PFAS in “European Law and Industry” – current and future challenges

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Short about Stefan Posner and Swerea IVF

Stefan Posner

Polymer and textile chemist with over 30 years experience in research on chemicals in textiles and polymeric materials in cooperation with international companies, authorities and academia in several international projects over the years. Stefan is since many years working with legal preparatory work on chemicals for UNEP Stockholm Convention, EU Commission and several National Authorities and is deeply involved in research to substitute hazardous chemicals with a recent certain focus on highly fluorinated substances and flame retardants but other groups of hazardous chemicals have been in focus in the past.

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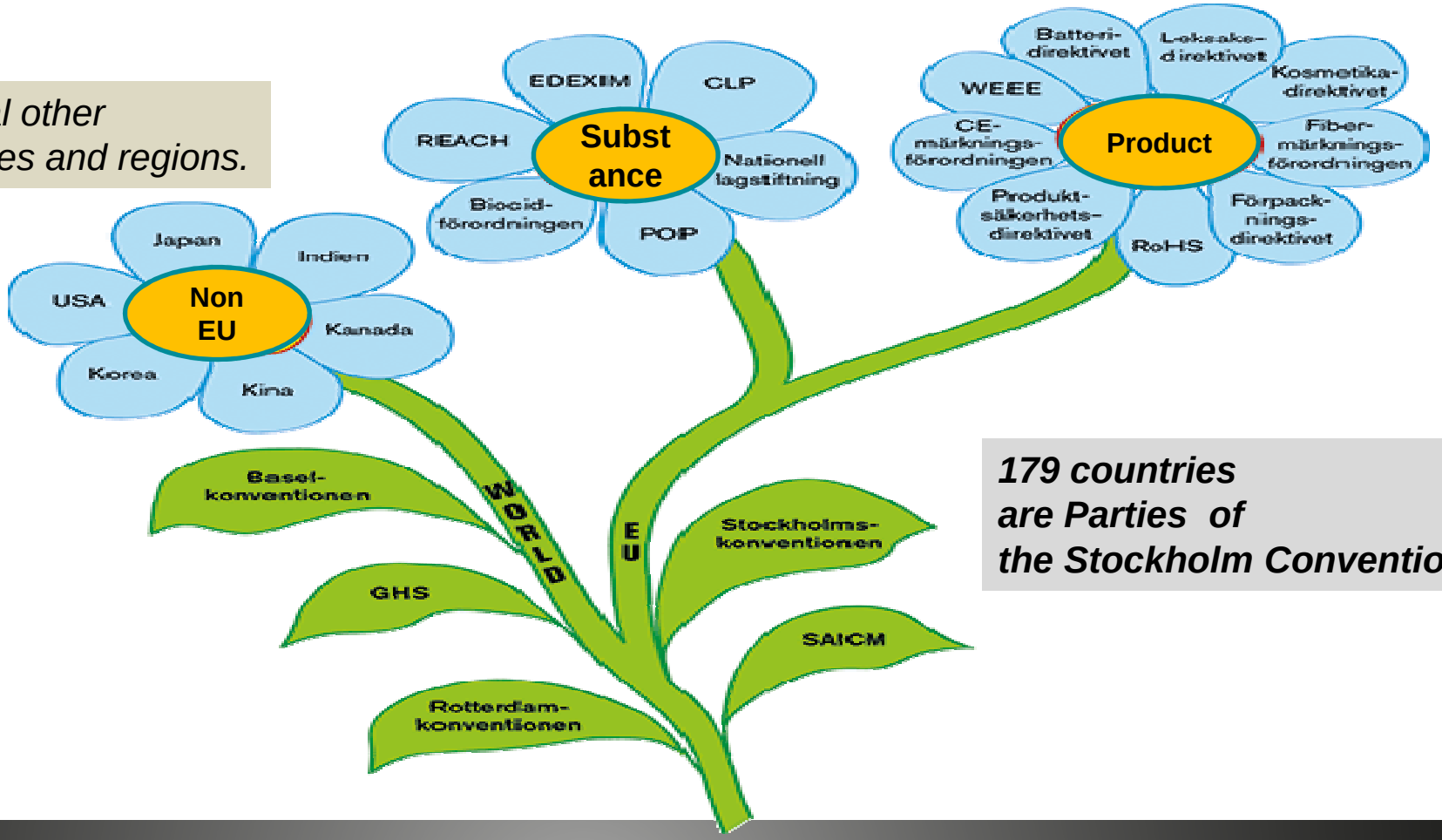
Binding International Conventions and Regulations

Several other countries and regions.



179 countries are Parties of the Stockholm Convention

Substances eliminated (Annex A) or restricted (Annex B) under the Stockholm Convention are called POPs

- **POP** is an abbreviation for **P**ersistent **O**rganic **P**ollutants and have the following characteristics

- Highly toxic to humans and the environment
- Persistent in the environment, resisting bio-degradation
- Taken up and bio-accumulated in terrestrial and aquatic ecosystems
- Capable of long-range, transboundary atmospheric transport and deposition

Criteria for certain hazardous substances of very high concern in EU.

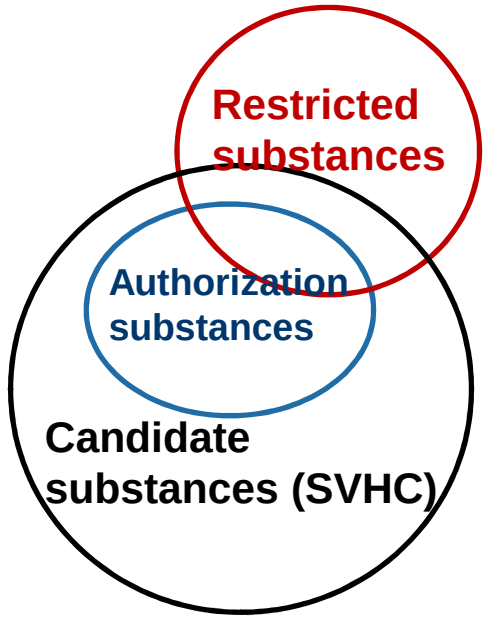
a) Carcinogenic (Category 1a & 1b)

b) Mutagenic (Category 1a & 1b)

c) Reproductive toxic (Category 1a & 1b)

d) Persistent and Bioaccumulative and Toxic* (PBT)

e) Very Persistent and very Bioaccumulative (vPvB)



f) Substances (P B or vPvB) but that are not toxic in the manner specified in d) but leading to a corresponding concern for which there is scientific evidence of probable serious effects to human health or the environment. (include endocrine toxic (ED) and allergenic)

** With toxic refers to both acute toxicity and chronic toxicity.*

Current legal PFAS status - International Conventions and EU Regulation (April 2015)

Fluoro chemicals (PFAS)	Abbr.	CAS RN	Norway	REACH candidate List (SVHC)	REACH annex XVII	EU POP Regulation	Stockholm convention
Perfluorooctane sulfonic acid and related substances	PFOS	1763-23-1				X	Restriction annex B
Perfluorohexane sulfonic acid	PFHxS	108427-53-8					Pending
Perfluorooctanoic acid and related substances	PFOA	335-67-1	Restricted *(PFOA and 7 related substances)*		Restriction proposal		Proposal
Pentacosafluorotridecanoic acid	PFTrDA	72629-94-8		X			
Tricosafluorododecanoic acid	PFDoA	307-55-1		X			
Henicosafluoroundecanoic acid	PFUnA	2058-94-8		X			
Heptacosafluorotetradecanoic acid	PFTA	376-06-7		X			

Strong international trend to less harmful DWR alternatives switch over.

