Highly fluorinated chemicals
A legal and technical challenge

Stefan Posner
stefan.posner@swerea.se

Stefan Posner
Senior researcher

Swerea IVF
P.O. Box 104, SE-431 22 Mölndal, Sweden

What are highly fluorinated compounds/ polymers?

- Surfactants
  - extremely low surface tension

- Side chain fluorinated polymers
  - extremely low surface energy

- Fluoropolymers e.g PTFE - *another chemistry*

Terminology

PFAS; chemicals that contain one or more perfluoroalkyl moieties, – $CnF2_{n+1}$.

In the past, PFASs were often referred to as "PFCs" (per- and polyfluorinated chemicals)

The family of PFAS

- PFAA; Perfluoroalkyl acids
- PFCA; Perfluoroalkyl carboxylic acid
- PFSA; Perfluoroalkane sulfonic acids
- Compounds derived from perfluoroalkane sulfonyl fluoride (PASF)
- Fluorotelomer (FT)-based compounds
- Per- and polyfluoroalkyl ether (PFPE)-based compounds

Electrochemical fluorination - ECF

Input PFAS

$H(CH_2)_nSO_2F$ (n = 4, 6, **8 ,** 10)

e^- + HF | ECF

$F(CF_2)_nSO_2F$

Perfluoroalkyl sulfonyl fluoride

Perfluoroalkyl sulfonamide

$F(CF_2)_nSO_2NH_2$

Perfluoroalkyl sulfonate

$F(CF_2)_nSO_3M$ M = H, NH_4, K, Na, …

$F(CF_2)_nSO_2NH_2$

Perfluoroalkyl sulfonamide

R = H, Me, Et, Bu

$F(CF_2)_nSO_2N(R)CH_2CH_2OH$

N-Alkyl Perfluoroalkyl sulfonamido alcohol

R = H, CH_3

$F(CF_2)_nSO_2N(R)CH_2CH_2OC(O)CR=CH_2$

(Meth)acrylate monomer

$F(CF_2)_nSO_2N(R)CH_2CH_2CH_2N(CH_3)_2$

Surfactants
- **Amide**
- **Ethoxylate**
- **Oxazolidinone**
- **Phosphate**
- **Silane**
- **Sulfate**

Surfactants
- **Adipate**
- **Fatty acid ester**
- **Phosphate**

Oligomeric Surfactants

Surfactants
- **Betaine**
- **Sulfobetaine**
- **Cationic**

Transformation

Output PFAS

Final degradation products are perfluorinated sulfonic acids (PFSA)

n = 4 formation to PFBS
n = 6 formation to PFHxS
n = 8 formation to PFOS
n = 10 formation to PFDS

