Persistent Organic Pollutants Review Committee on the work of its second meeting. Risk Profile on perfluorooctane sulfonate».

⁴⁴ Pistocchi y Loos, «A Map of European Emissions and Concentrations of PFOS and PFOA»; Pim de Voogt, «Perfluorinated Organic Compounds in the European environment (PERFORCE). Final Scientific Report»; Hansen et al., «Quantitative Characterization of Trace Levels of PFOS and PFOA in the Tennessee River».

⁴⁵ John Jensen, «Risk evaluation of five groups of persistent organic contaminants in sewage sludge.», 201.

⁴⁶ Government of Canada, «Archived - Environment and Climate Change Canada - Draft Screening Assessment Perfluorooctanoic Acid, Its Salts, and Its Precursors».

The FP6-PREFORCE Project evaluated the concentration of **four different PFCs** (PFHx, PFHpA, PFOA, and PFNA) in **14 European rivers**. Danube and Rhine watersheds are the main sources of these compounds arctic Due to the negligible retention of PFOA and PFOS in solids, authors estimated the annual emissions of these compounds in 10, 2 and 20 tons of PFHxA, PFHpA, and PFOA respectively⁴⁴. The final report concludes that **levels of PFOS in water sediments have increased from 1990 to 2005, pointing WWTP as the main source** of PFOS and PFOA to the environment.

Another estimation of the global emissions of PFOA/PFOS compounds into European rivers was performed by Pistocchy et al⁴⁴. The authors estimated PFCs discharges into the European water courses and coastline in **20-30 tons per year**, mostly emitted from wastewater treatment plants from both industrial and domestic origin. As Figure 8 shows, **greater emissions are located in the course of the main rivers** (Danube, Rhine, etc.) and industrial areas.

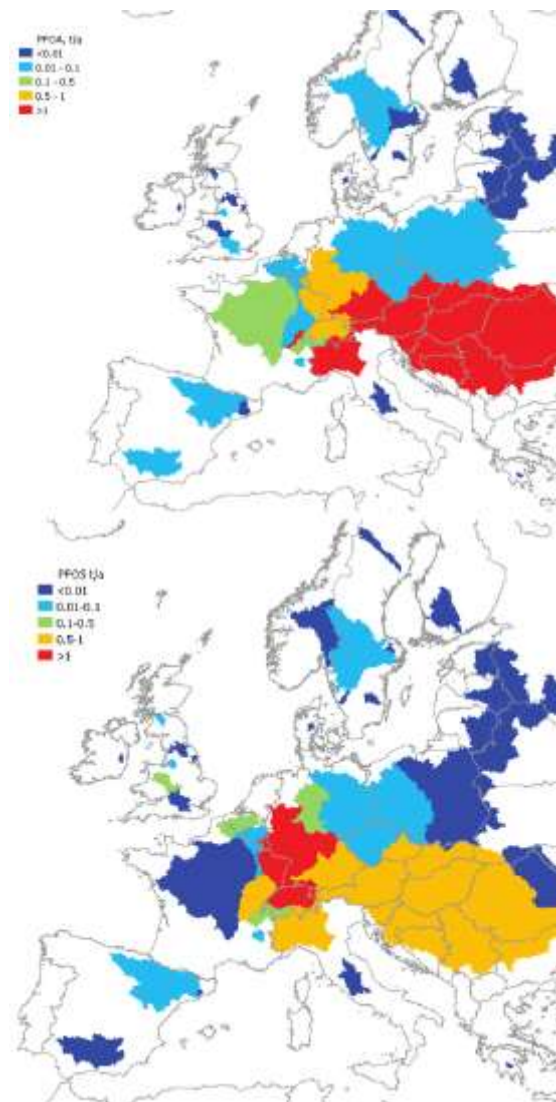


FIGURE 8. EMISSIONS OF PFOA AND PFOS FOR MONITORED CATCHMENTS IN EUROPE⁴⁴.

4.1.2.4 Ecotoxicity and bioaccumulation

Bioaccumulation of PFCs and its potential toxicity is one of the greatest concerns involving the use of C-8 DWORs and long-chain fluorochemicals.