- There is an international voluntary phase out of long chain flurotelomers and the related perfluorinated carboxylic acids (incl. PFOA) by the end of 2015.
- If the phase out is not performed, additional international regulatory actions taken in 2014 and 2015.
- Usage has now moved towards more short-chain molecules where human and ecotoxicity is still largely unknown, but there are indicators of their potential hazards to humans and environment.
- Non fluorinated alternatives are known to replace fluorochemicals for water repellent properties, but there is concern and still data gaps on their health and environmental characteristics.

Stockholm Convention
PFOS and related substances

- The production and use of perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF), hereafter called PFOS, should be eliminated by all parti… …ed as acceptable purposes and s… …B to the Conventio…

- Eva… …d sp… er…
  - …
  - Info…
  - Informa…
  - Information o… …reliance on such alternatives.

- The evaluation shall take place no later than 2015 and every four years thereafter in conjunction with regular meetings of the Conference of the Parties.

Global intention to eliminate PFOS and related substances

Acceptable purposes and specific exemptions for PFOS and related substances in the Stockholm Convention (SC) Annex B (April 2015)

Acceptable purposes	Specific exemptions
A. Photo-imaging B. Photoresist and anti-reflective coatings for semiconductors C. Etching agent for compound semiconductors and ceramic filters D. Aviation hydraulic fluids E. Metal plating (hard metal plating) only in closed-loop systems F. Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters) G. Fire fighting foam H. Insect baits for control of leaf-cutting ants from genus Atta *spp.* and *Acromyrmex spp*	1. Photo masks in the semiconductor and liquid crystal display (LCD) industries 2. Metal plating (hard metal plating) 3. Metal plating (decorative plating) 4. Electric and electronic parts for some colour printers and colour copy machines 5. Insecticides for control of red imported fire ants and termites 6. Chemically driven oil production 7. Carpets 8. Leather and apparel 9. Textiles and upholstery 10. Paper and packaging 11. Coatings and coating additives 12. Rubber and plastics

Currently allowed uses for PFOS and related substances in EU (April 2015)

Allowed uses (March 2015) in EU/EEA according to Regulation (EC) No 850/2004 and its amendments	Acceptable purposes and specific exemptions for PFOS, its salts, and PFOSF according to Annex B of the Stockholm Convention.
Photoresists or anti photolithotogra	nti-reflective coatings for nductor and dustries
Hydrau	
Photogra papers, or p	
Mist suppressants f chromium plating in closed	metal plating) only in p systems
No corresponding use	Metal plating (decorative plating)

PFOS and related substances are banned in EU but may be in textile articles as contaminants or intentionally used in third countries outside EU

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Stockholm Convention
PFOA and its compounds

- The European Commission will issue an Annex D screening dossier for PFOA and its compounds for possible inclusion in Annexes A, B or C of the Stockholm Convention.

- The screening dossier should be submitted to the Secretariat of the Stockholm Convention in May 2015.

The first proposal by Germany and Norway on restriction of PFOA and related substances in the EU under REACH Annex XVII

Perfluorooctanoic acid (PFOA, CAS 335-67-1, EC 206-397-9), including its salts and any other substance having linear or branched perfluoroheptyl derivatives with the formula C_7F_{15}- as a structural element, including its salts except those derivatives with the formula C_7F_{15}-X, where X= F, Cl, Br and any other substance having linear or branched perfluorooctyl derivatives with the formula C_8F_{17}- as a structural element, including its salts, except those derivatives with the formula C_8F_{17}-X, where X= F, Cl, Br or, C_8F_{17}-SO_2X', C_8F_{17}-C(=O)OH or C_8F_{17}-CF_2-X' (where X'=any group, including salts)	1. Shall not be manufactured, used or placed on the market - as substances, - as constituents of other substances in concentrations equal or above 2 ppb of a single substance, - in a mixture in concentrations equal or above 2 ppb of a single substance 2. Articles or any parts thereof containing one of the substances in concentrations equal to or greater than 2 ppb of a single substance shall not be placed on the market. 3. Paragraph 1 and 2 shall apply from (18 months after entry into force). 4. By way of derogation, paragraph 2 shall not apply to the placing on the market of second-hand articles which were in end-use in the European Union when the restriction becomes effective.

European Committe for Standardization (CEN) – New Work Item (NWI) validated test method for the determination of PFOA and related substances in textiles.

Proposed title:

Textiles and textile products — Perfluorinated Compounds - Part 1 - Determination of Extractable Long Chain Perfluorinated and Polyfluorinated Substances in Textile Materials (Method using Methanol)

- **Scope**

  This standard specifies a test method for detection and quantification of extractable long chain perfluorinated and polyfluorinated substances in textile products. As well as PFOA, long chain per- and poly-fluorinated compounds from C_7 – C_{14} are used in soil and water repellent finishes. Classes of compounds include acids, telomers.

A new research project on alternatives to PFCs in textiles

Funded by a Governmental Research Fund FORMAS (Sweden).

1, 7 M€ , 2013 - 2017

www.supfes.eu

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Long term goal of SUPFES

The results will be generalized to a methodology for practical substitution of priority substances; realistic testing of alternatives from both eco toxicity and health perspective as well as from a technically functional standpoint.