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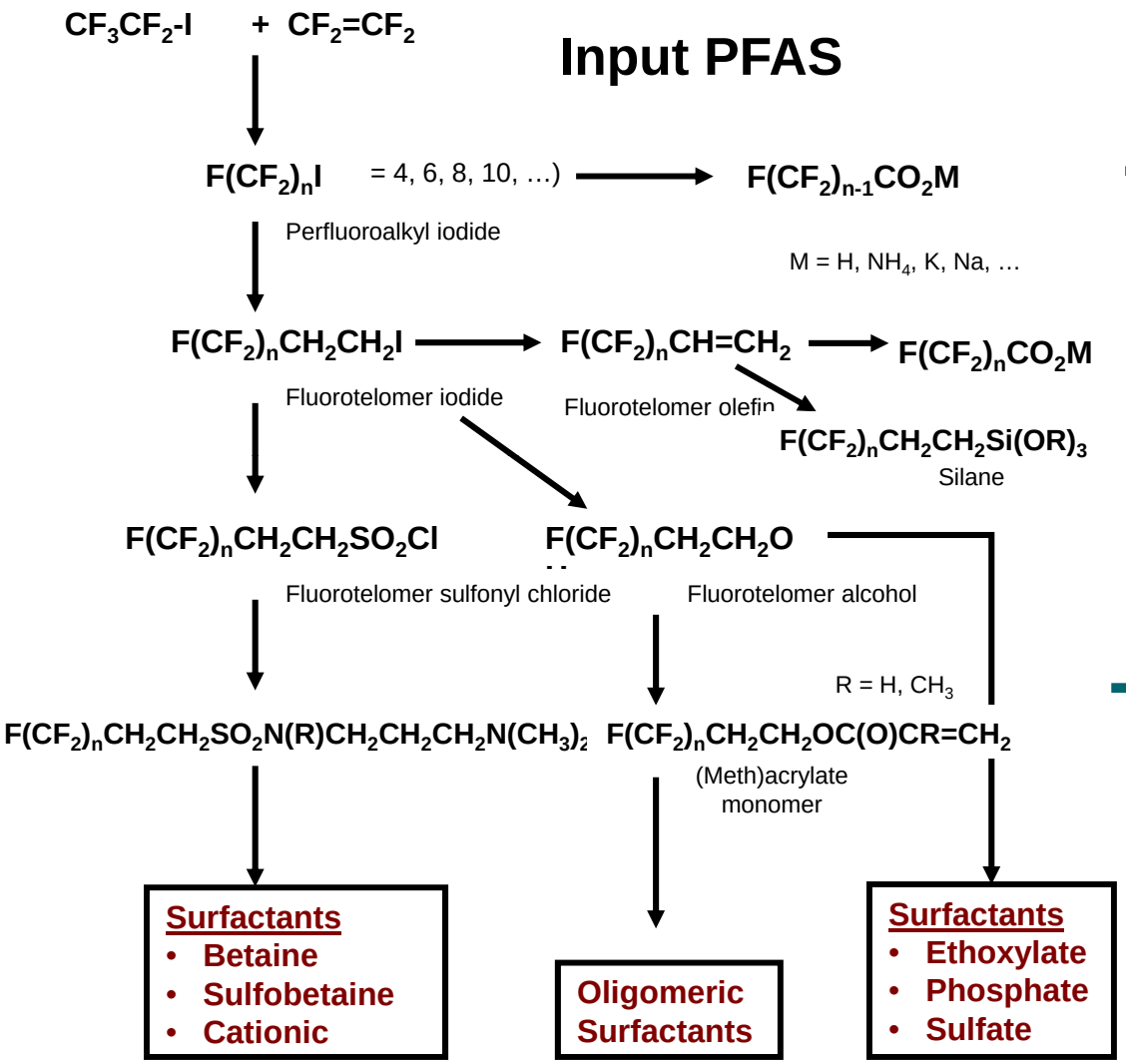
Telomerization



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The fluorinated surfactant

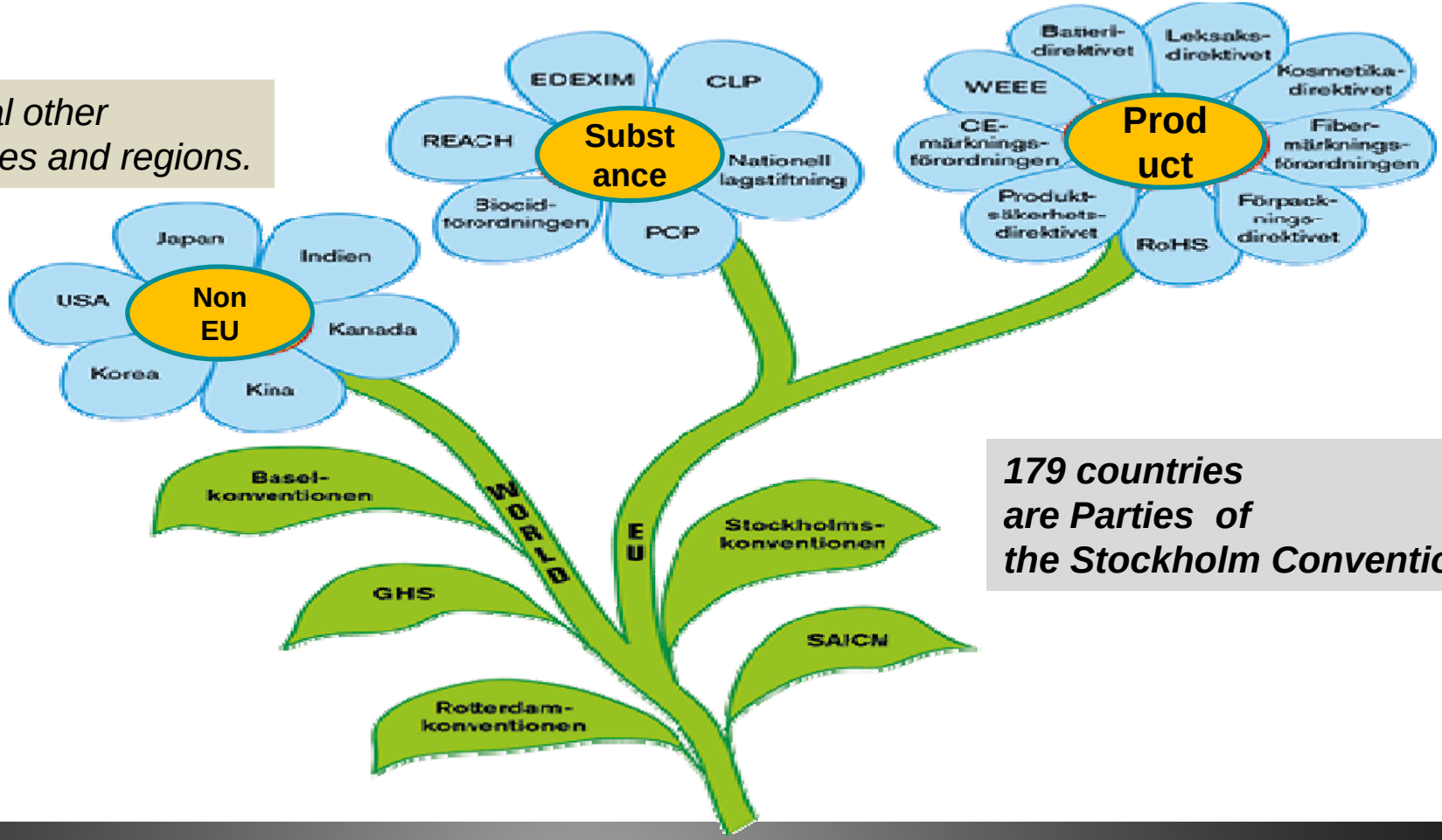
- The fluorinated ”tail” is both hydrophobic and oleophobic – unique.

