Introduction to fluorinated POPs (PFOS, PFOA, PFHxS and other PFAS) related to polymers and plastics

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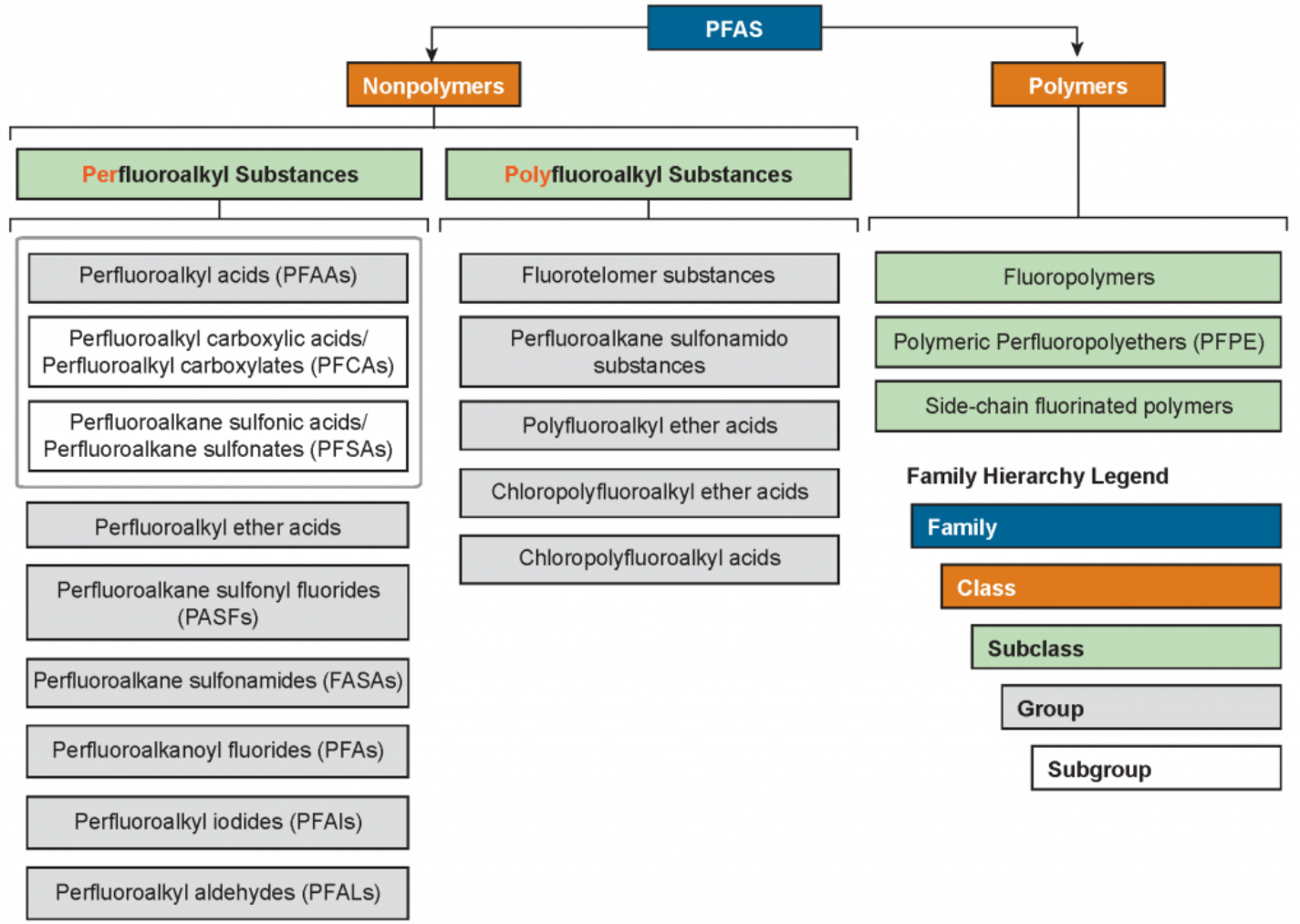
April 25th, 2023

IPCP Webinar Series: POPs in plastic and monitoring approaches

Outline

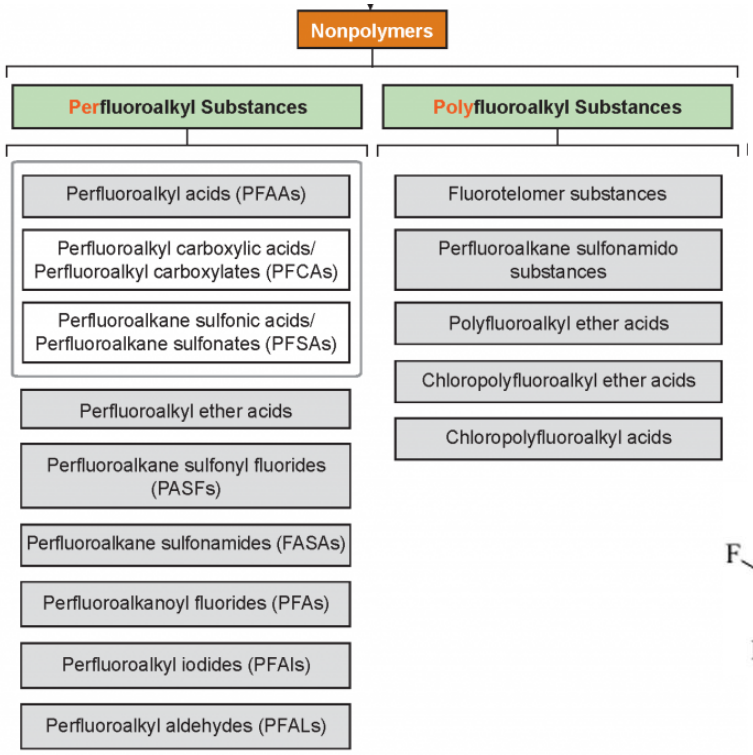
- Introduction and overview of different PFAS and different types of fluorinated polymers
- Fluoropolymers
- Side-chain fluorinated polymers
- Fluorinated high-density polyethylene (HDPE) containers
- Conclusions
- Questions and answers

PFAS Universe

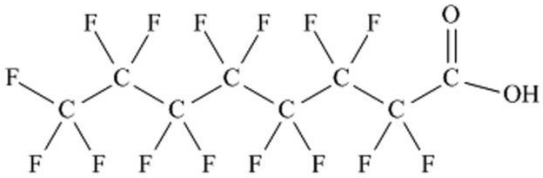


https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/

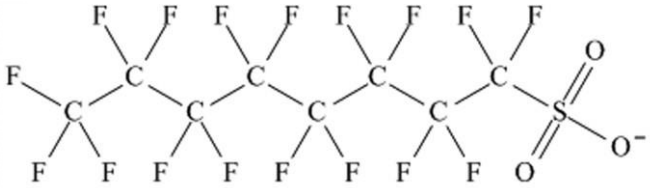
Non-polymeric PFAS



Legacy

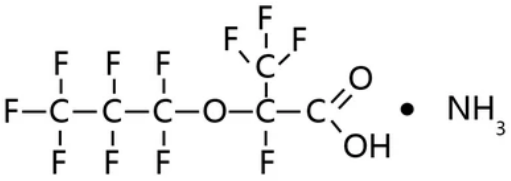


Perfluorooctanoic acid (PFOA)

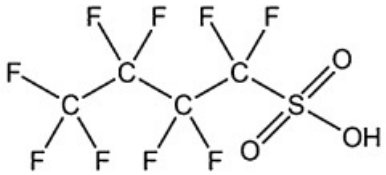


Perfluorooctane sulfonic acid (PFOS)

Replacements



C3 dimer salt ("GenX")



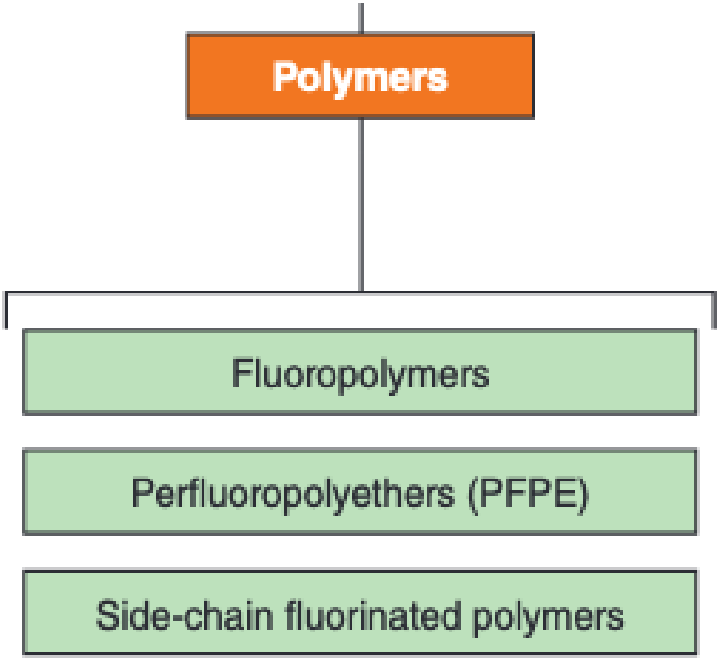
Perfluorobutane sulfonic acid (PFBS)

PFAS listed in the Stockholm Convention

- PFOS, its salt and PFOSF
- PFOA and related compounds
- PFHxS and related compounds

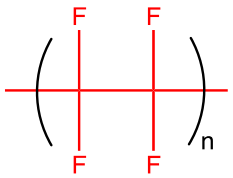
Long-chain perfluoroalkyl carboxylic acids (C9-C21 PFCAs) are being evaluated in POPRC for their POP properties and possible listing in the Convention.