First relevant tests to evaluate bioaccumulation and toxicity of PFCs were internally addressed by 3M and DuPont, between 1961 and 1981. These studies reported the presence of PFOA in workers blood, showing evidence of serious health problems such liver damage in workers and birth defects in children.

Bioaccumulation and toxicity of PFCs have been widely tested during the last decades. These tests have shown a different pattern of bioaccumulation, comparing with other persistent pollutants. **PFOA and PFOS binds to proteins** and not to lipids, so accumulation occurs mainly in blood, organs (liver and kidney) and muscle but not in lipid tissues. Despite of differences found between tests, it is globally accepted that **aquatic animals are less affected** by PFOA, which is quickly excreted by gill

permeation. Thus fishes are not considered a relevant endpoint of this substance. In contrast, **air-breathing homeotherms are unable to eliminate PFOA**⁴⁷ and PFOS/PFOA levels in different tissues have been widely reported, **increasing with its position in the food chain**. Bioaccumulation along the trophic chain has been also reported in areas where PFOA contaminated sludge was used as fertilizer, such in Decatur's PFCs contamination episode.

The **highest concentrations of PFOS** are characteristically observed in **high trophic level organisms**, indicating that PFAs may have also a significant bioaccumulation potential. Sulfonates bioaccumulated to a greater extent than carboxylates of equivalent perfluoroalkyl chain length, indicating that the acid function must be considered⁴⁸. **PFOA is ubiquitously present in terrestrial top predator species**, even those from remote areas, such Arctic region, indicating the bioaccumulation potential of PFOA.

Bioaccumulation in humans shows similar patterns than in animals, with highest concentrations found in lungs, kidneys, liver and blood. Elimination rates for people highly exposed to PFOS/PFOA such workers, have been reported to range between 2 and 4 years.

Olsen et al.⁴⁹ also reported the presence of **eleven perfluorinated alkyl acids (PFAAs)** in plasma from a total of 600 American Red Cross adult blood donors between 2000 and 2010. Results showed a decline of PFOS over 76% and 48% for PFOA, as suggested consequence of the phase-out period in the United States. In contrast, PFOS and PFOA concentrations in human serum reported in China shows an increasing trend, as result on the displacement of PFC production and use from US to China⁵⁰. The **halving time** (time needed for decrease of the concentration of these compounds in blood by half) was approximately 4.3 years.

A number of modeling studies have suggested food contamination as the responsible of the human exposure to PFCs in non industrialized areas. Sea fish and other seafood may account for the majority of human exposure. Also crops grown in contaminated soils can accumulate PFCs and might be another source of human exposure⁵¹.

⁴⁷ ECHA, «Member State Committee support document for identification of pentadecafluorooctanoic acid (PFOA) as a substance of very high concern because of its CMR and PBT properties».

⁴⁸ Martin et al., «Dietary Accumulation of Perfluorinated Acids in Juvenile Rainbow Trout (*Oncorhynchus Mykiss*)».

⁴⁹ Olsen et al., «Temporal Trends of Perfluoroalkyl Concentrations in American Red Cross Adult Blood Donors, 2000–2010».

⁵⁰ Lim et al., «Emission Inventory for PFOS in China»; Choudhury, «Environmental Impacts of the Textile Industry and Its Assessment Through Life Cycle Assessment».

⁵¹ Lindstrom, Strynar, y Libelo, «Polyfluorinated Compounds».

4.2 Alternative DWOR products

As consequence of the increasing concern of the negative effect of long-chain PFCs over human health and environment, an industrial transition started in 2000s decade aiming to replace long chain fluorochemical in water and oil repellent coatings.

Current tendency is to replace this C8-fluorocarbon chemistry by **short-chain fluorocarbon products** (C6 or C4) or even **fluorine-free water repellents**. In fact, several chemical industries already switched to these short-chain PFCs in its commercial products (i.e. based in C4 fluorocarbons). In addition to these products, other alternatives based on natural compounds have been also developed, such paraffin waxes, silicones, dendrimers and inorganic nanoparticles.

