Basis for Developing a Methodology to Estimate Fluorinated GHG Emissions from the Fluorinated Treatment of Textile, Carpet, Leather, and Paper

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Textile Industry

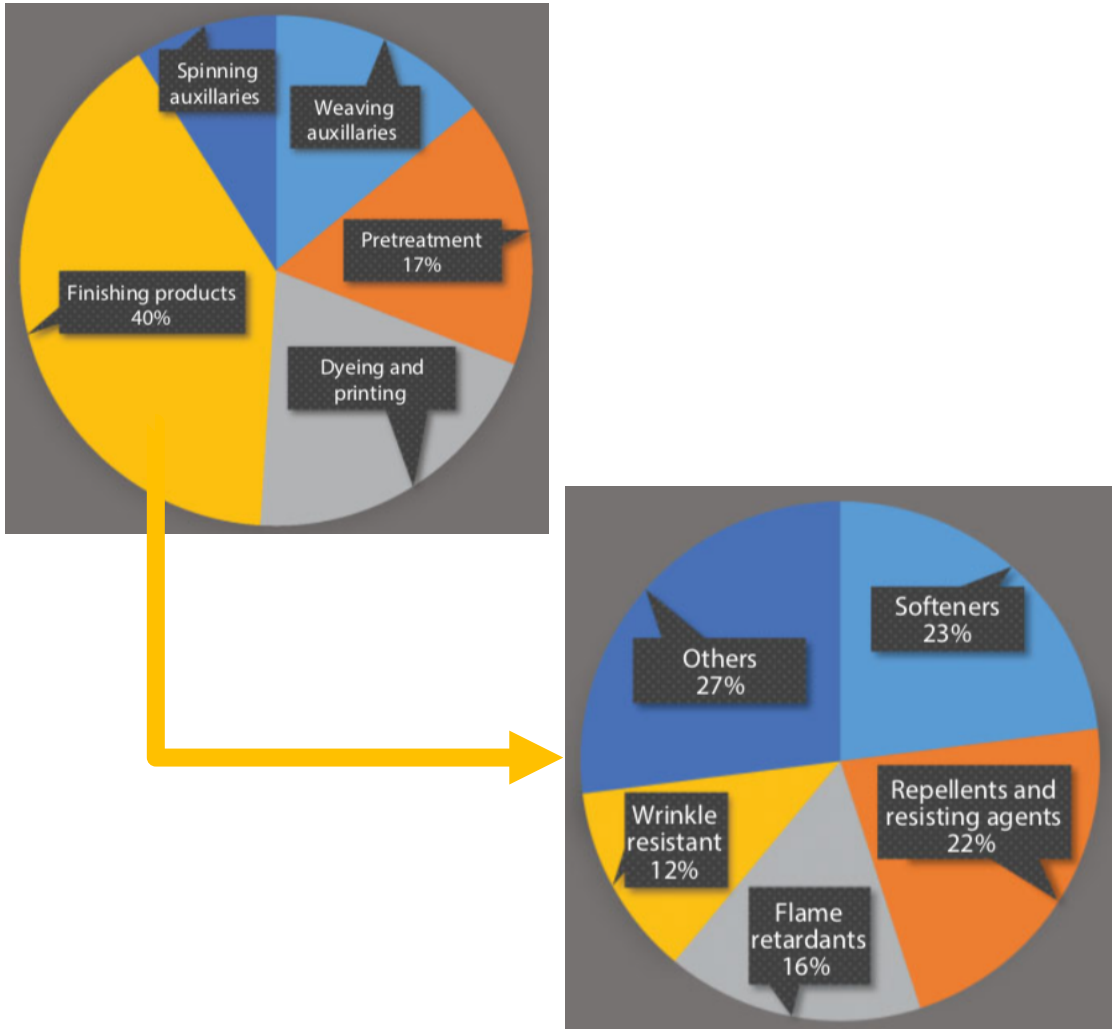
- The total **greenhouse gas (GHG) emissions from textile production** currently stands at **1.2 billion tonnes annually**, which is more than emissions from all international flights and maritime shipping combined. (Source: Editorial "The price of fast fashion" *Nature Climate Change.* Volume 8, page1, 2018).
- Responsible for **10% of the global carbon emissions**, **20% of global wastewaters** and, according to the UNFCCC, the sector's emissions are expected to rise by more than 60 per cent by 2030 (Source: https://unfccc.int/news/fashion-industry-un-pursue-climate-action-for-sustainable-development).
- Yet, potential GHG emissions from the fluorinated treatment (finishing) of textiles have – so far – never been accounted for.