Polymeric PFAS

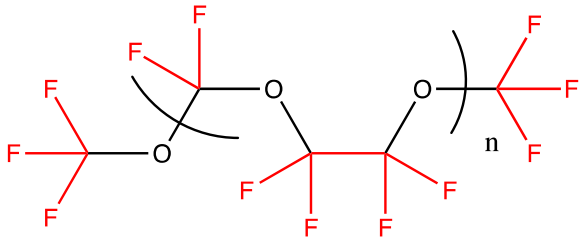


- Fluorinated polymers = all polymers for which one or more of the monomer units contains F, in the backbone and/or in side chains (Buck et al., 2011), including

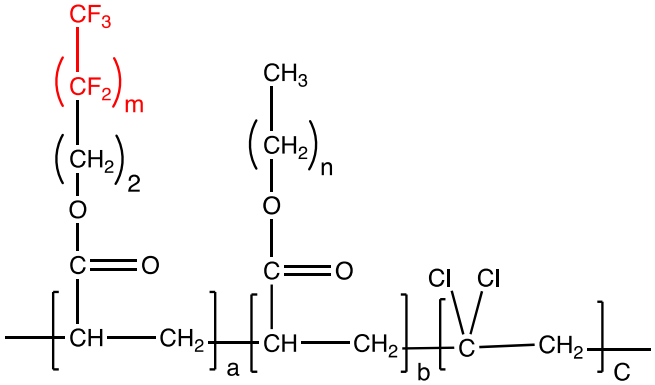
fluoropolymers



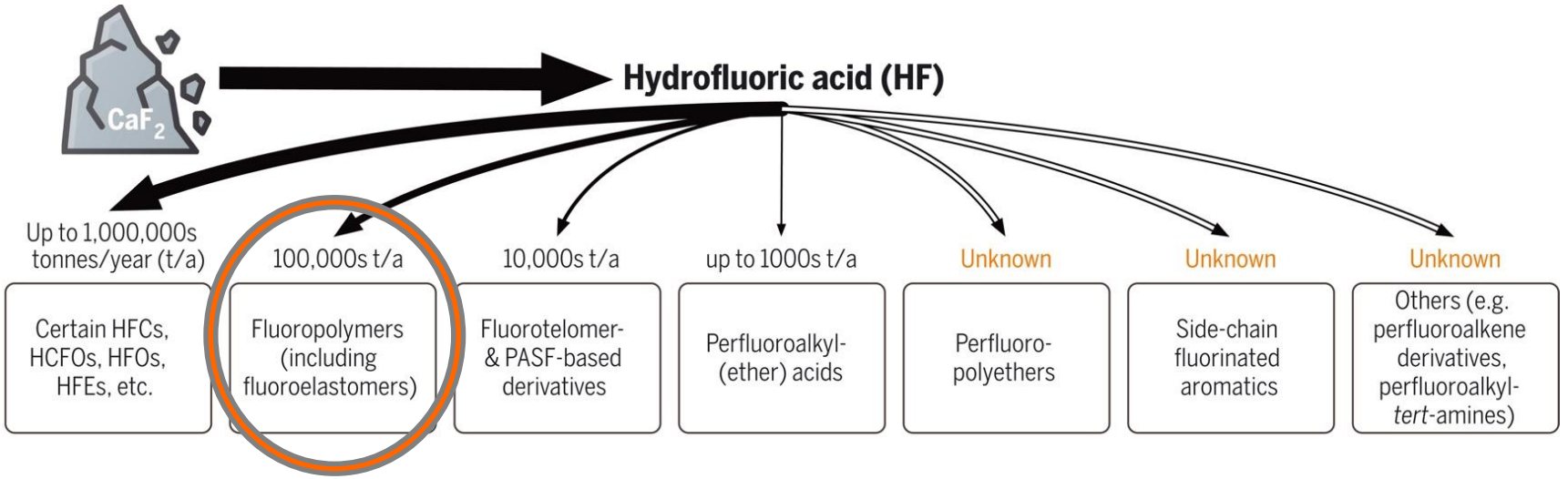
perfluoropolyethers



side-chain fluorinated polymers



The Importance of Fluoropolymers

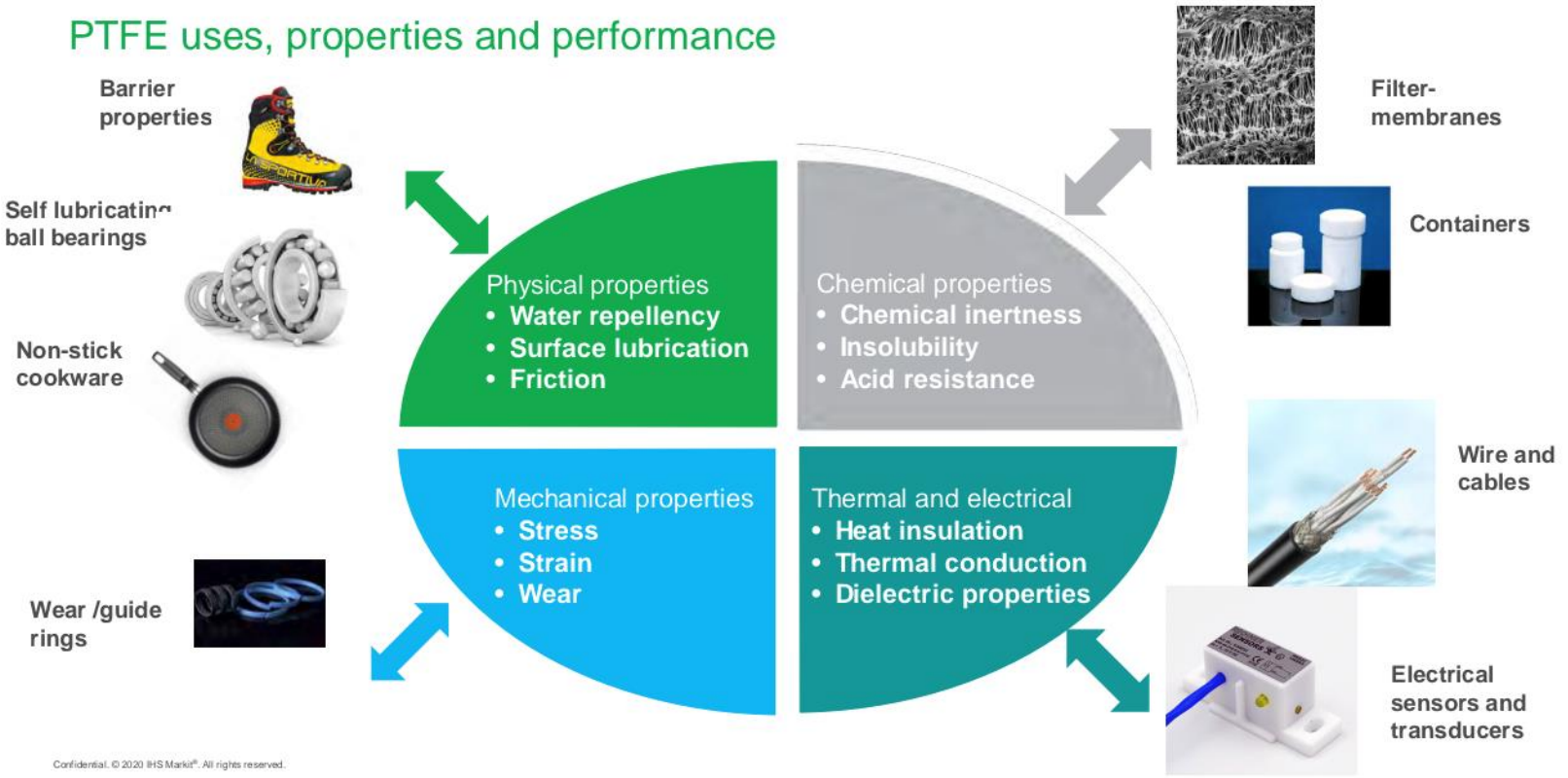


https://www.science.org/doi/abs/10.1126/science.abg9065

320 000 tonnes in 2018

https://www.agcce.com/fluoroplastics/;
https://hal.archives-ouvertes.fr/hal-02926117/document

Properties and uses of fluoropolymers



Wietlisbach S. (2020). Fluorochemicals Outlook. Fluorine Forum 2020.