Besides the performance of these alternative DWORs and its feasibility for industrial scale application, the environmental impact of these new compounds must be addressed in order to ensure that they do not represent a similar threat than those compounds aiming to replace.

According to the selected DWORs in Action A.1.1, next section will evaluate the environmental impact of the alternative finishing products according on its chemical composition.

4.2.1 Short Chain (C6) fluorocarbon based DWORs

As mentioned before, short-chain DWORs are the **most extended alternatives to the conventional PFCs**, due to its higher performance and superior surface-active⁵² properties comparing with other alternatives in both water and oil repellency.

According to the review on the state of the art and the survey performed in the textile sector, four PFOA-free C6 based DWORs will be evaluated in MIDWOR-LIFE project.

Besides the different characteristics of those products, which will lead to different performances and application methods, **all four products are based in C6 fluorocarbon chemistry**, which will be the key factor when analyzing its impact in the environment. Thus, the environmental pre-screening will focus on short-chain PFC chemistry from a comprehensive perspective.

4.2.1.1 Main characteristics of short chain (C6) DWORS

As mentioned before, the most extended alternatives to PFOS and PFOA at present are other fluorinated chemicals with shorter chain length (four to six carbons), due to its higher performance and durability in garments. The most important short-chain perfluoroalkylsulfonic acids are **perfluorobutane sulfonic acid** (C4, **PFBS**) and **perfluorohexane sulfonic acid** (C6, **PFHxS**), which also exist as various salts. The only difference to PFOS is the shorter perfluorinated chain (*“tail”*).

As in PFOS, these short chain alternatives have many derivatives. Among the perfluorocarboxylic acids (PFCAs), the main short-chain alternatives are perfluorobutanoic acid (PFBA) and perfluorohexanoic acid (PFHxA) and their

⁵² Jesper Kjølholt, Allan Astrup Jensen, y Marlies Warming, «Short-chain Polyfluoroalkyl Substances (PFAS)».

derivatives⁵². Production and uses of short chain fluorocarbons have increased since 2000s, and it is estimated that **in the next 5-10 years annual consumption of PFHxS and its derivatives will surpass the 1,000 tons**⁵³.

Despite **toxicity of PFCs have been proved to decrease with carbon chain length**, its similar composition and structure, combined with its similar persistence in the environment has raised concerns regarding its safeness as alternative to long-chain PFCs.

4.2.1.2 Environmental Impact of short-chain (C6) DWORs

Short-chain perfluoroalkyl acids have been reported to be **less bioaccumulative and toxic** than its long chain alternatives. However they may **still** have hazardous properties such **persistence, bioaccumulation and long-range transport potential**, and thus may pose risk to human health and environment⁵⁴.

Short chain PFCs, as happens with its long-chain homologues, are not degraded neither by abiotic mechanisms (such hydrolysis, photolysis, etc.) or biological processes. Degradation process follow a similar scheme to long-chain PFCs, with a primary degradation of the functional group, leaving the highly persistent perfluorinated backbone intact⁵². Several studies suggest that **short chain perfluorinated acids are nearly as persistent as long-chain homologues**⁵⁴.

Due to its higher solubility, short-chain PFAS have shown a **higher long-range transportation potential in water bodies than its long-chain homologues**⁵⁵. ENVIRON assessment on short-chain PFAS⁵⁶ reported the presence of 6:2 FTOH in remote environments, as well as the presence of PFHxA, a transformation product. It has been reported that short-chain are predominantly found dissolved in water bodies, while long-chain PFAS appeared to bind more strongly to particles.

Despite there is less studies regarding the emission of short-chain PFCs, **elevated levels of these compounds have been measured** in water bodies around the world. PFBS and/or perfluorobutanoic acid (PFBA, an impurity in PBSF-based derivatives) have been monitored in water samples from the Rhine watershed⁵⁷, and also in the

⁵³ Wang et al., «Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFASAs) and their potential precursors».