Textile Finishing agents

- The highest usage of chemicals (around 40%) in textile is related to finishing. The world market of textile finishing agents has been estimated to be **111.2 million tons in 2015**. In addition, it is predicted to expand at 5.3% from 2017 to 2021.

- Repellents and resisting agents that made a large use of fluorocarbons are around 22% of the finishing market (**~ 24 million tons in 2015)**.

- Source: Shahid-ul-Islam and B.S. Butola "Advanced Textile Engineering Materials" John Wiley & Sons, Inc. 2018



The Fluorinated GHG Emissions Gap*

- During the 2015-2016 Technical Assessment of the 2006 IPCC Guidelines on National GHG Inventories, possible reasons for explaining the gap between top-down and bottom-up estimates of perfluorinated (PFC) emissions were examined.
- Among other potential new (unaccounted for) sources of PFC emissions, those originating from the fluorinated treatment of textiles were identified.
- Several peer-reviewed papers and a significant number of patents filed in the last decade indicated that PFC emissions may occur from these processes, in particular for plasma-based treatment.
- **Yet, no information was found to be available in the open literature to estimate emission factors from the fluorinated treatment of textiles.**

* Kim, J., et al. (2014), Quantifying aluminum and semiconductor industry perfluorocarbon emissions from atmospheric measurements," Geophys. Res. Lett., 41, 4787-4797, doi: 10.1002/2014GL059783

Fluorine-based treatment of textiles

- **Fluorochemical finishes** have been widely used to functionalize fibres for water or oil repellence, soil and stain release, improving textile breathability, softening, dyeing ability, increasing mechanical strength, providing antibacterial and anti-odour finishes, and for fabricating wrinkle-free materials. Only fluorocarbon finishes can repel both oil and water.

- The conventional processes used for increasing the water repellence of fibres use perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs), commonly referred to as ‘C8’ chemistry because the precursor molecules contain 8 carbon atoms. Such processes can lead to the formation of perfluoroalkylated acid, and in particular to the environmental release of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), two chemicals of concern due their persistent and bio-accumulative nature.

Fluorine-based treatment of textiles

- As a result, the use of C8 fluorinated polymers in textiles, carpet, leather, and paper has been restricted in some regions (Europe), and the industry is moving towards shorter chained chemistry (from ‘C8’ to ‘C6’ and ‘C4’).

- However, the C6 and C4 chemistries have been reported to perform more poorly than the conventional C8 chemistry (Davies 2014), and the C8 chemistry continues to be widely used in regions with large textile production capacities, particularly in developing countries (e.g China, which represents 50% of the world’s textile chemical consumption).

Fluorine-based treatment of textiles

- Two main methods are most used to apply finishes onto textiles: **continuous and exhaust/batch**.

- **For continuous application**, the pad–dry–cure method is mostly used. The padding step involves the uniform application of the chemical finish onto the fabric, and the drying step (110-130 ºC) is responsible for water removal. Finally, the curing/fixation step (150-190 ºC) involves the bonding or fixation of the finish onto the textile fabric.

- **For exhaust application** of the finish, chemical usage is a function of the weight of the fabric (% OWF (weight of fabric) or % OWG (weight of good)).