Screening of DWR chemicals

Chemical screening of materials

- Screening DWR
- Target analysis

Toxicity screening

- Raw chemicals
- Complex chemical mixtures DWR

Technical performance

- Leaching and emission
- Weathering (washing, abrasion)
- Non-mechanical agening (UV, humidity, temp)

Selection alternatives

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Information in process:

Deliveries of information about leaching and emissions, toxicity of PFAS vs. alternatives from textiles

- **Obtained information (for further processing):**
- Information on which PFASs are used in which textile products (response from approx 50 companies based on upstream information)
- **Ongoing:**
  - Information on complex chemical mixture of DWR
  - Processes used to prepare DWR for textiles
  - Chemistry taken place by producing DWR coating
  - Delivery of alternative compounds
  - Availability of toxicity data on PFASs and alternative compounds

Stakeholders in SUPFES

Stakeholder	Category
The Chemicals Group at Swerea IVF European Outdoor Group	Retailers
Outdoor Industry Association	Retailers and producers
KEMI, Swedish Chemicals Agency Swedish Environmental Protection Agency German EPA, UBA US EPA Norwegian EPA UNEP (Stockholm Convention and CiP) Others…	Authorities
TEGEWA	Textile Chemicals Industry Association (Europe)
International fluorochemicals producers	
International non fluoro chemicals producers	

Characterization of PFASs in diffuse sources

Ike van der Veen, Pim Leonards and Jana Weiss
Institute for Environmental Studies, VU University
Amsterdam, Netherlands

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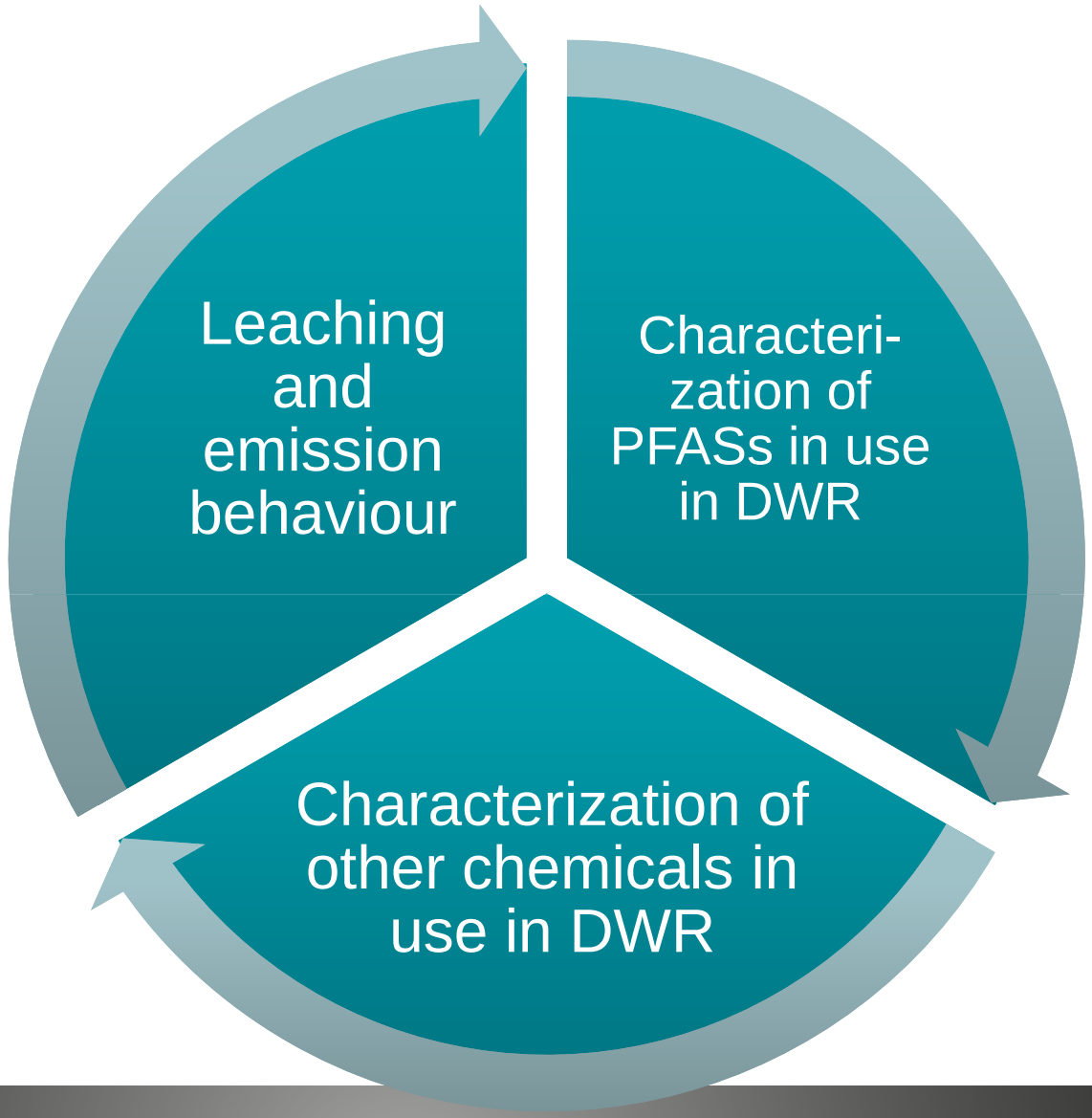

Leaching and emission behaviour
Characteri-zation of PFASs in use in DWR
Characterization of other chemicals in use in DWR

Work performed so far..... (April 2015)

- Screening PFASs in textile samples with LC-MS/MS
- Optimization and validation of extraction method
- Analyses of PFASs in textile samples with validated method