Uses of fluoropolymers in Europe

Industrial sectors	Uses	Sales in 2015 [t]
Transport	Seals and rings; fuel management systems	18 500
Chemical & power	Polyolefin processing; anti-dripping agents; gaskets, vessel liners, valve and pipe liners, tubing, coatings, cable coatings, filters	16 500
Cookware	Non-stick cookware	3 500
Electronics	Semiconductor manufacturing (process surfaces, wafer carriers, tubing, valves, pumps, and fittings), wire and cable insulation, connectors, optical fibers	3 500
Food & pharma	durable processing equipment covering	3 000
Textiles & architecture	Coated fabrics and films for buildings and roofs, clothing, etc.	3 000
Medical applications	Cardiovascular grafts, heart patches, ligament replacement, catheters, guide wires, filters and pumps	1 500
Renewable energy	Front/backside films in solar applications, PEM fuell cells, lithium-ion battery	500
Others	Copier roller	2 000

https://fluoropolymers.plasticseurope.org/application/files/7816/1167/4026/Final_SEA_Fluoropolymers_summary2017_3.pdf

Uses of PFAS

Environmental Science Processes & Impacts

ROYAL SOCIETY OF CHEMISTRY

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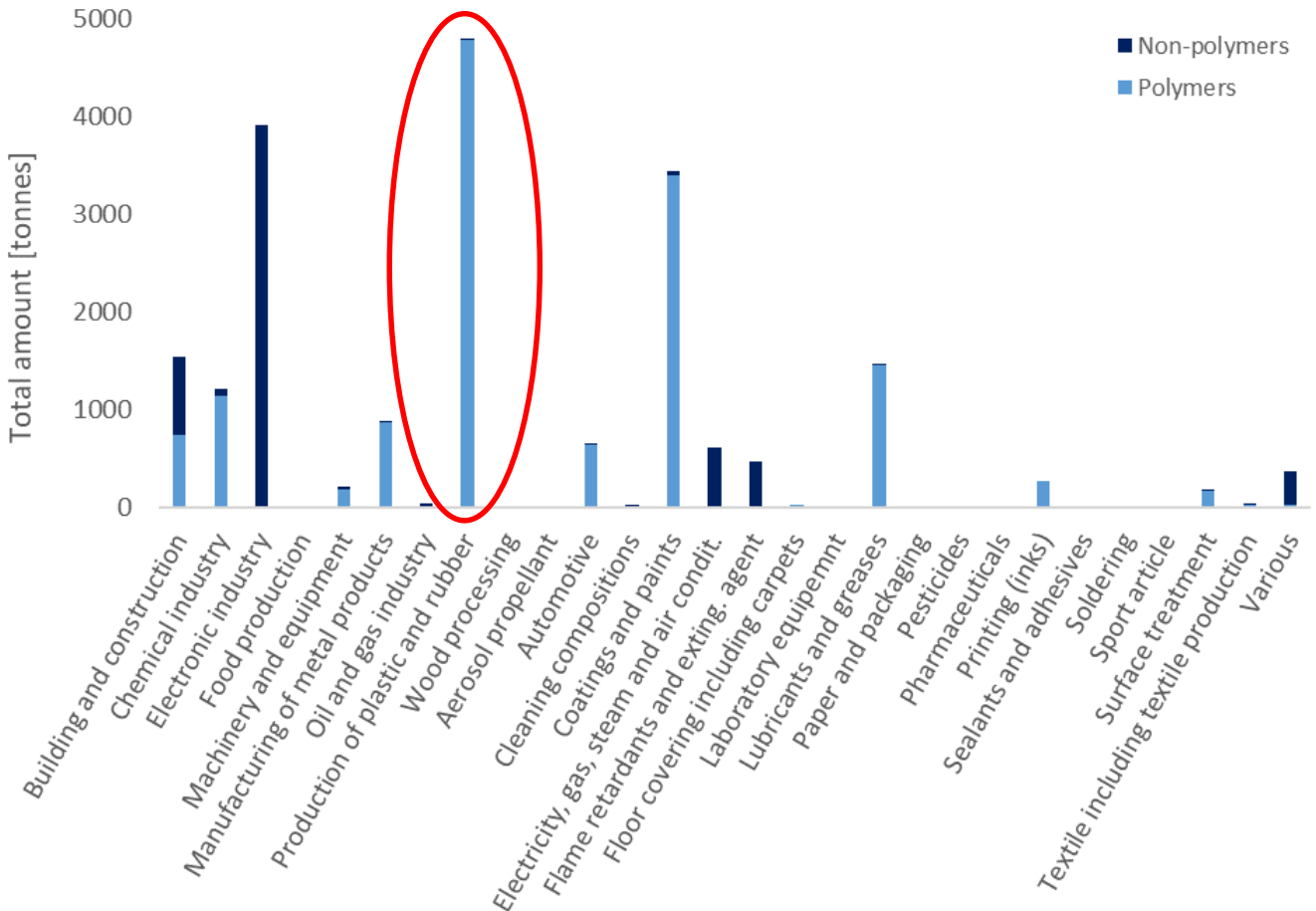
Cite this: DOI: 10.1039/d0em00291g

An overview of the uses of per- and polyfluoroalkyl substances (PFAS)†

Juliane Glüge, *[a] Martin Scheringer, [a] Ian T. Cousins, [b] Jamie C. DeWitt, [c] Gretta Goldenman, [d] Dorte Herzke, [ef] Rainer Lohmann, [g] Carla A. Ng, [h] Xenia Trier [i] and Zhanyun Wang [j]



More than 200 uses identified for more than 1400 PFAS

Polymers dominate use

Fluoropolymer additives to non-fluorinated plastics

- PTFE added as **anti-dripping agent** (“flame retardant synergistic agent”) and **anti-wear agent**
- **Polymer processing additives** added (50-1000 ppm added) to improve **moulding/extrusion** of non-fluorinated polymers
- If you measure F in non-fluorinated plastics don’t be surprised

Global Production/Consumption Volumes

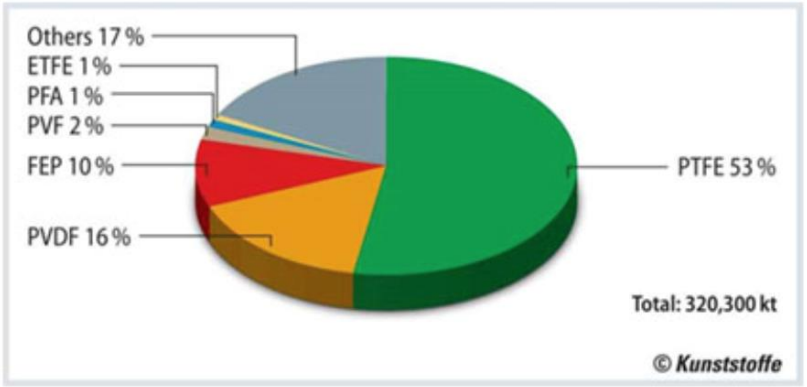


Fig. 1. Worldwide consumption of fluoroplastics in 2018 by type (sources: Fluoropolymers, IHS Markit; Recent Challenges in Fluoropolymer Business, FPS GmbH)

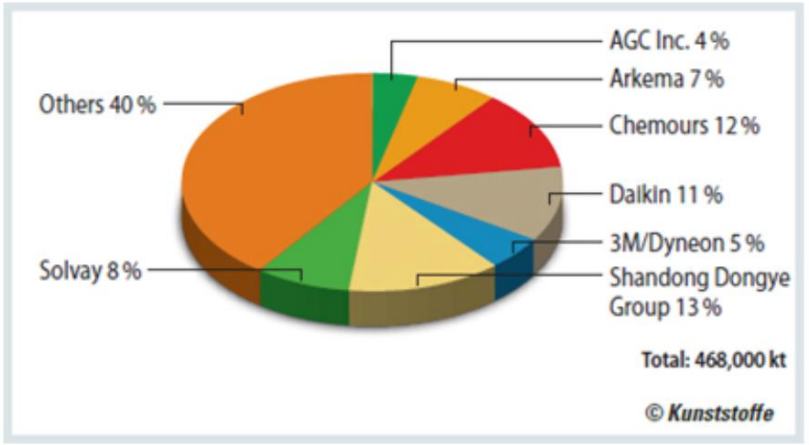


Fig. 3. Production capacities of the six most important fluoroplastics manufacturers represented worldwide as well as the Chinese Shangdong Dongye Group
(sources: Fluoropolymers, IHS Markit)

Fluoroelastomers (FKM + FFKM)
in 2018/2019: ca. 35 kt

FFK = Fluorinated Kautschuk Material
FFKM = Fully Fluorinated Kautschuk Material

Kautschuk = rubber in German

https://www.agcce.com/fluoroplastics/;
https://hal.archives-ouvertes.fr/hal-02926117/document

Global Consumption

Country / region	Consumption in 2018 [kt]
China	120.1
USA	69.0
Western Europe	50.9
Japan	18.2
Others	62.1
Total	320.3