Fluorine-based treatment of textiles

- **Fluorine-based plasma treatment of textile, carpet, leather, and paper** has received increased interest and has been a fertile subject for research and development (R&D) since the early 2000s, in part due to the fact that plasma technologies provide excellent performance and that plasma processes can be tailored to achieve many desirable properties.

- **Plasma-based processes using fluorinated compounds** in the textile industry are expected to result in emissions of unreacted fluorinated compounds and by-products with high global warming potentials (GWPs - e.g. CF_4, C_2F_6, CHF_3, SF_6). **However, the extent to which plasma processes have been introduced in volume manufacturing is not clear.**

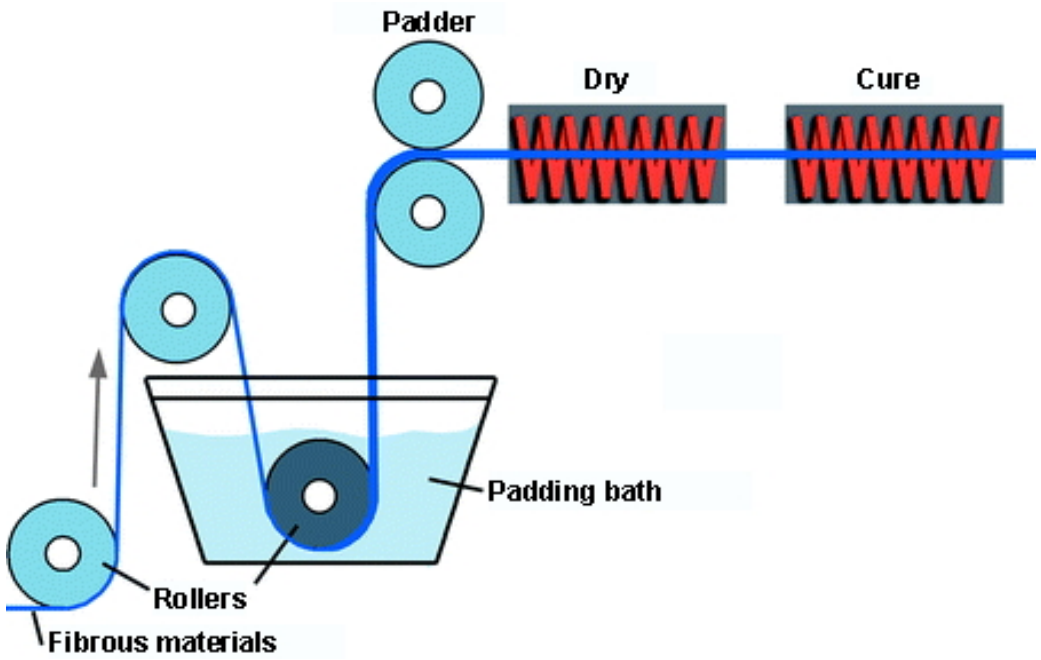
Fluorine-based treatment Emissions

- Although several international and national reports refer to the possible off-gas emissions of fluorinated compounds into the atmosphere due to textile treatment (wet or plasma), no emission factors appear to be available in the open literature to estimate greenhouse gas emissions from such processes (EPA 1997; Schönberger & Schäfer 2003; MoEU 2012; DEPA 2013; UNIDO et al. 2017).

- As a consequence, the authors of the IPCC 2019 refinement were not able to estimate the volume of PFCs that are emitted by the textile, carpet, leather, and paper industries. Nevertheless, PFC emissions in this sector could represent a significant new source, due to the large volume of substrates (i.e., product classes) treated and the sheer size and global nature of the industry.

Fluorine-based Wet-based treatment

Wet treatment processes include several application techniques but about 80% of the processes use the pad-dry-cure method, where the dry fabric is immersed in the finishing liquor and then squeezed between rollers before being dried and finally cured, usually at a temperature of between 150 and 180 ºC. Other techniques include vacuum extraction, spray applications, foam finishing, coating, and lamination.