Analyses of PFASs in textile samples with validated method

44 different textile products

+

5 products contained two different colors

↓

49 samples analysed

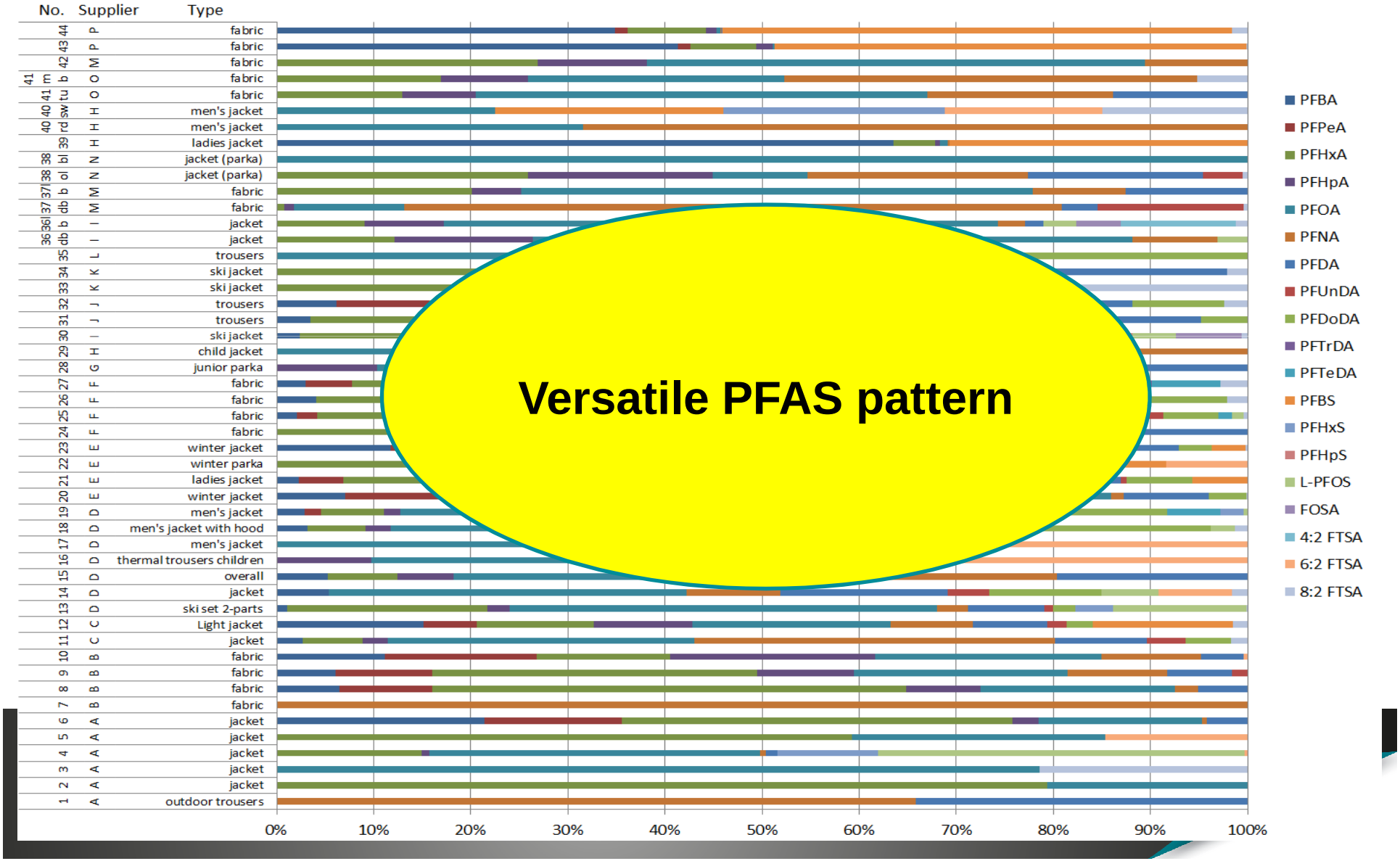
Results of PFASs in textile samples with validated method

Main PFASs compounds detected in textile samples:

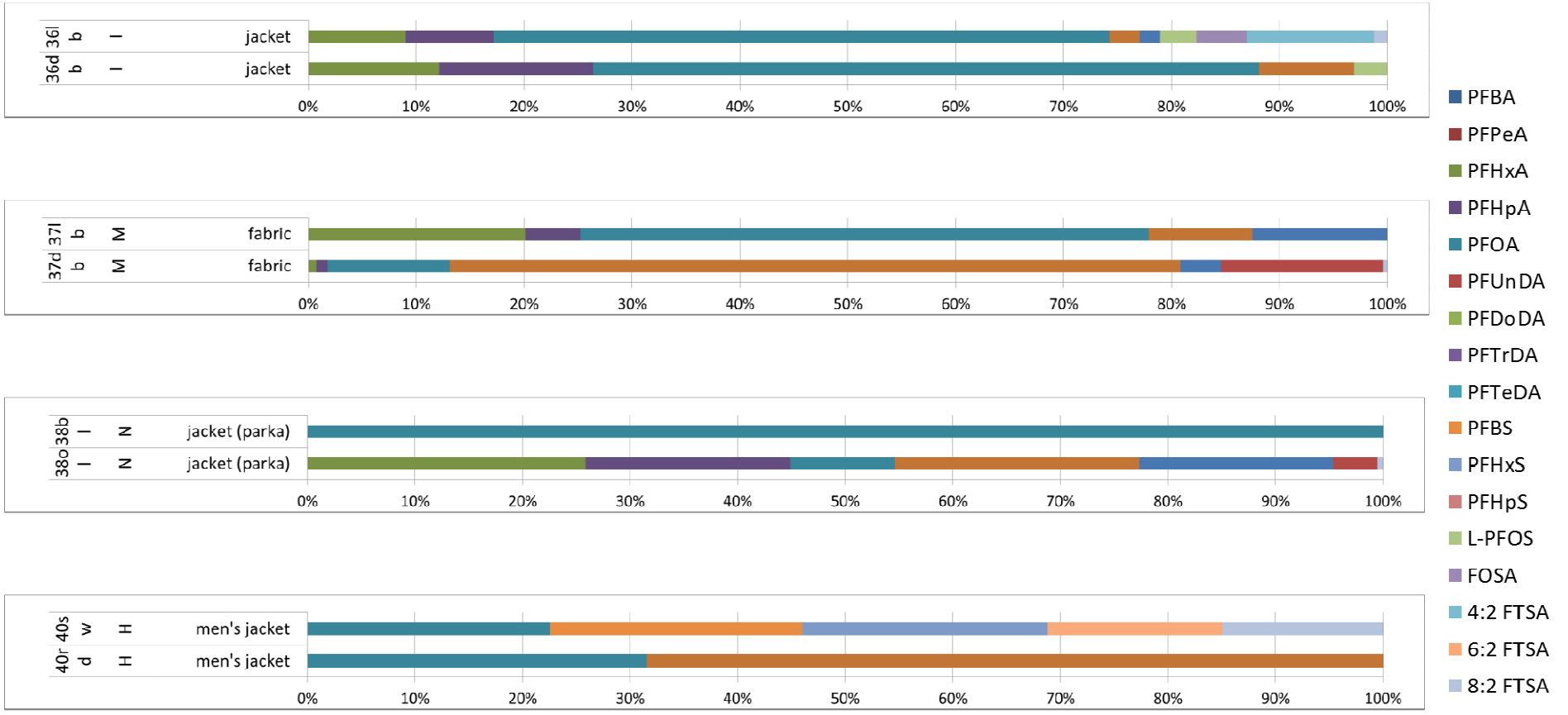
- PFBA
  - 47% of samples
  - 0.02-28 µg/m^2
- PFOA
  - 96% of samples
  - 0.01-5.1 µg/m^2
- PFBS
  - 18% of samples
  - 0.02-42 µg/m^2
- PFHxA
  - 76% of samples
  - 0.03-6.4 µg/m^2
- PFNA
  - 78% of samples
  - 0.01-2.8 µg/m^2
- L-PFOS
  - 18% of samples
  - 0.02-3.2 µg/m^2

- **Commission Regulation (EU) No 757/2010 of 24 August 2010 (POP Regulation 840/2004 amendment) : PFOS < 1 µg/m^2**
- **Norway: PFOA < 1 µg/m^2**