- Long chain PFAS – the fluorinated ”tail” contain
  - More than or equal to 7 perfluorinated carbons if a PFCA
  - More than or equal to 5 perfluorinated carbons if a PFSA
  - Precursors that can degrade to the above compounds.

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

Binding International Conventions and Regulations

Several other countries and regions.



179 countries are Parties of the Stockholm Convention

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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.

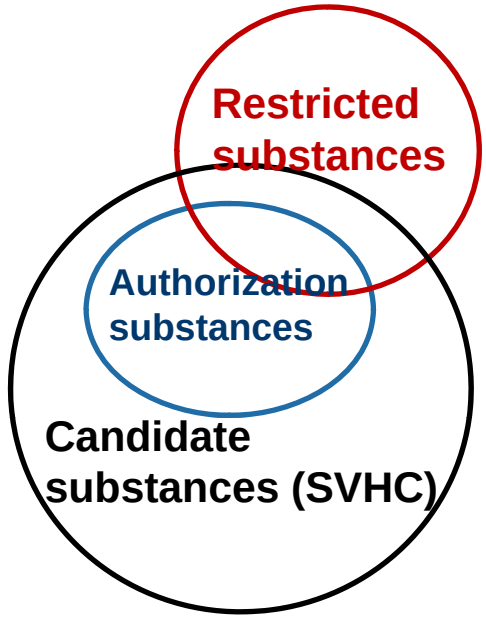
a) Carcinogenic (Category 1a & 1b)

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.*

Examples – chemicals of your concern and their practical substitution to less harmful feasible alternatives

Substance group	REACH SVHC (candidate list & annex XIV)	REACH restriction annex XVII	RoHS (Electronics)	Stockholm Convention ------ POPs legislation	CLP harmonized classification and labelling (chemical products)	Feasible alternatives (some examples)
Specific substance groups						
Toxic metals	X	X	X		X	Calcium/zinc stabilizers
Phthalate plastizisers	X	X (children products)			X	Adipates, citrates, phosphor organic etc
Halogenated flame retardants	X	X	X	X DecaBDE proposed for annex A	X	Halogen free flame retardants
Poly and perfluorinated substances	**X (PFOA and higher homologues)**			**X (PFOS and related substances)**	**X**	**Silicone-based products, stearamidomethyl pyridine chloride, perfluorobutane sulfonate for leather. Dendrimers.**
Nonlyphenols (NP) and nonylphenoletoxylates (NPE)	X (branched and linear NP)	X (detergents)				Alcohol ethoxylates, both linear and branched, glucose-based carbohydrate derivatives such as alkylpolyglucoside, glucamides, and glucamine oxides.
General substance groups						
Substances that are classified as CMR, endocrine toxic, neurotoxic, strong sensitisers, PBT, vPvB		CMR must not be used within EU.			X	Practical substitution for materials development recommended for each specific case