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List of most important input chemicals used in wet treatment

Chemical name	Vapour pressure (mm Hg @ 25°C)	Chemical name	Vapour pressure (mm Hg @ 25°C)
Vinylidene fluoride	30000	Heptafluorobutyric acid - C4HF7O (PFBA)	10
Tetrafluoroethylene	24500	Fluorotelomer alcohol 6:2 FTOH	6,6 - 0,1
Vinyl fluoride	19800	1H,1H,2H-Perfluoro-1-decene	6,36
Hexafluoropropene	4900	Perfluorooctane sulfonyl fluoride (POSF)	5,75
Chlorotrifluoroethylene	4590	(perfluorooctyl)ethylene (PFOE)1	3,6
1,1,2,2-Tetrafluoroethyl methyl ether	1280	Polyfluorinated fluorotelomer iodides (6:2 FTI)	2,9
Perfluoromethylvinyl ether	765	Perfluorohexanoic acid (PFHxA)	1,98
C5F12 (PFC-41-12)	610	Fluorotelomer alcohol 8:2 FTOH	1,9 - 0,03
Perfluoropropylvinyl ether	534	PFOA isomers	1,26 - 2,04
C5F11NO	274	Fluorotelomer alcohol 10:2 FTOH	1,1 - 0,001
C6F14 (PFC-51-14)	232	Perfluoro-3,6-dioxaheptanoic acid (PDHA)	1,06
Perfluorobutyl iodide	158	Ethyl perfluorooctanoate (EPFO)	0,97-1
(Perfluorohexyl)ethylene	43,8	3-(Perfluorobutyl)propanol (PFBP)	0,7
C8F18	29	n-methyl perfluorobutane sulfonamidoethanol (Me-FBSE)	0,05
Fluorotelomer alcohol 4:2 FTOH	12,5 - 1,6	Perfluorobutane sulfonic acid (PFBS)	0,027
Perfluorobutanoic acid (PFBA)	10 (20ºC)	Perfluorooctane sulfonic acid (PFOS)	0,002

High vapour pressure **Medium vapour pressure** **Low vapour pressure**

Neutral and ionic PFAS concentrations [ng/(sample.day)] and estimated volume (µg and pg /m^3) in outdoor air in a Textile factory in China

Neutral PFAS	6:2 FTOH	8:2 FTOH	10:2 FTOH	12:2 FTOH	6:2 FTAC	8:2 FTOH	MeFBSA	MeFOSA	EtFOSA	MeFBSE	MeFOSE	EtFOSE
Site 1	132.8	441.9	149.5	1.33	0.64	0.47	0.36	0.06	(0.004)	0.01	<MDL	<MDL
Site 2	38.6	185.7	143.2	0.90	0.65	0.85	0.43	0.09	<MDL	<MDL	<MDL	<MDL

Ionic PFAS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	06:02 FTUCA*	08:02 FTUCA*	10:02 FTUCA*
Site 1	<MDL	0.69	0.47	0.68	0.20	1.62	0.18	0.40	0.10	0.03	n.d.	n.d.	4.12	2.29	2.45
Site 2	<MDL	0.82	0.25	0.32	0.14	1.78	0.19	0.46	0.11	n.d.	n.d.	n.d.	0.83	1.07	1.75

8:2 FTOH	10:2 FTOH	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
[µg/m3]	[µg/m3]	[pg/m3]	[pg/m3]	[pg/m3]	[pg/m3]	[pg/m3]	[pg/m3]	[pg/m3]	[pg/m3]	[pg/m3]	[pg/m3]	[pg/m3]	[pg/m3]
23.0	2.7	<MDL	173	117	169	50	405	44	99	24	7	n.d.	n.d.
9.7	2.6	<MDL	206	63	81	35	444	49	114	27	n.d	n.d.	n.d.