Profiles of PFASs in textile samples



Profiles of two fabrics of one product



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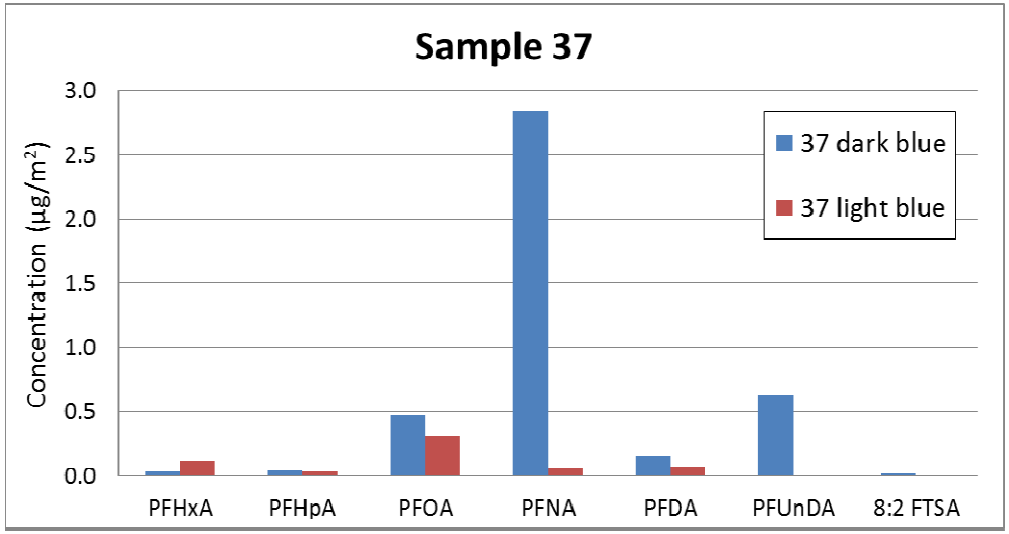
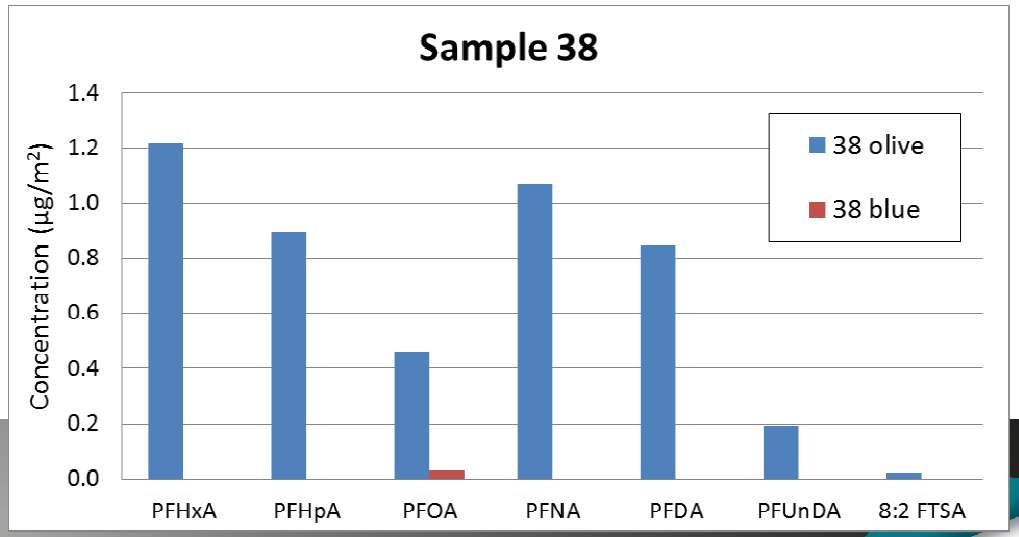
Different fabrics of the same product





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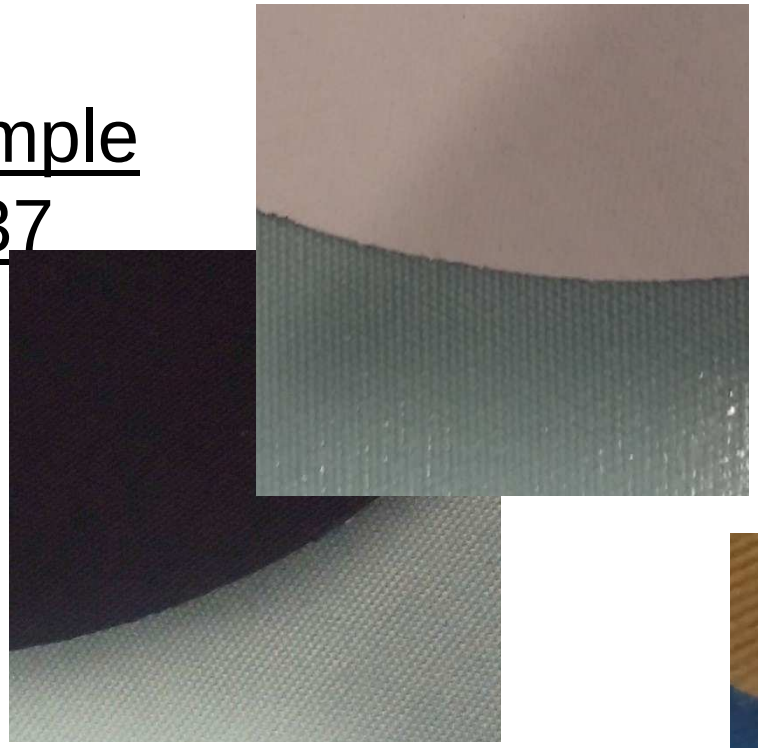
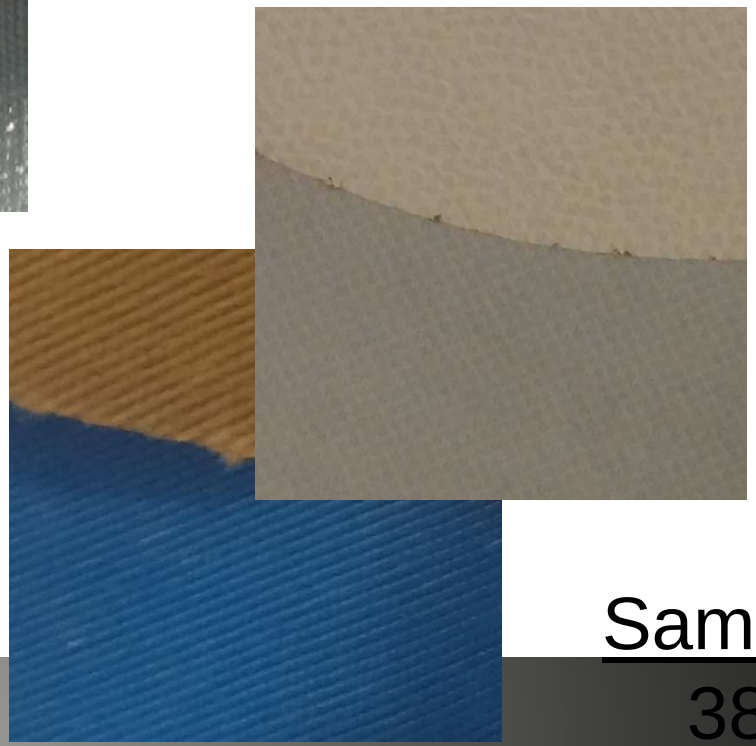
Textile structures of samples