Source: Fluoropolymers, IHS Markit

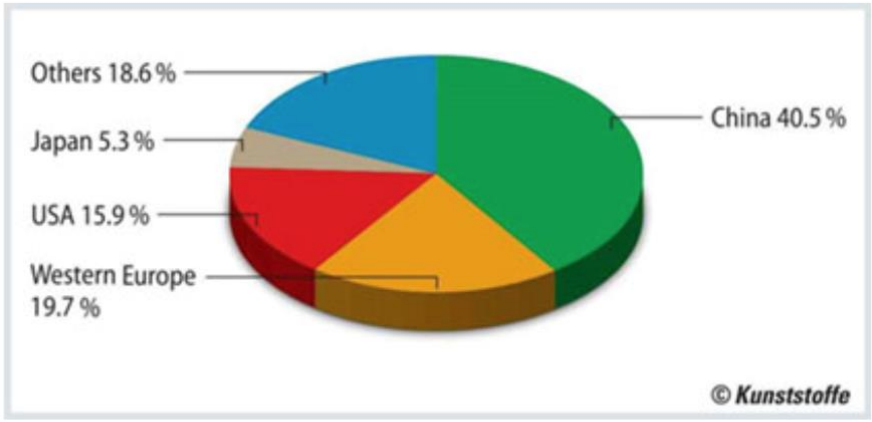


Fig. 2. Largest buyers of PTFE 2018 by region
(sources: Fluoropolymers, IHS Markit)

https://www.agcce.com/fluoroplastics/

Production trends

TREND
Polymers for the Future

Macromolecular Chemistry and Physics
www.mcp-journal.de

The Promising Future of Fluoropolymers

Bruno Améduri

~ 320 300 t in 2018, and production steadily increasing

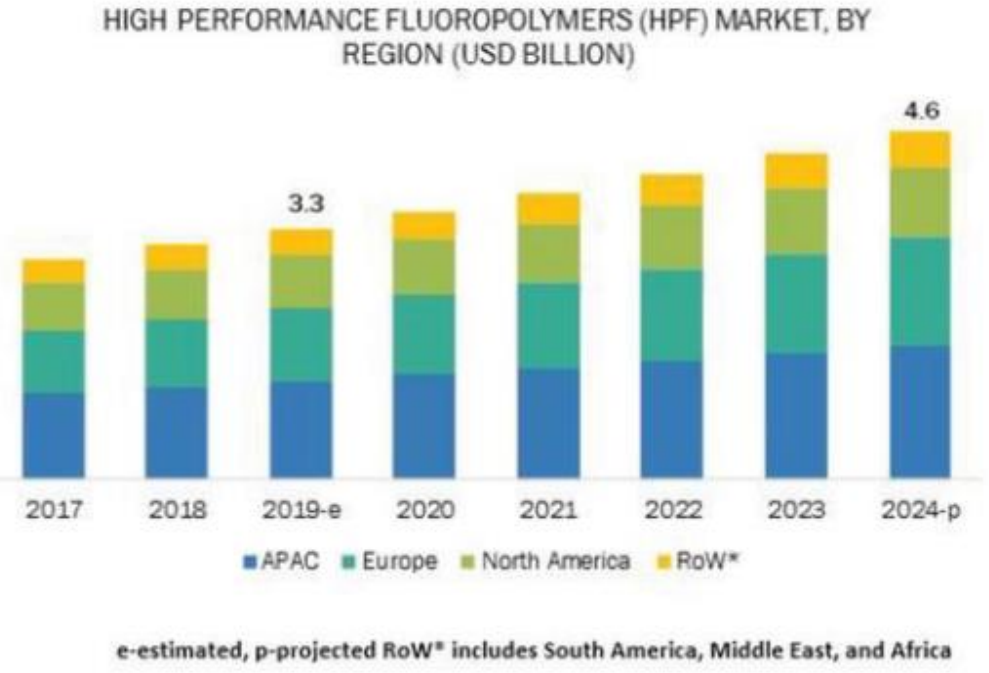
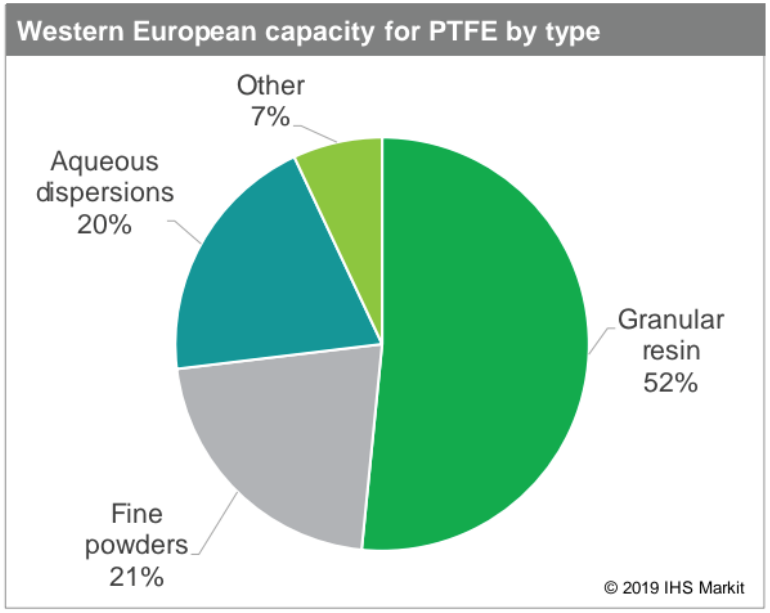


Fig. 2. represents the fast growing market for high performance FPs to 2024.

Relevance of fluoropolymers to Stockholm Convention?

- Salts of PFCAs (e.g. ammonium salts of PFOA and PFNA) were used as "processing aids" in the polymerization of certain types of fluoropolymers historically
  - Large releases of PFOA and PFNA to environment from fluoropolymer manufacturing
  - not all fluoropolymer manufacturing requires polymerization aids (emulsion polymerization does but not suspension polymerization)
  - residuals of PFOA and PFNA (and other PFAS) in fluoropolymer products
- PFOS or PFHxS were not used in fluoropolymer manufacture
  - But very relevant to side-chain fluorinated polymers

Types of PTFE



Granular resin

- Thick walled tubing
- Molded parts

Fine powders

- Sintering and stretching
- Extruding thin sections

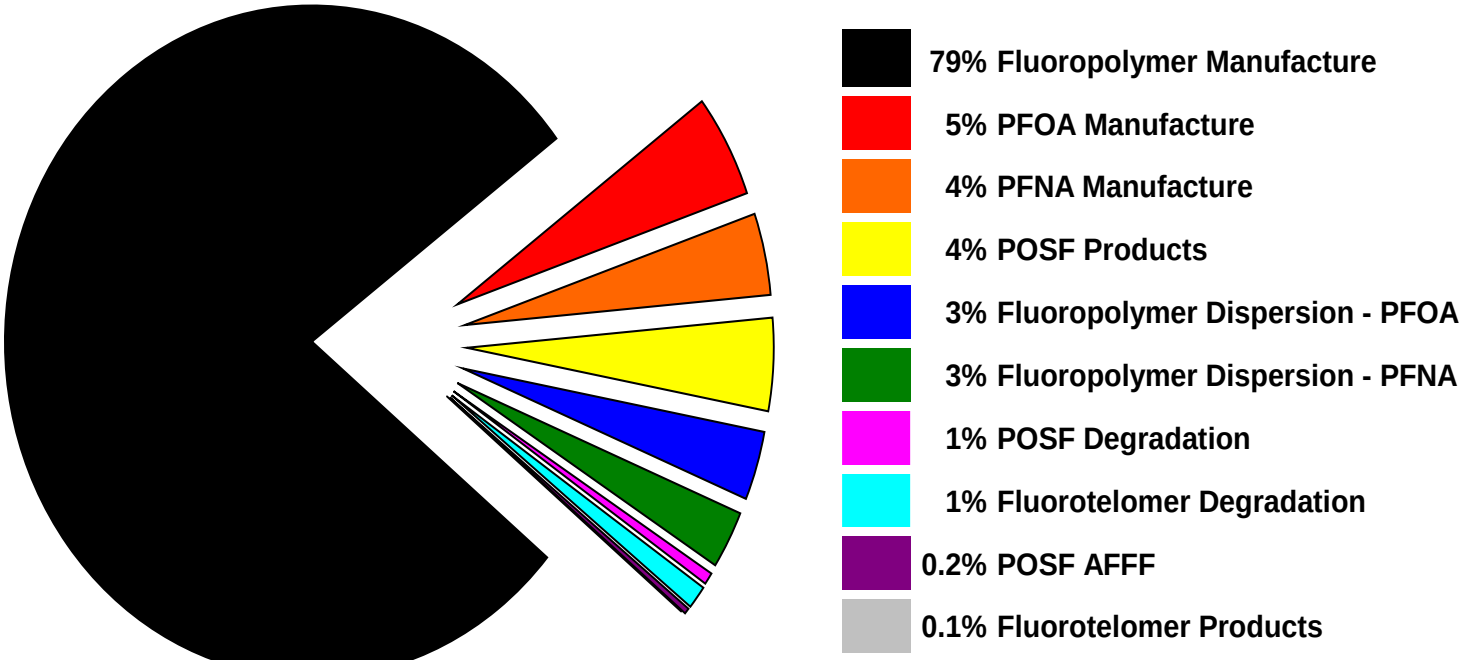
Aqueous dispersions

- Tough coatings
- Fibre impregnation
- Fibre production

- Fine powders and aqueous dispersions (small particle sizes) are made by emulsion polymerization and thus require surfactant processing aids
- Granular resins (coarser particles) can be made by suspension polymerization and do not require surfactant processing aids