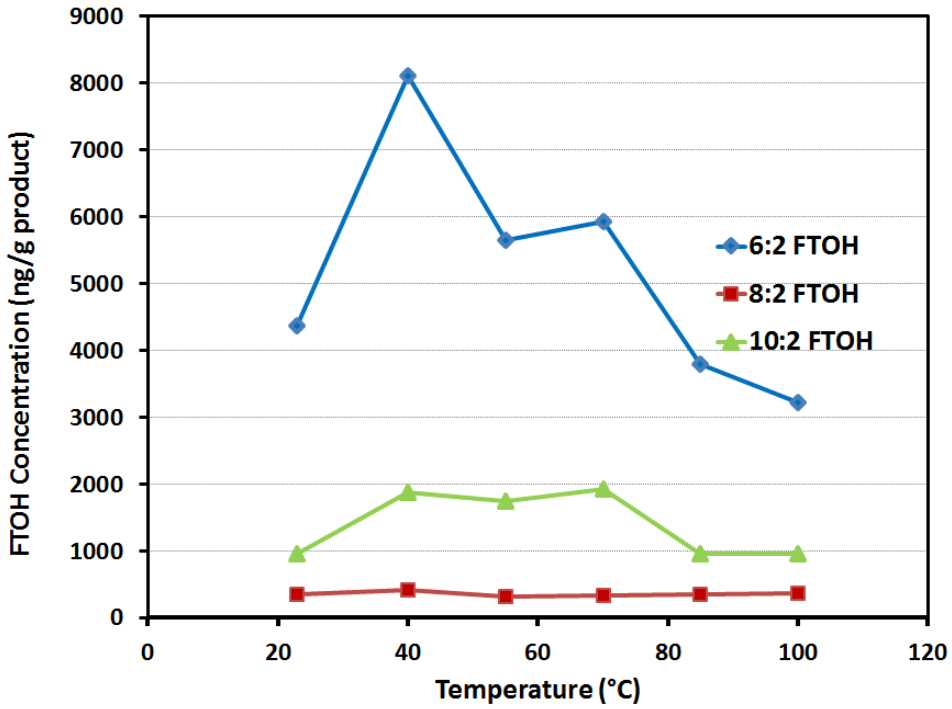
Source: Heydebreck, F., Tang, J., Xie, Z., & Ebinghaus, R. (2016). *Emissions of Per- and Polyfluoroalkyl Substances in a Textile Manufacturing Plant in China and Their Relevance for Workers' Exposure. Environmental Science & Technology, 50(19), 10386-10396. D*oi:10.1021/acs.est.6b03213.

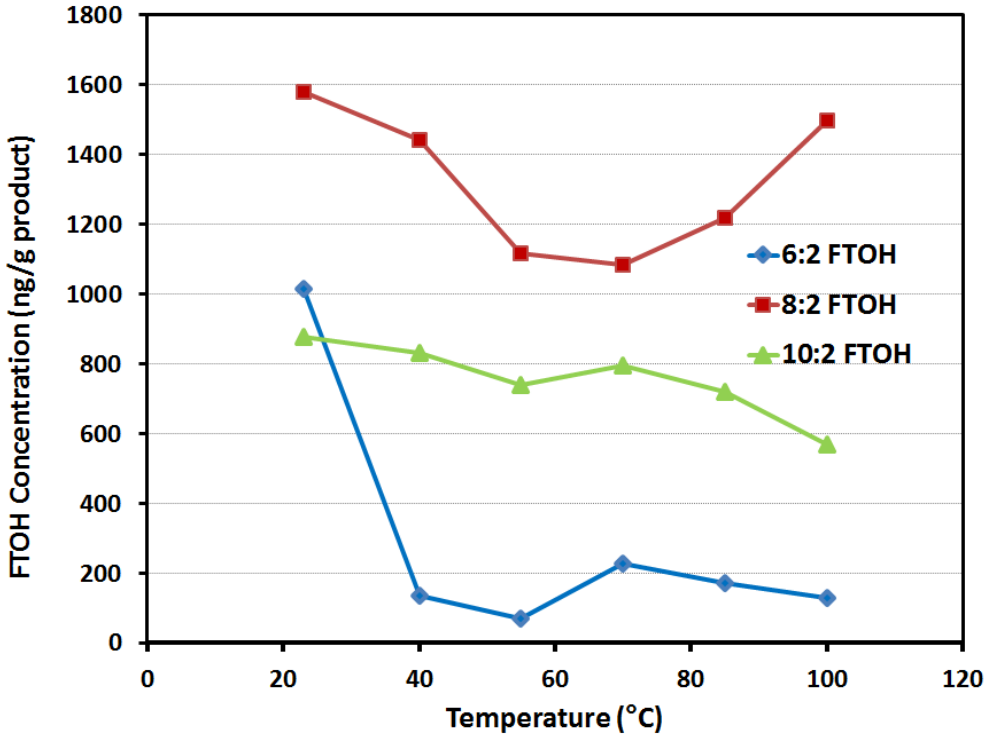
FTOH Concentrations (ng/µL) of measurements performed at room temperature on the off-gases directly from liquid preparations