⁵⁴ Wang et al., «Hazard assessment of fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors».

⁵⁵ Jesper Kjølholt, Allan Astrup Jensen, y Marlies Warming, «Short-chain Polyfluoroalkyl Substances (PFAS)».

⁵⁶ ENVIRON, «Assessment of POP Criteria for Specific Short-Chain perfluorinated Alkyl Substances. Report prepared for FluoroCouncil, Washington, DC. Project Number: 0134304A».

⁵⁷ Lange et al., «Occurrence of Perfluoroalkyl Sulfonates and Carboxylates in German Drinking Water Sources Compared to Other Countries»; Möller et al., «Distribution and Sources of Polyfluoroalkyl Substances (PFAS) in the River Rhine Watershed».

German coast⁵⁸, Tokyo Bay in Japan⁵⁹, and Northwest Pacific Ocean⁶⁰, indicating an **increase in the use and release of PFBS and other short-chain PFCs**⁶¹.

It is globally accepted that toxicity of PFCs increases with its fluorocarbon chain length, and thus **short-chain PFCs are less harmful than C8-C10 compounds**⁶². However, toxicity it is also related with the functional group of the fluoropolymer. Thus **sulfonic acids (PFSA) are more bioaccumulative than carboxylic acids (PFCA)** of the same carbon chain length⁶³. As result of these, 6:2 FTOH has shown a higher endocrine disrupting effect in animals than the longer chain 8:2 FTOH⁶⁴. Several authors point out that, despite its low environmental degradation rate, **bioaccumulation potential of short-chain PFCs are significantly lower than long chain homologues**⁶⁵. In this line, short-chain PFCA have a **low biomagnifications potential in food webs** comparing with the conventional alternatives⁶⁶.

Among the different short-chain PFCs developed to replace C8 chemistry, some producers in China and Italy have initiated the production of perfluorohexane sulfonyl fluoride (PH_xSF, C₆F₁₃SO₂F)-based derivatives as alternatives in surface treatment products. **PFH_xS**, has been pointed to have a **similar toxicity than PFOS/PFOA, considered also as an long chain PFSA precursors**⁵³.

There is a general data gap over toxicological and environmental effects of short-chain PFAS. Often results are based in conclusions extrapolated from the long-chain PFCs, far more studied. **Short-chain PFAS have shown to have shorter half-life and higher elimination rates** than its long-chain homologues⁶⁷. **Acute toxicity also have been observed to be lower, except for PFH_xS**. Renal elimination is the main mechanism for PFAA elimination from the body for both short and long chain PFCs.

The relative high concentrations of short chain PFHAs in human tissues observed (specially PFBA)⁶⁸, suggest that **bioaccumulation and elimination routes may**

⁵⁸ Ahrens et al., «Sources of Polyfluoroalkyl Compounds in the North Sea, Baltic Sea and Norwegian Sea».

⁵⁹ Ahrens et al., «Distribution of Polyfluoroalkyl Compounds in Water, Suspended Particulate Matter and Sediment from Tokyo Bay, Japan».

⁶⁰ Cai et al., «Occurrence of Perfluoroalkyl Compounds in Surface Waters from the North Pacific to the Arctic Ocean».

⁶¹ Barmentlo et al., «Acute and chronic toxicity of short chained perfluoroalkyl substances to *Daphnia magna*».

⁶² Buhrke, Kibellus, y Lampen, «In vitro toxicological characterization of perfluorinated carboxylic acids with different carbon chain lengths»; Ding et al., «Acute Toxicity of Poly- and Perfluorinated Compounds to Two Cladocerans, *Daphnia Magna* and *Chydorus Sphaericus*».

⁶³ Ding y Peijnenburg, «Physicochemical Properties and Aquatic Toxicity of Poly- and Perfluorinated Compounds».

⁶⁴ Liu et al., «Waterborne Exposure to Fluorotelomer Alcohol 6».

⁶⁵ Lassen et al., «Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances»; Zhou et al., «Occurrence and Transport of Perfluoroalkyl Acids (PFAAs), Including Short-Chain PFAAs in Tangxun Lake, China».