Current legal PFAS status - International Conventions and EU Regulation (October 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)*	X	Restriction proposal for annex A		POP candidate
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).
- If the phase out is not performed, additional international regulatory actions are currently taken.
- 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
PFOA and its related 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 was submitted to the Secretariat of the Stockholm Convention in May 2015 and met the annex D criteria meaning a POP candidate.

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 li… branched perfluorohept… formula C_7F_{15}- as … its salts except… C_7F_{15}-X, wh… substance… perfluoro… as a struc… except tho… X, where X=… C(=O)OH or C_8… including salts)	1. Shall not be manufactured, used or placed on the market - as substances, …f other substances in …ve 2 ppb of a single …r above 2 …ne of …r …all …18 …ph 2 shall not …e market of second- …which were in end-use in the European Union when the restriction becomes effective.

ECHA committees SEAC and RAC suggested a higher restriction level to 1000 ppb for articles due to

- **Cross contamintion**
- **No international standard method yet**

That may influence such low values of 2 ppb.

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.

SUPFES - Substitution of prioritized poly- and perfluorinated substances to eliminate diffuse sources

Funded by a Governmental Research Fund FORMAS (Sweden).

1, 7 M€ , 2013 - 2017

www.supfes.eu

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SUPFES - partners

HAGLÖFS

IVM VU
Institute for Environmental Studies

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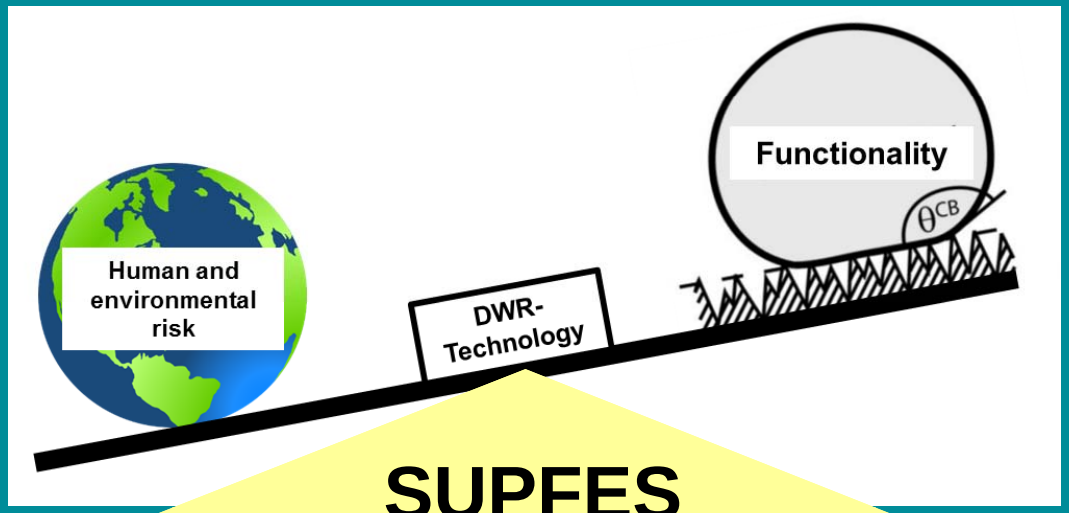
UNIVERSITET STOCKHOLMS
Stockholm University

Swerea IVF is coordinator
Project duration until 2017
Project budget: 1,85 M€



SUPFES

Swerea IVF Textile Research	VU University Amsterdam	Stockholm University	Chalmers University
Performance Testing LCA, LCC	Chemical Screening & Leaching Studies	Hazard Assessment: Measure & Model	Risk & Life Cycle Assessment (LCA)

SUPFES' objective:
Characterize the physical performance and assess the risks of alternative Durable Water Repellent (DWR) chemistries for textiles

A unique consortium of scientific and industrial partners with strong stakeholder involvement

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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	