	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH
Masurf FS-115	26.1	578.5	106.8	43.0
Zonyl FSA	9.4	948.1	130.7	17.9
Capstone FS-35	6.7	644.6	–	–
Arctic 3 AFFF	–	1.6	0.3	–

Source: Riedel, T. P., Lang, J., Strynar, M. J., Lindstrom, A. B., & Offenberg, J. H. (2019). Gas-Phase Detection of Fluorotelomer Alcohols and Other Oxygenated PFAS by Chemical Ionization Mass Spectrometry. Environmental Science & Technology Letters. doi:10.1021/acs.estlett.9b00196

FTOH Concentrations (ng/g product) emitted at diferente temperatures





Source: Liu, X., Guo, Z., Folk, E. E., & Roache, N. F. (2015). *Determination of fluorotelomer alcohols in selected consumer products and preliminary investigation of their fate in the indoor environment. Chemosphere, 129, 81–86.*
doi:10.1016/j.chemosphere.2014.06.012

Fluorine-based wet-based treatment (methodological framework)

- The **Tier 1** method is the least accurate estimation method and should be used only in cases where site-specific data on the consumption of input chemicals are not available.
- The **Tier 2a** method calculates emissions for each input chemical used on the basis of site-specific data on chemicals consumption and emissions control technologies. The Tier 2a method does not distinguish between processes, substrate types, or site-specific processes.
- The **Tier 2b** method is similar to the Tier 2a approach but the Tier 2b factors account for the types of wet production processes '*p*' and/or classes of products.
- The **Tier 3** method uses the same set of equations as the Tier 2b method. However, compilers need to interpret '*p*' in these equations as a specific production process using a specific 'recipe'.
  - **Currently, due to the absence of Tier 1 and Tier 2 default emission factors, only the Tier 3 method can be applied through the measurement of recipe-specific emission factors.**

Fluorine-based Plasma treatment

- Plasma processes used for the treatment of textiles can be divided into three process types:

1) **Plasma treatment** consists of using inert gases such as Ar, He, N_2, and chemically active molecules such as fluorinated gases such as CF_4, C_2F_6, C_3F_8, C_4F_8, C_5F_{10}, CHF_3, SF_6, and other (larger size) fluorine-containing molecules such as perfluoroalkyl acrylates to introduce chemical functionalities onto the target surface that and *graft* other molecules to attain specific surface properties.
2) **Plasma etching** is a process type where the substrate is bombarded with ions from the plasma to clean, sterilize, or enhance surface adhesion of the fabrics. Also in this case fluorinated gases can be used (e.g. CF_4).
3) **Plasma polymerization** is a process type where a monomer (e.g. CF_4, C_2F_6, C_3F_6, or larger fluorinated molecules such as fluorodecylacrylate) in vapour phase is converted into reactive fragments to deposit a thin film onto the substrate.