Sample 37



Inside

Outside



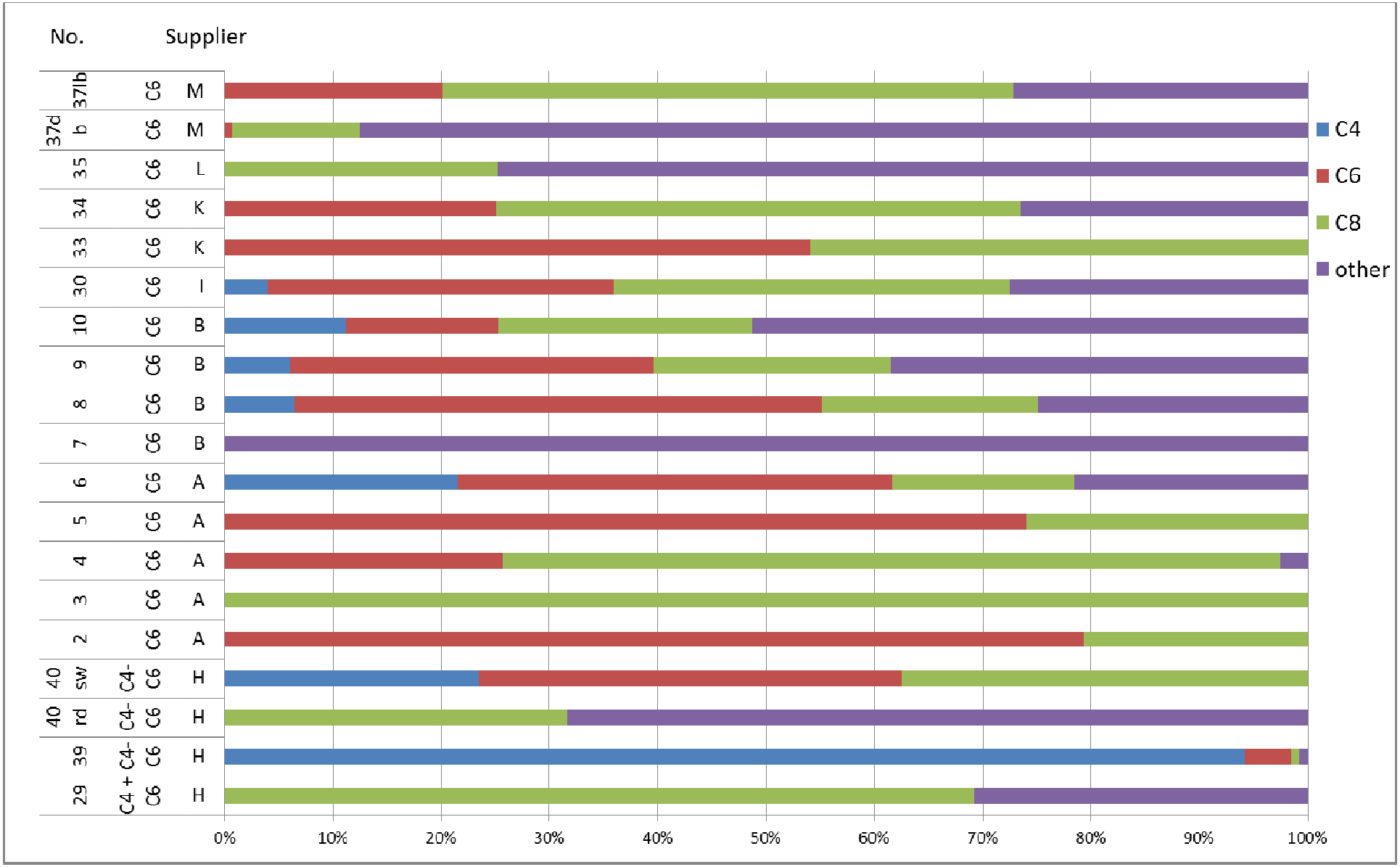
Inside

Sample 38

Outside

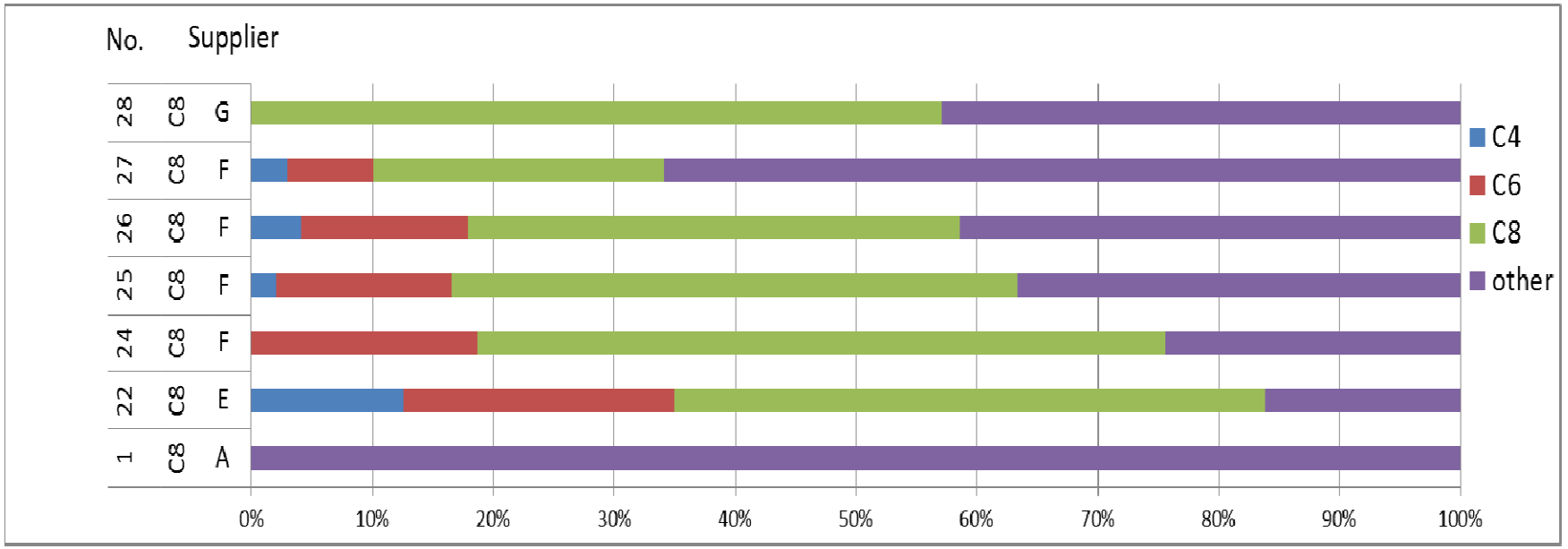
Screening for PFASs with LC-MS/MS
→ Preliminary Results