Prioritization process of DWR chemicals in SUPFES

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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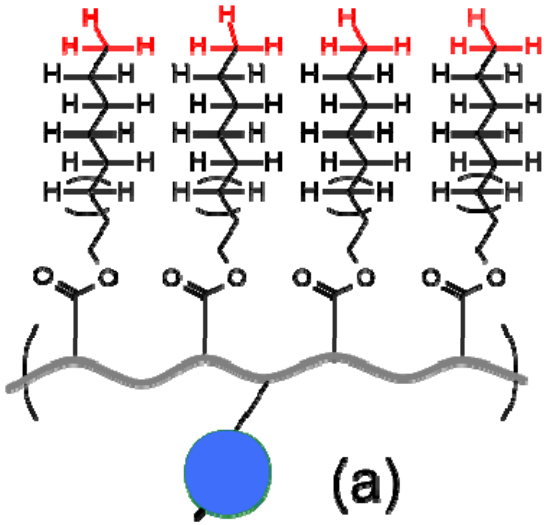
DWR chemistry

- Fluorocarbon-based
- Silicon-based
- Hydrocarbon-based polymers

Also looking into plasma technology as a feasible option to PFAS

Group	γ_c [mN/m]
CF_3	6
CF_2	18
CH_3	22
CH_2	31

decreasing repellency



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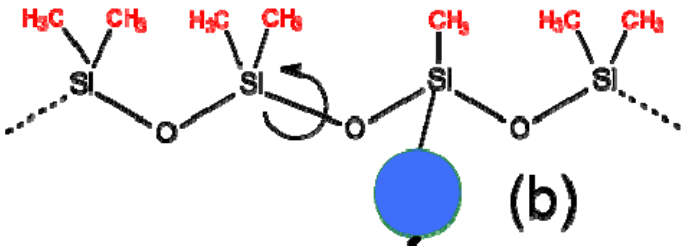

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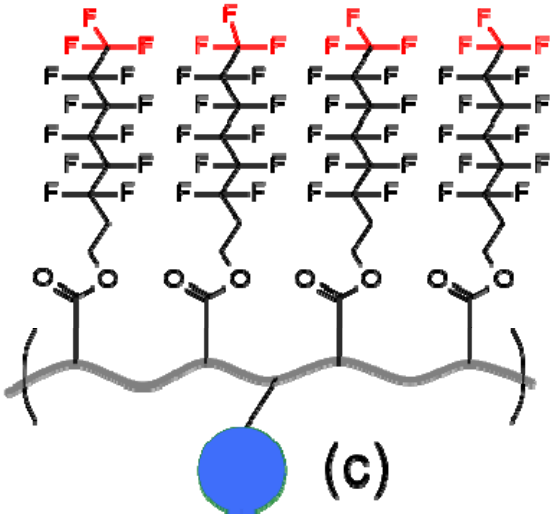

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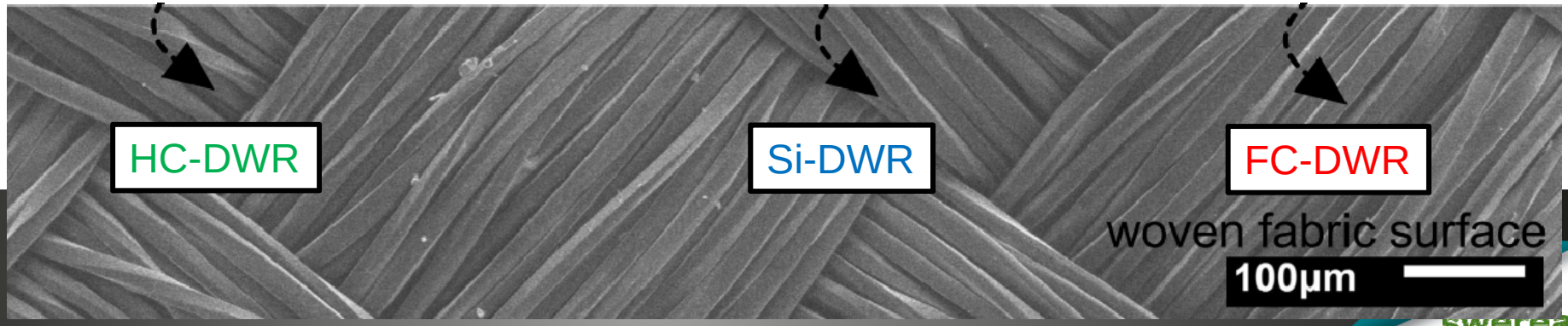
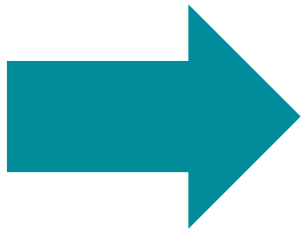