⁶⁶ Ding y Peijnenburg, «Physicochemical Properties and Aquatic Toxicity of Poly- and Perfluorinated Compounds».

⁶⁷ Chang et al., «Comparative Pharmacokinetics of Perfluorobutyrate in Rats, Mice, Monkeys, and Humans and Relevance to Human Exposure via Drinking Water».

⁶⁸ Pérez et al., «Accumulation of perfluoroalkyl substances in human tissues».

significantly differ between humans and laboratory animals, as result of differences in its renal function. Human toxicity of DWOR based on short-chain PFCs will be addressed in Action B2.

Thus, review on the state of the art of DWORs based in long and short chained fluoropolymers suggest that **products based on C4 and C6 chemistry are less harmful for both environment and human health**. However, further research must be addressed to ensure the harmlessness of these products and those generated on its partial degradation. In addition, fluorine-free DWORs may become a safer alternative if better performances are achieved.

4.2.2 Alternative DWORs non based on fluorinated chemistry

4.2.2.1 SOL-GEL based DWOR

Sol-Gel process consists in the production of inorganic networks by the hydrolysis of a metallic oxide precursor. A colloidal suspension (sol) is formed that gels to form a continuous network on the textile surface which gives the garment stain and water repellency. Organosilicones are a wide used precursor of a sol.

Currently **sol-gel is one of the most relevant emerging technologies in the textile industry**, due to its potential application to produce **functionalized fabrics** such, UV protection, antibacterial, flame retardant, water repellency and self-cleaning properties. **Sol-Gel is expected to lead the production of these types of garments**, due to its low cost, use of less chemicals and thus less environmental impact⁶⁹.

Regarding DWOR finishing, silica nanosols containin perfluoroalkyl compounds has been used to achieve ultrahydrophobic, oleophobic and soil repellent functional properties. Later, non-fluorinated nanosols based on long-chain alkylsilane additives have been used to avoid the environmental impact of PFCs⁶⁹.

Environmental Impact of SOL-GEL based DWORs

Overall **environmental impact of sol-gel DWORs is considered low** compared with perfluorocarbon-based DWORs (both long and short-chain). Only when **sol-gel includes perfluoroalkyl compounds**, may be considered harmful for the environment, as perfluorinated chains can be severed from the sol-gel structure, acting as long-chain PFSA precursors in the environment.

Sol-gel DWOR selected in MIDWOR is fluorine-free, and thus there is not significant impact over the environment, animals or human health as result of its application.

⁶⁹ Ismail, «Sol-gel Technology for Innovative Fabric finishing—A Review».

4.2.2.2 Silicon based DWOR

Silicon based DWORs are composed by a polydimethylsiloxane (PDMS) backbone. The hydrophobic methyl groups on the siloxane backbone will orientate away from the fibre surface fabric, while the fibre bonding is realised between the hydrophilic Si-o-Si chain and polar surface groups⁷⁰.

Environmental Impact of silicone based DWORs

Silicone base DWORs have been **pointed out as one of the most environmentally friendly alternatives** for achieves water repellency of fabrics⁷⁰. Only the presence of residual cyclic siloxanes, and the presence of solvents in its composition may suppose an hazard for the environment or human health.

Residual cyclic methyl siloxanes are considered the main environmental hazard of Fluor-free silicone based DWORs⁷⁰. Various silicone DWORs have shown to contain residual levels of cyclic volatile methyl siloxanes such octamethylcyclotetrasiloxane (D4) or decamethylcyclopentasiloxane (D5) in concentrations that may range between 400 and 3.300 ppm, as consequence of the formation of DWORs of high molecular weight based on silicones. However the **hazard of these compounds it is not clear**, and they can also being found in personal care products (such as cosmetic products and skin- and hair-care products), and household/industrial cleaning products.

Moreover, residual levels of D4 or D5 found as result of application of silicon based DWORs should evaporate during the curing stage in the fibre treatment, thus its presence in the finished garment should be lower⁷⁰.