C6 Chemistry

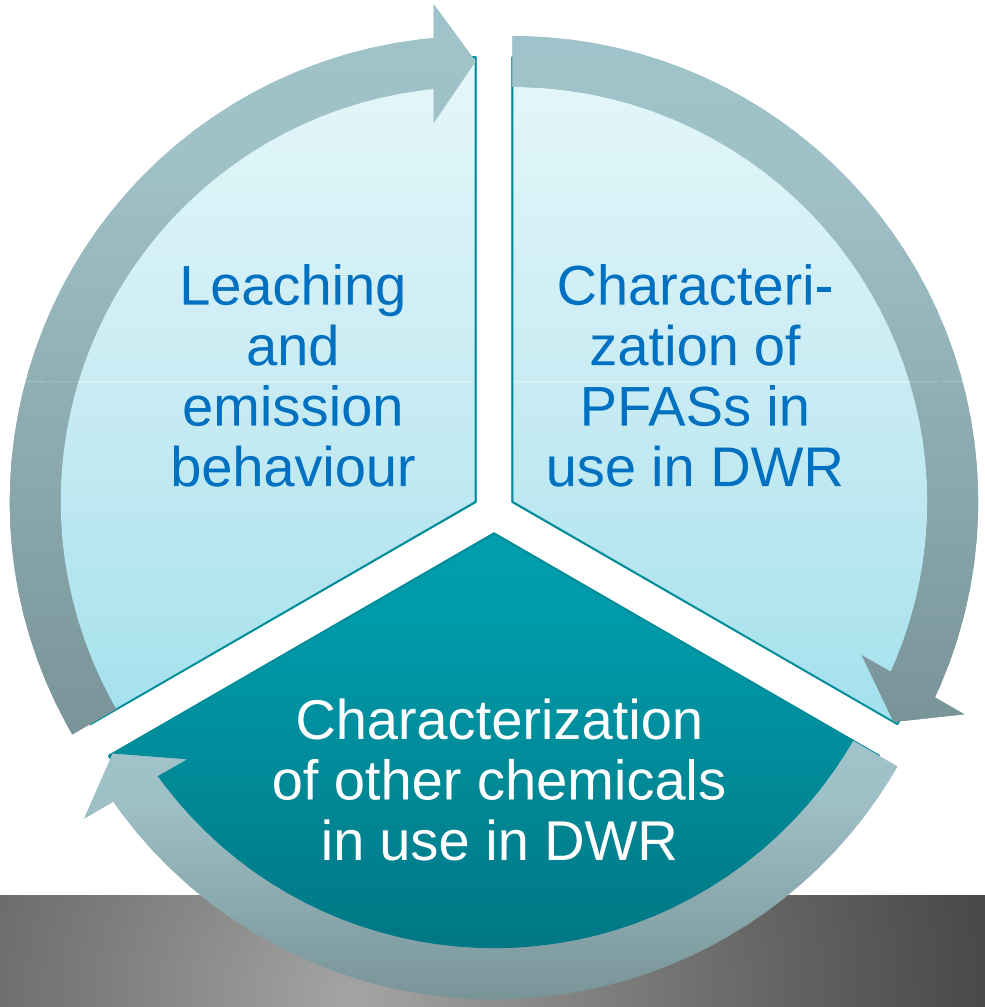


Screening for PFASs with LC-MS/MS
→ Preliminary Results

C8 Chemistry



Characterization of other chemicals in use in DWR



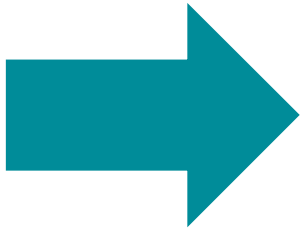
Characterization of other chemicals in use in DWR

- Other PFASs: e.g. Flourotelomer alcohols (FTOHs), fluoro sulfonamides/amide ethanols (FOSAs/ FOSEs), fluorotelomer acrylates (FTACs)
- Polymers
- Waxes
- Siloxanes
- Dendrimers

Water repellent polysiloxanes

Some manufactured intermediates

Abbreviation	Name	CAS no.
D4	Octamethyl cyclotetrasiloxane	556-67-2
D5	Decamethyl cyclopentasiloxane	541-02-6
D6	Dodecamethyl cyclohexasiloxane	540-97-6
MM (or HMDSO)	Hexamethyl disiloxane	107-46-0
MDM	Octamethyl trisiloxane	107-51-7
MD2M	Decamethyl tetrasiloxane	141-62-8
MD3M	Dodecamethyl pentasiloxane	141-63-9



Polysiloxanes

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POP assessment (Stockholm Convention (SC)) of siloxanes

Substance	Persistence Annex D 1. (b)	Bio accumulation Annex D 1 (c)	LRT Annex D 1 (d)	Adverse effects: ecotoxicity Annex D1 (e)	Adverse effects to human health Annex D1 (e)
Decamethyl cyclopentasiloxane (D5) ***vPvB***	Yes	Yes	Yes	No	No
Dodecamethyl cyclohexasiloxane (D6)	Yes	No	Yes	No	No
Decamethyl tetrasiloxane (MD2M)	Equivocal data	No	Yes	No	No
Octamethyl cyclotetrasiloxane (D4) ***vPvB and T, pot. POP***	Yes	Yes	Yes	Yes	Yes
Octamethyl trisiloxane (MDM)	Equivocal data	Yes	Yes	No	No

Source: ***UNEP/POPS/POPRC.10/INF/8/Rev.1***

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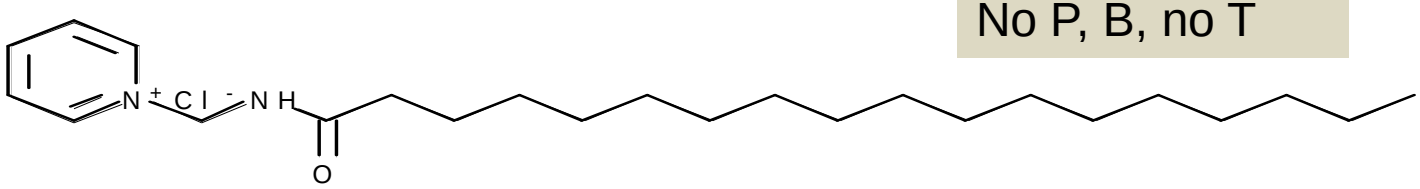
Water repellent cotton and cotton/PET blends

- A classic cationic textile surfactant is 1-(stearamidomethyl) pyridinium chloride

SC assessment:
No P, B, no T



- The substance reacts with cellulose at elevated temperatures to form a durable water-repellent finish on cotton
- There are also other similar resins used to water repellent cotton
- Sometimes these treatments are adressed as paraffin wax treatments

Superhydrophobic repellents

- Hyperbranched hydrophobic polymers (dendritic, i.e., highly branched polymers) and specifically adjusted comb polymers as active components

- Superhydrophobic means contact angles larger than 150° that can be applied in coatings, textile, leather etc.
- Dendrimers may be in the region of nano sized materials meaning features with an average diameter between 1 to 100 nm

- There are now cationic dendrimers applied to improve bonding to cotton.