Most important input chemical monomers used in plasma treatment

ATMOSPHERIC PLASMA	LOW PRESSURE PLASMA
$C_{11}H_7F_{13}O_2$	CF_4 (PFC-14)
$C_{13}H_7F_{17}O_2/C_{15}H_7F_{21}O_2$	C_2F_4 (PFC-1114)
Unidyne TG-571®	C_3F_6 (Perfluorocyclopropane)
CF_4 (PFC-14)	C_2F_6 (PFC-116)
CHF_2CF_3 (HFC-125)	C_3F_8 (PFC-218)
CHF_3 (HFC-23)	C_4F_{10} (PFC-31-10)
C_3F_6 (Perfluorocyclopropane)	C_6F_{14} (PFC-51-14)
C_2F_6 (PFC-116)	C_4F_8 (PFC-318)
$C_8F_{17}CH_2CH_2OCOCH=CH_2$	CHF_2CF_3 (HFC-125)
C_3F_8 (PFC-218)	SF_6 (Sulfur hexafluoride)
$C_{13}H_7F_{17}O_2$	CF_3SO_3H (co-monomer)
SF_6 (Sulfur hexafluoride)	C_2ClF_3 (co-monomer)
$H_2C=CHCO_2CH_2CH_2(CF_2)_7CF_3$	C_6F_6 (co-monomer)
$C_6H_{13}F_3O_3Si$ (FAS-3)	HC_6F_5 (co-monomer)
$C_6F_5Si(OC_2H_5)_3$ (FAS-5)	$CF_3(CF_2)_7CH=CH_2$
$C_{13}H_{13}F_{17}O_3Si$ (FAS-17)	1,1,2,2, tetrahydroperfluorodecyl acrylate (AC8)

Fluorine-based treatment Emissions (methodological framework)

- The **Tier 1** method is the least accurate estimation method and should be used only in cases where site-specific data on the consumption of input chemicals are not available.
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    - **Currently, due to the absence of Tier 1 and Tier 2 default emission factors, only the Tier 3 method can be applied through the measurement of recipe-specific emission factors.**

CONCLUSIONS AND PERSPECTIVES

- PFAAs, PFOS, PFOA and telomeric alcohols are not relevant as GHG. However, Some literature refer to possible emissions of fluorocarbon in the atmosphere due to wet and plasma coating of textiles, but no data or estimations of emissions can be found.

- Several telomeric preparations are frequently mixtures of short and long perfluoroalkyl chains (C6, C8, C10 of Fluorotelomer acrylates, Fluorotelomer methacrylates and Per-fluoroalkane sulfonamidoethanols).

- It is not clear whether fluorinated ethers, perfluoropolyethers, unreacted monomers or by-products formed during the pad-dry-cure (150-190 ºC) process or other thermal coating process in textile, leather and paper industry can produce relevant GHG gases.

CONCLUSIONS AND PERSPECTIVES

- Some commercial processes for producing functionalized fluoroalkyl intermediates such as electrochemical fluorination of hydrocarbon structures and telomerization could produce non-CO_2 GHG gases.

- Some replacements of PFASs, fluorinated ethers, fluototelomers and short-chain PFASs less toxic but more persistent in the environment and with higher mobility could be relevant as GHG gases.

Source: 1) Brendel S et al. (2018). Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH. *Environmental sciences Europe*, *30*(1), 9. doi:10.1186/s12302-018-0134-4; **2)** Dumoulin R et al. (2005) Laboratory measurements of the infrared absorption cross sections of fluorotelomer alcohols. In: *European Geosciences Union*, p. 10257. Vienna, Austria: Geophysical Research Abstracts.

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Thank you for your attention

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