PFCA emissions from fluoropolymer manufacturing

Stockholm University



% of total historical (1950-2004) global PFCA emissions

Sources, Fate and Transport of Perfluorocarboxylates

KONSTANTINOS PREVEDOUROS,† IAN T. COUSINS,*,† ROBERT C. BUCK,‡ AND STEPHEN H. KORZENIOWSKI‡

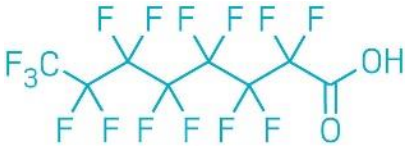
Estimated PFCA emissions by carbon chain length

PFCA	Σ (1950-2004) MIN [t]	MAX [t]	% Direct Sources	% Indirect Sources
PFB 4	1	55	0%	100%
PFP 5	1	32	0%	100%
PFHx 6	40	355	77%	23%
PFHp 7	18	265	63%	37%
PFO 8	2720	5940	94%	6%
PFN 9	360	1340	99%	1%
PFD 10	4	55	31%	69%
PFUn 11	92	345	99%	1%
PFDo 12	1	12	58%	42%
PFTe 13	23	86	99%	1%

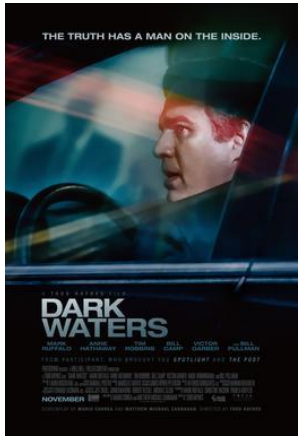
- PFOA dominates global historical emissions of PFCAs from PTFE manufacturing
- PFNA emissions from PVDF manufacturing also high

Pollution resulting from use of PFCAs in fluoropolymer manufacturing

PFOA – e.g., W Virginia
(C8 study)

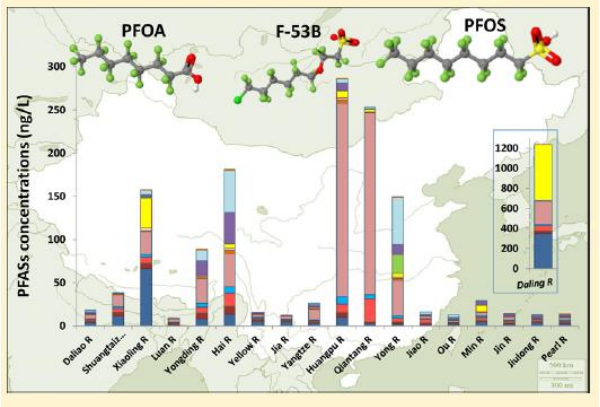


PFNA – e.g., New Jersey
(NJ suing Solvay)



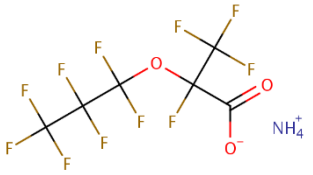
Mostly phased out under US EPA 2010/15 Stewardship Program

PFOA still used as a processing aid in China; high PFOA emissions in Chinese/Asian rivers (Wang et al., 2016)

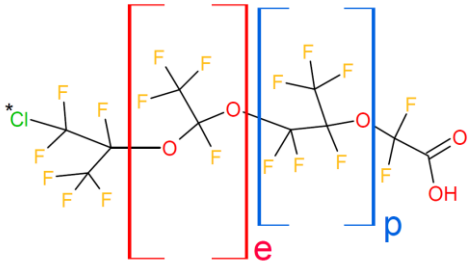


Substitute PFAS processing aids

a) Ammonium salt of hexafluoropropylene oxide dimer acid (HFPO-DA, CAS 62037-80-3, or GenX, Chemours) detected in the environments of North Carolina and the Netherlands.



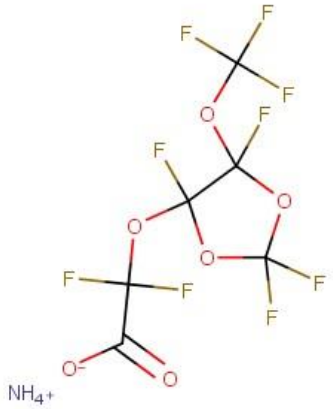
b) Functionalized PFPE reported in Wang et al. 2013 (CAS 329238-24-6, Solvay) now observed in Bormida River (Italy) and New Jersey (Washington et al., 2020).



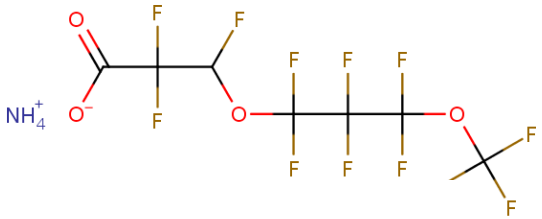
Note: the e = ethyl group can range from 0 - 2 units and p = propyl group can range from 1 – 4 units with the ethyl group most likely being closest to the chlorine. Additionally, the chlorine can be on the terminal carbon as shown or on the C2 position as $CF_3CF(Cl)CF_2$-O.

More substitute PFAS processing aids

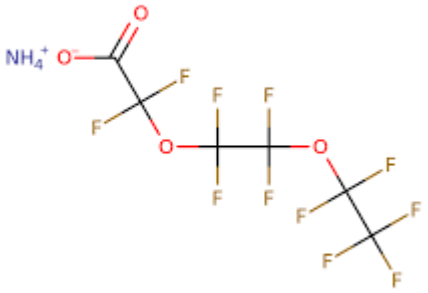
c) Perfluoro{acetic acid, 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt (CAS No 1190931-27-1) (cC604, Solvay) now observed in ground- and surface water in the Veneto region (Italy).
https://echa.europa.eu/substance-information/-/substanceinfo/100.207.411



d) Ammonium 4,8-dioxa-3H-perfluorononanoate (CAS 958445-44-8) (ADONA, 3M) detected in the Rhine River and serum samples.



e) ammonium difluoro[1,1,2,2-tetrafluoro-2- (pentafluoroethoxy)ethoxy]acetate (CAS 908020-52-0) (EEA, Asahi Glass) detected in water and air near Thornton Cleveleys, Lancashire.



Non-fluorinated processing aids

Stockholm University

GFL
GUJARAT FLUOROCHEMICALS
VALUE THROUGH GREEN CHEMISTRY
CIN : L24304GJ2018PLC105479

Gujarat Fluorochemicals Limited

Corporate Office: INOX Towers, Plot No. 17, Sector-16A, Noida-201301, Uttar Pradesh, India.
Tel: +91-120-6149600
Fax: +91-120-6149610 | www.gfl.co.in

25.08.2022

Company Announcement

Gujarat Fluorochemicals Limited (GFL) is pleased to announce a successful development in the production process of FKM (fluoroelastomers).

Based on this development, GFL shall stop the use of fluorinated polymerization aids (PFAS) in the manufacture of FKM terpolymers, which was a necessary requisite in previous production processes. GFL is not using fluorinated polymerization aids in the manufacture of FKM copolymers.

FKM products manufactured with the updated technology exhibit technical properties that are equivalent in performance in various applications of interest, compared with previous FKM commercial grades. Commercial production of FKM terpolymers with the updated technology has started already.

This is a significant step forward in our ambition to discontinue the use of fluorinated polymerization aids in the manufacturing process of fluoropolymers, in line with our previous announcement dated 9 March 2022, in which we communicated our pioneering successful development involving the use of non-fluorinated polymerization aids in the emulsion process to obtain PTFE aqueous dispersions.