Cationic properties needs to be considered concerning cytotoxicity

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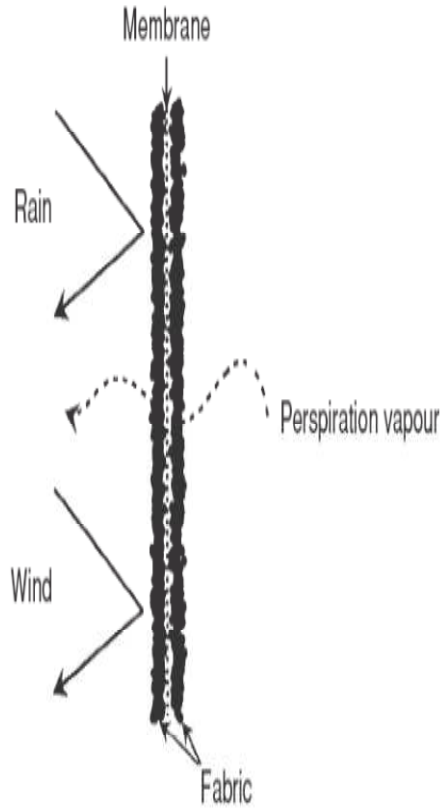
Fluoro silicone structures for DWR treatment

- SiO_2 (silicon dioxide) molecules which are perflourinated. formula contains SI-F, that means, that the fluorine is bonded to the silicon dioxide.

- *Still very little information of this groups of alternative DWR treatments on textiles.*

Membranes

- Membranes are extremely thin films made from polymeric material and engineered in such a way that they have a very high resistance to liquid water penetration, yet allow the passage of water vapour.
- A typical membranes is only 10 µm thick and is laminated to a conventional textile fabric to provide the necessary mechanical strength.
- This is a thin film of polytetrafluoroethylene (PTFE) polymer with 1.4 billion holes per cm^2.
- These holes are much smaller than the raindrops (2-3 µm compared with 100 µm), yet very much larger than water vapour molecule (0.0004 µm).



12.4 Schematic diagram of a typical membrane system.

PFOA is used as an emulsifier for production of PTFE membranes – observe possible residues

Are non fluoro treated fabrics completely free from fluoro chemicals?

Unfortunately NO.

There may still be traces of stable fluorinated degradation products in the fabric such as

- perfluorinated carboxylic acids (PFCAs) such as PFOA
- perfluorinated sulfonic acids (PFSAs) such as PFOS

Why?

PFSA and PFCA substances are not used in production, but occur as contaminants through water and food chains and appear everywhere.

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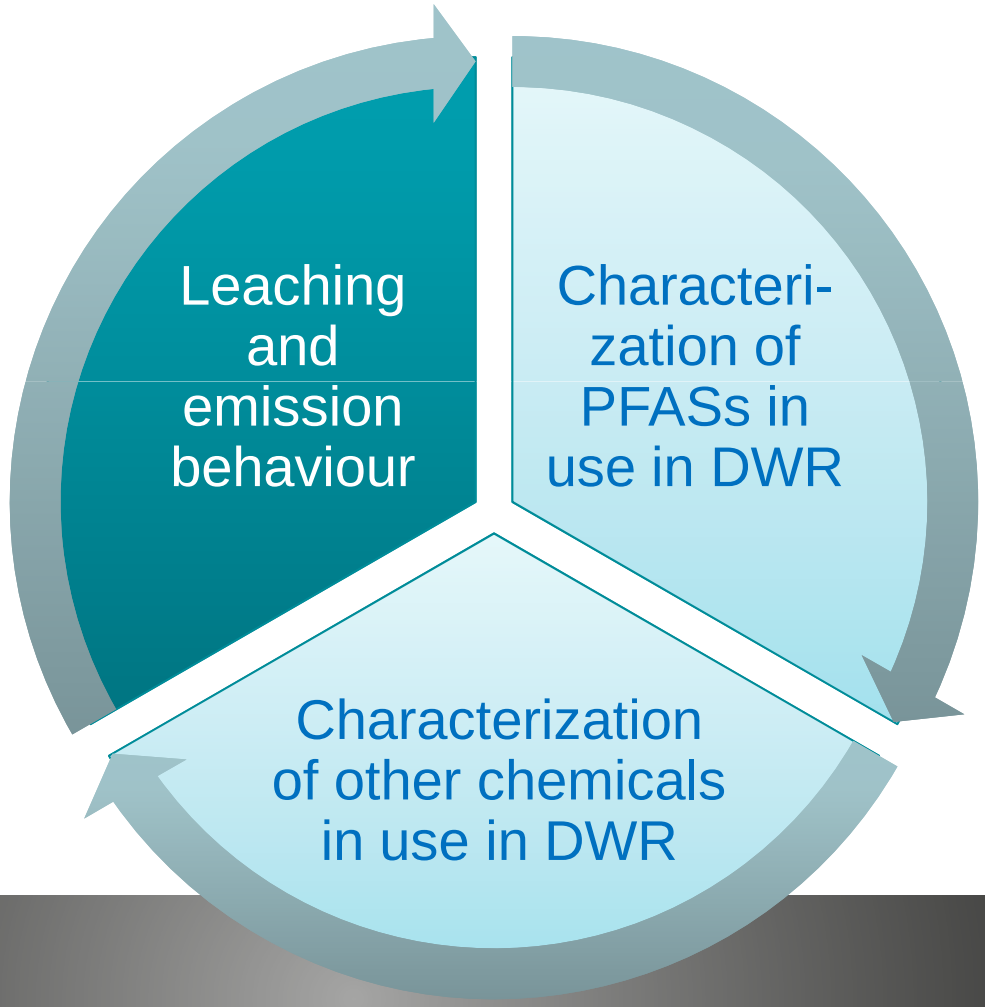
Leaching and emission studies in SUPFES



Leaching and emission behaviour

- Leaching
- Weathering
- Washing

- **Information used for life cycle assessment studies**

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Summary and conclusions

- A method is developed and validated for the analyses of PFASs in textiles
- PFASs are detected in textile samples
- Some samples contain PFOS and PFOA levels above the norm of 1 µg/m^2
- Other chemicals used in DWR will be characterized and (semi)-quantified
- Leaching, weathering and washing studies will identify what and how much is leaching of DWR by different DWR technology and will be used for life cycle assessment studies


Thanks for your attention!