Water repellent polysiloxanes

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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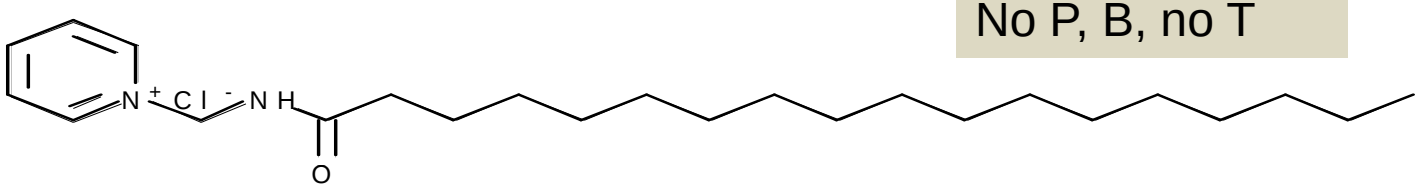
Water repellent cotton and cotton/PET blends

- 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

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.*

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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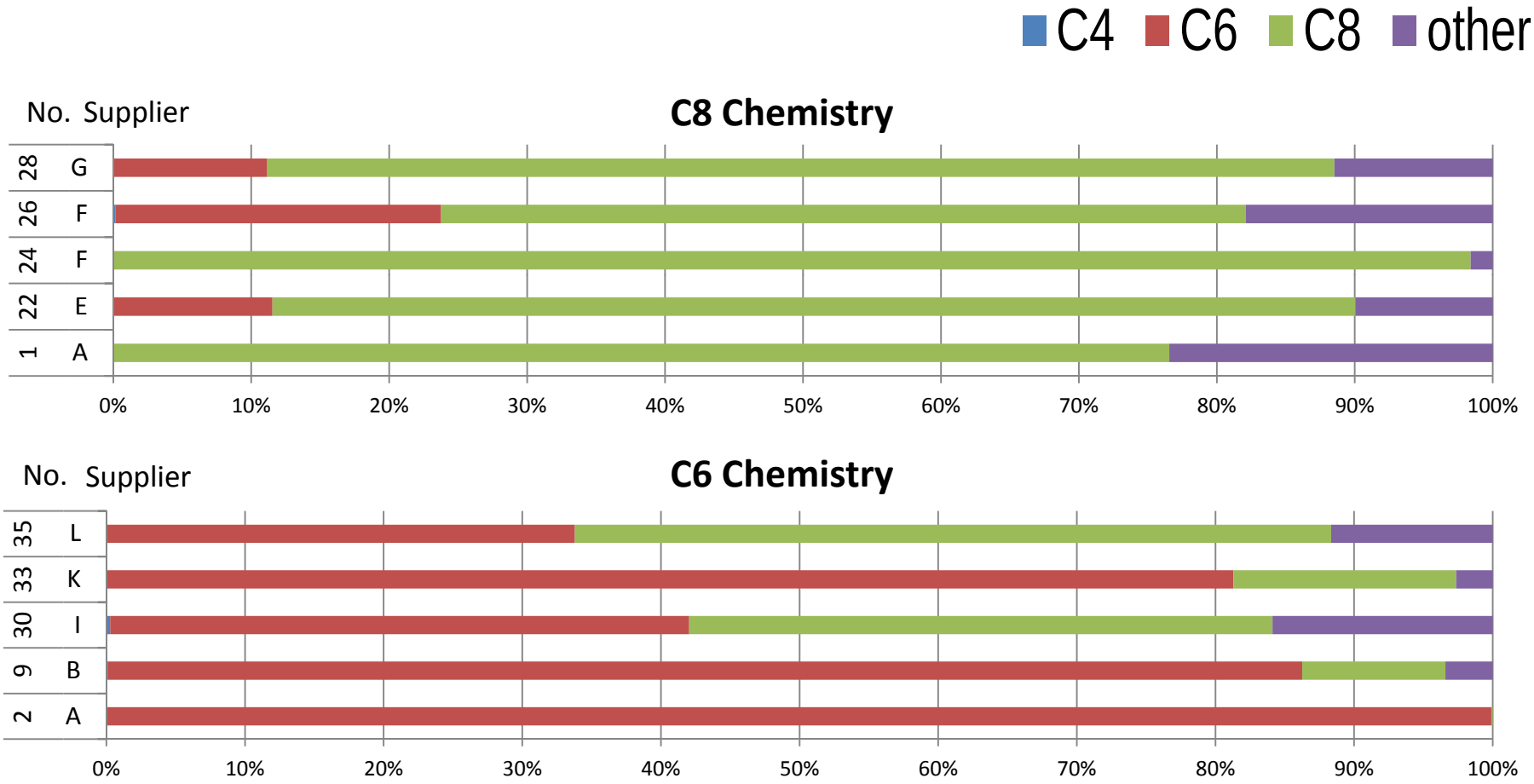
Main PFASs detected in textile samples