Non-fluorinated processing aids

Stockholm University

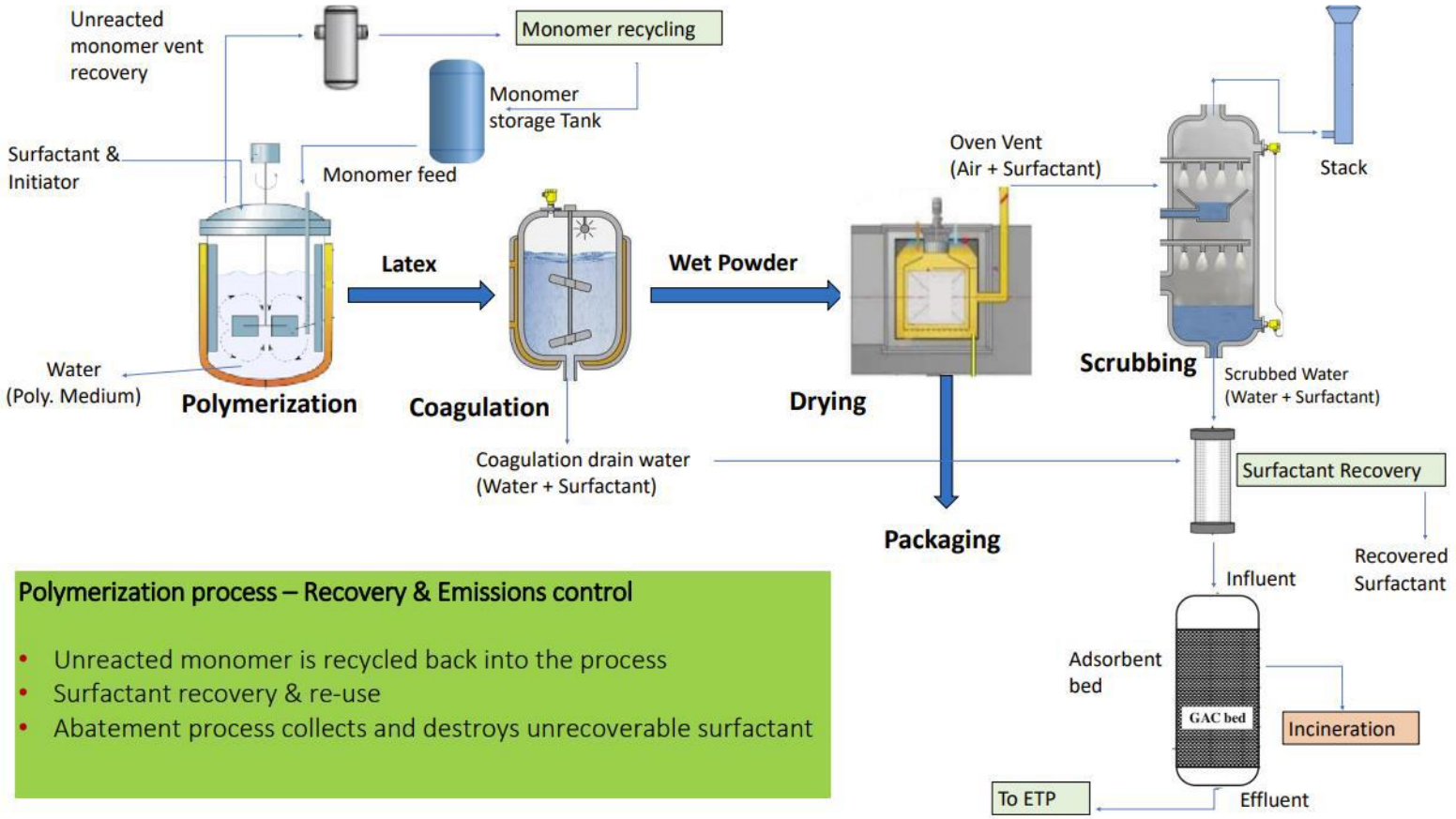
Table 1. Global production of fluoropolymers and use of FPAs.

Fluoropolymers	Volume (tonnes)	% of total volume	Use of FPAs	% volume that does not require the use of FPAs	% volume that will not require the use of FPAs[1]
PTFE Total	169,759	53%			
PTFE Suspension	84,879.5	26.5%	N	26.5%	26.5%
PTFE Emulsion	84,879.5	26.5%	Y		26.5%
PVDF (Homopolymer + Copolymer)	51,248	16%	N	16%	16%
FKM	35,000	10.9%			
FKM Copolymer	25,000	7.8%	N	7.8%	7.8%
FKM Terpolymer[2]	10,000	3.1%	Y/N	1.6%	3.1%
FEP	32,030	10%	Y		
PVF	6,406	2%	Y		
PFA	3,203	1%	Y		
ETFE	3,203	1%	Y		
THV	800	0.3%	Y		
ECTFE (Copolymer + Terpolymer)	2,200	0.3%	N	0.3%	0.3%
PCTFE	8,600	2.7%	N	2.7%	2.7%
Others	7,851	2.5%			
TOTAL	**320,300**			**54.8%**	**82.9%**

Courtesy of Jaime Sales from Chemservice

CHEMSERVICE

Emission reductions



Polymerization process – Recovery & Emissions control

- Unreacted monomer is recycled back into the process
- Surfactant recovery & re-use
- Abatement process collects and destroys unrecoverable surfactant

Abatement techniques achieve 99% recovery of surfactant

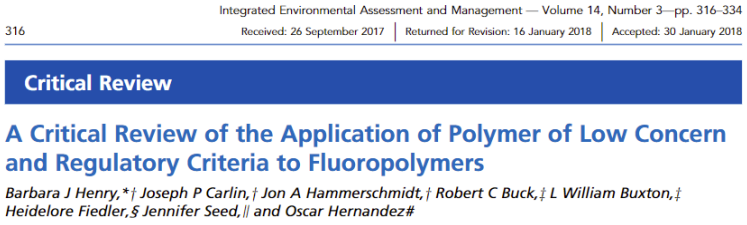
CHEMSERVICE

It's not just about processing aids!

- Many ultrashort-chain fluorinated by-products are highly volatile, difficult to capture, and have high GHG potential
- Detection of oligomers in stack emission samples (McCord et al, 2019)
- PVDF production (Decatur, AL): series of polyfluoroalkyl carboxylic acids with + CF_2CH_2 (Newton, 2017)
- Chemours (NC) confirmed > 250 novel, potentially unique PFAS in their effluents
  - Using non-fluorinated processing aids results in higher emissions of fluorinated byproducts

Fluoropolymer manufacturers' position

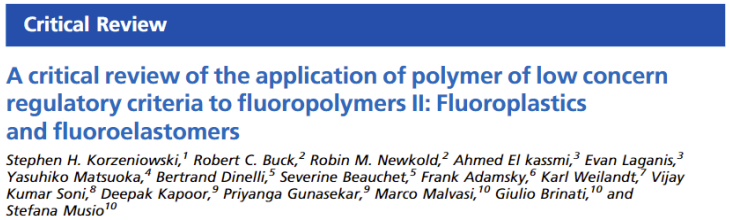
- Concern regarding how the broad PFAS regulations will affect business
- Believe that fluoropolymers should be considered as a separate family with regard to regulation using the following claims:
  - they meet the OECD "Polymer of Low Concern" (PLC) Criteria
  - Many industrial uses are essential for health and safety and critical to the functioning of society
  - Industry have made significant efforts to address lifecycle concerns


Integrated Environmental Assessment and Management — Volume 14, Number 3—pp. 316–334
316
Received: 26 September 2017 | Returned for Revision: 16 January 2018 | Accepted: 30 January 2018

Critical Review

A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers

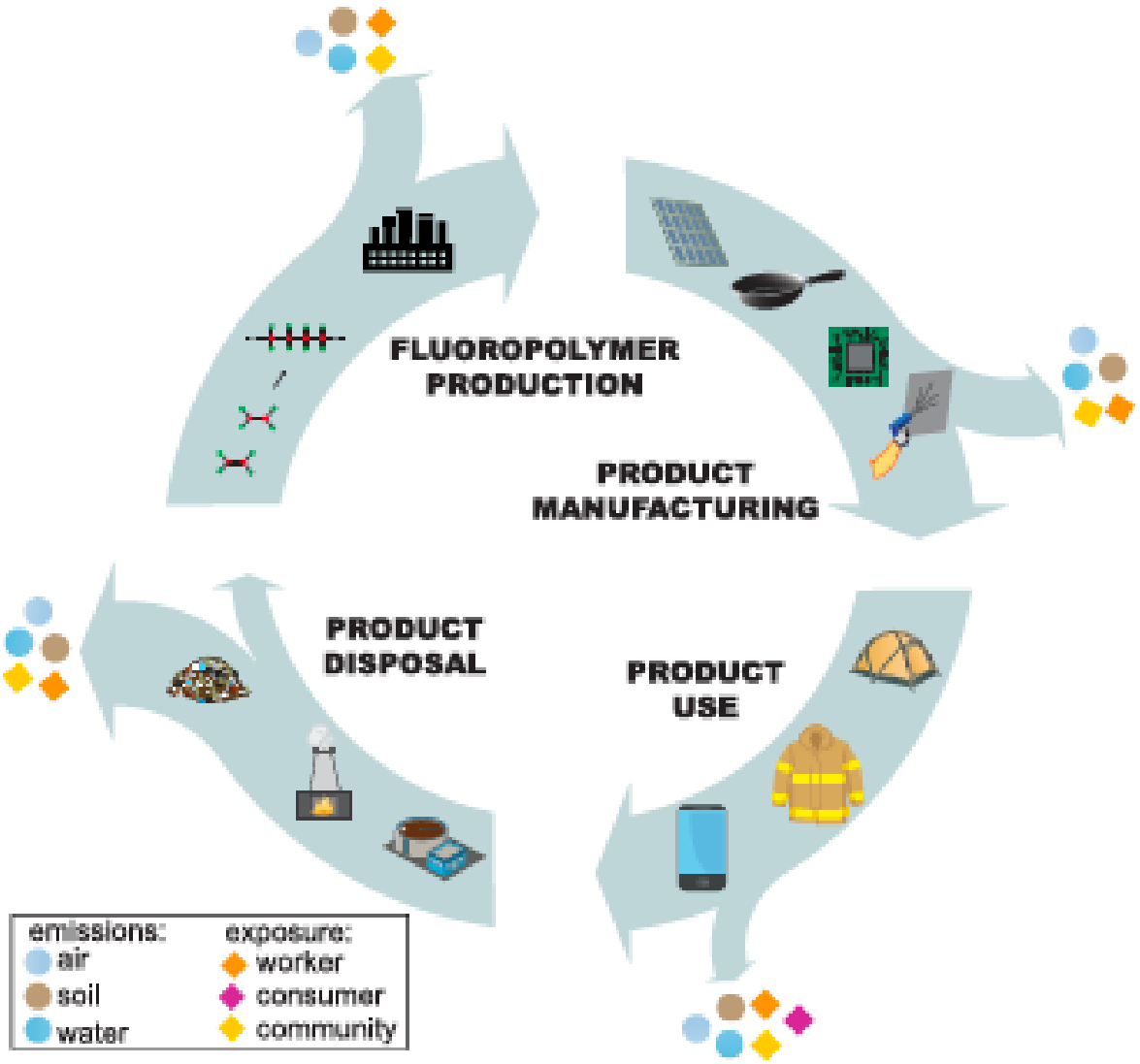
Barbara J Henry,*† Joseph P Carlin,† Jon A Hammerschmidt,† Robert C Buck,‡ L William Buxton,‡ Heidelore Fiedler,§ Jennifer Seed,‖ and Oscar Hernandez#