Studies on PDMS polymers showed a relatively fast depolymerisation process which leads to biodegradable compounds. According to the Risk evaluation performed by the UK Environment Agency, **no risks were identified from production and uses of D5 for the air, water soil or humans exposed** via the environment. Gravier et al.⁷¹ also conducted studies on PDMS degradation, concluding that most of these cyclic compounds ends up in the soil as result of the application of sludge from wastewater treatment plant as fertiliser. In the soil PDMS undergoes depolymerization through cleavage of the siloxane bonds to yield low molecular weight silanols. These silanols are sufficiently volatile to be transported into the atmosphere, where they are degraded by hydroxyl radicals to yield silica, water and carbonyl compounds. The rate of degradation of these compounds in upper atmosphere is 10-30 days, while in dry soil is faster (4-7 days).

The presence of other chemicals in the DWOR formulation may have also a relevant impact, depending on the type of compound and its composition. In example, the selected silicon-based DWOR contains Polyethoxylated aliphatic alcohol, and Isothiazol, which have a moderate toxicity to the aquatic environment.

⁷⁰ Holmquist et al., «Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing».

⁷¹ Graiver, Farminer, y Narayan, «A Review of the Fate and Effects of Silicones in the Environment».

4.2.2.3 Perfluorosilicon-based DWORs

Perfluorosilicones are alternative finishing products based on a **polydimethylsiloxane (PDMS)** backbone where **methyl groups have been replaced by fluoroalkyl acrylate copolymers** in order to improve its oil repellency⁷². These products improve the performance of silicon based DWORs, adding the repellency to oil.

Environmental Impact of Perfluorosilicon-based DWORs

Perfluorosilicone DWORs are based in the structural modification of a silicone polymer (PDMS) by a **fluoroalkyl** chain. Thus, despite it is not classified as a short-chain fluorocarbon, it **supposes a similar threat to the environment**.

Most perfluorosilicon DWORs include C6 perfluoroalkyl chains, which will eventually be released to the environment as the silicon backbone is degraded. Despite the amount of PFHxS which might be released to the environment is significantly lower than in short-chain DWORs, Perfluorosilicones must be also considered as a source of long chain PFSA precursors in the environment, as described in section 4.2.1.

⁷² Holmquist et al., «Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing».

5. Discussion

After doing a pre-screening of the technical performance and environmental impact of the selected DWOR repellents and their alternatives, it can be seen that the longer the chain, the better the oleophobic and hydrophobic properties.

In all the cases, good oleophobic properties result into good hydrophobic properties. However, in the opposite direction is not always true, since a fluorocarbon is needed for oleophobic properties, and silicones are presented as completely fluorine-free alternatives. As a result, these silicone-based products do not have acceptable oleophobic properties.

During the pre-screening, PHOA-free products have been widely mentioned, but it is important to take into account that this does not mean that are completely PFOA free, but they have a lower quantity than the one limited by law. This is the reason why nowadays C6 are the best alternative.

According to the information reviewed, short-chain fluorocarbon based DWORs are the finishing products which raise a greater concern for both environment and human health, among the different reviewed products. Due to its chemical composition, short-chain DWORs have a similar persistence, long-range transportation and bioaccumulation risks than conventional C8-based DWORs.

However, there is still lack of specific studies over these compounds, and many environmental assessments performed extrapolate conclusions from C8-based compounds, much deeper studied. Still, there is an overall agreement pointing out that C6-fluorocarbons have lower toxicity, higher elimination rates and lower biomagnification across the food chain. This fact, together with its higher performance as finishing agent compared with other alternative products, sets these compounds as the most available substitute to C8-DWORs at present.

With the only exception of perfluorosilicon-DWORs, all the remaining alternative DWORs selected in MIDWOR-Life are PFOA-free and do not arise any significant environmental hazard. Moreover, unlike fluorinated compounds, sol-gel and silicon based DWORs are completely degraded in wastewater treatment systems.

6. Recommendations

It is important to check during B1 and B2 actions the technical and environmental results, since they could not be very exact.