- **PFBA**
  - 47% of samples
  - 0.02-28 µg/m^2 (median 0.17 µg/m^2)
- **PFHxA**
  - 76% of samples
  - 0.03-6.4 µg/m^2 (median 0.21 µg/m^2)
- **PFOA**
  - 96% of samples
  - 0.01-5.1 µg/m^2 (median 0.25 µg/m^2)
- **PFBS**
  - 18% of samples
  - 0.02-42 µg/m^2 (median 0.69 µg/m^2)
- **L-PFOS**
  - 18% of samples
  - 0.02-3.2 µg/m^2 (median 0.09 µg/m^2)
- **6:2 FTOH***
  - 88% of samples
  - 0.43-360 µg/m^2 (median 24 µg/m^2)
- **8:2 FTOH***
  - 92% of samples
  - 1.5-380 µg/m^2 (median 17 µg/m^2)
- **10:2 FTOH***
  - 90% of samples
  - 0.06-130 µg/m^2 (median 4.1 µg/m^2)
- **8:2 FTAC***
  - 46% of samples
  - 0.29-280 µg/m^2 (median 2.6 µg/m^2)

Ionic PFASs *and* ***neutral PFASs*** *are detected in textiles of outdoor clothing at quantifiable concentrations.*

Neutral PFASs *are present at higher concentrations then* ***ionic PFASs****.*

Patterns of PFASs in textile samples



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Chemical hazard assessment of alternatives
Preliminary results

Substance	Hazard classification per endpoint											
	Human health								Ecotox		Fate	
	C	M	R	D	E	AT	ST	N	AA	CA	P	B
Benchmark												
PFOA	**H**	**L**	*H*	**H**	PEA	**M**	**H**	DG	**L**	*L*	**vH**	**H**
Fluorocarbons												
PFHxA	*L*	*L*	*M*	*M*	PEA	**L**	*M*	DG	*L*	*H*	**vH**	*L*
PFBS	DG	*L*	*L*	*L*	PEA	**L**	*L*	DG	*L*	*L*	**vH**	*L*
Silicones												
Short-chain silanols	DG	DG	DG	DG	DG	DG	DG	DG	DG	DG	DG	DG
DMSD	DG	DG	DG	DG	DG	DG	*M*	DG	DG	DG	*vH*	*L*
TMS	DG	*L*	DG	DG	DG	*M*	*M*	DG	**L**	DG	DG	*L*
D4	*L*	*L*	*L*	*L*	DG	**L**	**vH**	DG	*L*	**vH**	**vH**	*vH*
D5	*L*	**L**	*L*	*L*	DG	*H*	*H*	DG	*L*	*L*	**vH**	*vH*
Hydrocarbons												
Paraffin Wax	**L**	**L**	*L*	*L*	DG	**L**	DG	DG	**L**	**L**	**vL**	**L**
Nanotechnologies												
Dendrimers												
Inorganic nanoparticles												

L=low, M=moderate, H=high, vH=very high, DG=data gap, PEA=potential endocrine activity.
Classifications in *italics* are of low confidence and in bold of high confidence.

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Chemical hazard assessment of alternatives Conclusions so far in SUPFES.

- Our preliminary hazard ranking suggests that hydrocarbon-based polymers are the most environmentally benign, followed by silicone- and PFAS-based side chain polymers.
- The silicone industry is committed to reduce the levels of residual cyclic volatile methyl siloxanes present in the silicone-based DWR products and this will lower the actual risks.
- There is a lack of information on the hazards associated with DWR nanotechnologies and these data gaps must be filled.
- To assess the human and environmental risks of critical chemicals from DWRs the exposure has to be considered


Thanks for your attention!