Critical Review

A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers

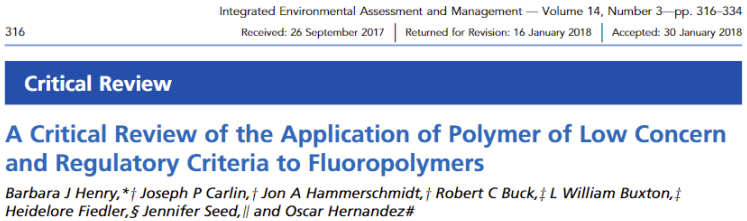
Stephen H. Korzeniowski,[1] Robert C. Buck,[2] Robin M. Newkold,[2] Ahmed El kassmi,[3] Evan Laganis,[3] Yasuhiko Matsuoka,[4] Bertrand Dinelli,[5] Severine Beauchet,[5] Frank Adamsky,[6] Karl Weilandt,[7] Vijay Kumar Soni,[8] Deepak Kapoor,[9] Priyanga Gunasekar,[9] Marco Malvasi,[10] Giulio Brinati,[10] and Stefana Musio[10]

The fluoropolymer lifecycle



The use phase

- OECD PLC criteria focus on use phase
  - Industry research shows that 18 different modern fluoropolymer products meet the PLC criteria
  - Stable, non-bioaccumulative, non-toxic, low leachables (<1 ppm, residuals removed), etc.
  - PFOA/PFNA largely phased out so zero residuals in modern products, historically 1 to >10 ppm residuals
- Some products may not meet the PLC criteria, e.g. Chinese imported fluoropolymer products?
- Overheating of cookware leads to release of short-chain PFCAs in the gas phase
  - Only solution is to follow normal operating procedures


Integrated Environmental Assessment and Management — Volume 14, Number 3—pp. 316–334
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Received: 26 September 2017 | Returned for Revision: 16 January 2018 | Accepted: 30 January 2018

Critical Review

A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers

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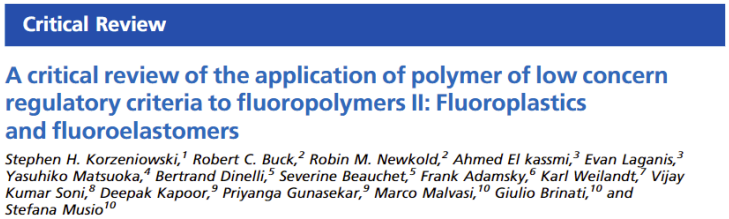
Critical Review

A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers

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End of Life –Waste Collection

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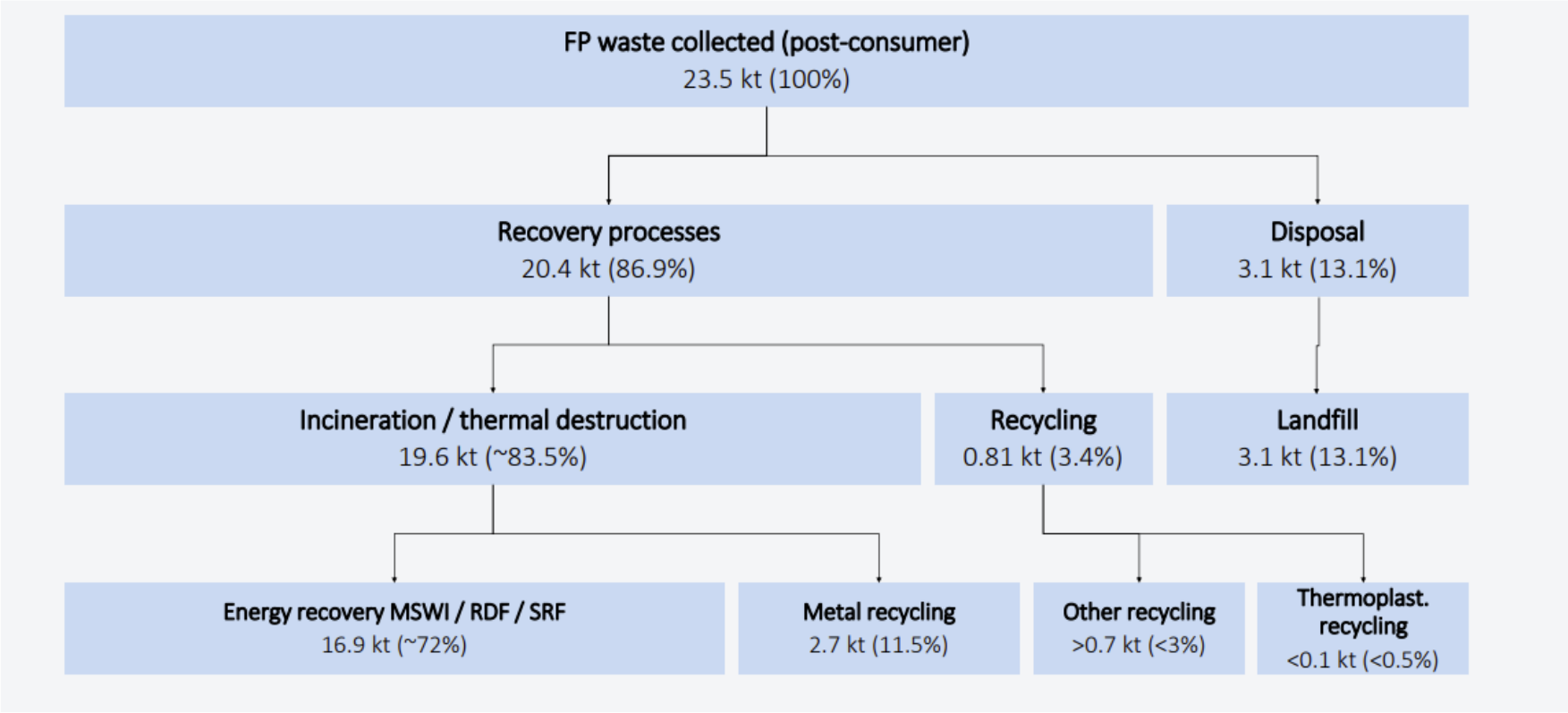
Collected FP waste by waste stream in the EU in 2020

FP relevant waste stream	Total waste collected in kt	Thereof plastics in kt	*Share in %*	Thereof FP in kt	*Share in %*
Residential household waste and municipal waste generated by commercial activities	148,500	10,300	*6.9*	2.2	*<0.01*
Electronic waste collection (WEEE)	5,000	1,170	*23.4*	2.3	*0.05*
ELV incl. auto-shredder residue (ASR)	10,000	1,190	*11.9*	3.0	*0.03*
Commercial & industrial (various streams; usually commingled)	400,000	4,700	*1.2*	15.1	*<0.01*
Total	**563,500**	**17,360**	***3.1***	**23.5**	***<0.01***
Other waste streams not further analysed / relevant *e.g., separate collection of LWP waste or separate collection of commercial packaging waste*	*51,500*	*12,090*	*23.5*	*<1 kt*	*<0.01*

Courtesy of Jaime Sales from Chemservice

CHEMSERVICE

End of life - treatment of waste



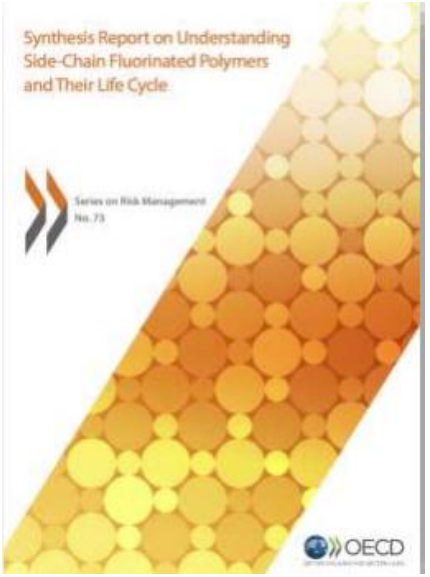
Courtesy of Jaime Sales from Chemservice

Emissions during incineration/thermal treatment

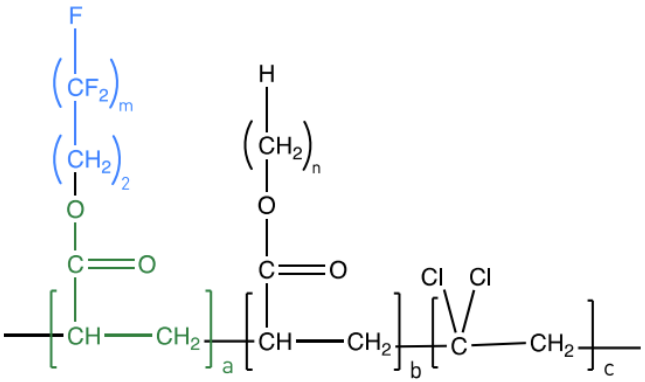
- Comprehensive review conducted by RIVM
- Concludes that PTFE will thermally break down (but mineralization uncertain) at operational temperatures (>850°C) into smaller fluorocarbon gases
  - could be strong greenhouse gases?
  - no evidence for POP PFAS releases
- International research ongoing to measure flue gases, fly ash, bottom ash, wastewater
- Metal recycling at lower temperatures

Side-chain fluorinated polymers (SCFPs)

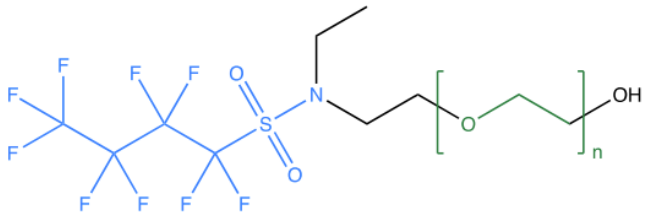
- Defined as polymers with a non-fluorinated polymer backbone and with PFAS moieties on the side chain(s)
- A non-exhaustive list of 103 SCFPs and 42 PFAS monomers in report by Zhanyun Wang
  - acrylates, urethanes, oxetanes, ethoxylates, etc.
  - Often exact structures cannot be identified
- Used (<10,000 tonnes/y) in:
  - surface treatments (textiles, carpets, food contact paper and board)
  - fluorosurfactants (e.g. in some firefighting foams, paints, laquers, varnishes, reprographic agents, adhesives, binding agents, printing inks, and glossing agents)



Key aspects of the chemistry of SCFPs



A. an example of fluorotelomer acrylate SCFPs



D. an example of PASF-based ethoxylate SCFPs
CASRN 68298-79-3

They have different non-fluorinated copolymers (A is an acrylate and D is an ethoxylate)

They can be flurotelomer(FT)-based or perfluoroalkane sulfonyl-fluoride(PASF)-based (A is FT-based and D is PASF-based)

The fully fluorinated carbon side chains can be of different lengths (typically 4, 6, 8 or 10 carbons)

Large historical use of perfluorooctane sulfonyl fluoride-based SCFPs

Stockholm University

Estimated total yearly use areas PFOS in the EU (for 2000)

Industrial application	EU consumption (Tonnes/year	PFOS & PFOS-related chemical
Verchromung **Plating**	10	PFOS, FOSE
Fotolithografie	0,47	
Fotografie	0,85	FOSAAcOH
Photographic	0,75	Polymer
Luftfahrt **Aviation**	0,73	Perfluorsulfonate
Feuerlöschmittel **AFFF**	0,57	FOSA
Faserveredelung **Fiber coating**	240	FOSE-Polymere
Papierveredelung **Paper**	160	FOSE-Polymere
Beschichtung **Coating**	90	

Source: Risk and Policy Analysts (2004); Fricke & Lahl, UWSF 17, 36 – 49 (2005)

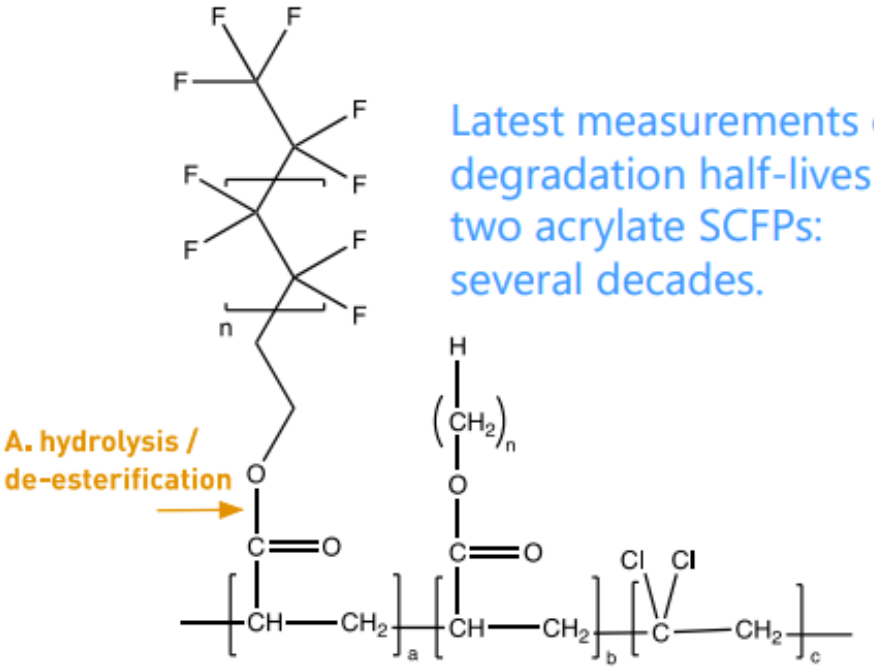
Use of FOSE-polymers in food contact materials probably highly important historical human exposure pathway for PFOS and PFOA

Key aspects of the chemistry of SCFPs

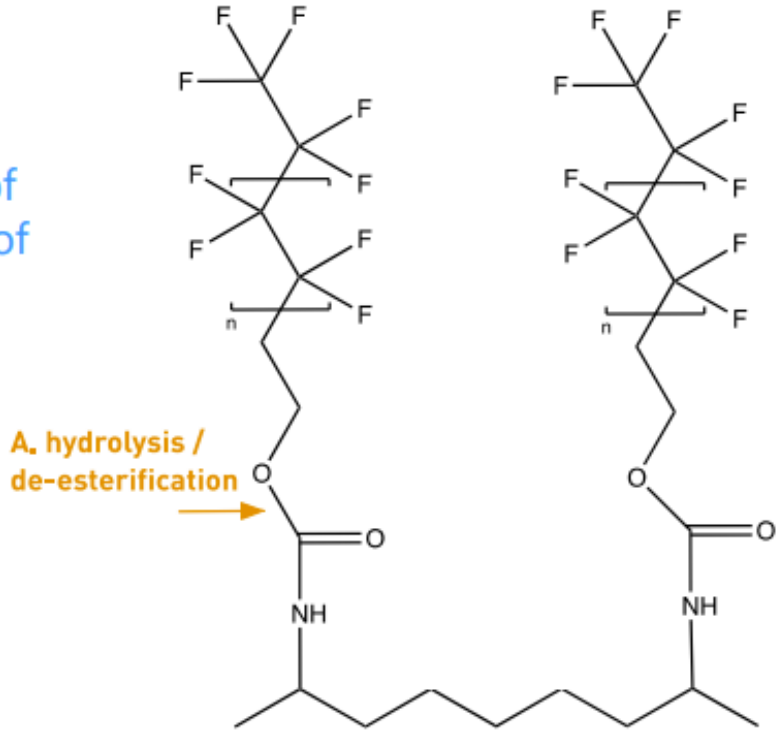
- The fluorinated side-chains do not cleave easily under environmental conditions
  - But the products contain impurities of perfluoroalkyl acids (PFAA) and PFAA precursors (at % levels) which leach out of the products
- PASF-based SCFPs with 8 fully fluorinated carbons contained PFOS, PFHxS and PFOA, and their precursors
- FT-based SCFPs with 8 fully fluorinated carbons contained PFOA, other PFCAs and their precursors
- Modern PASF-based SCFPs have 4 fully fluorinated carbons and modern FT-based SCFPs have 6 fully fluorinated carbons

Degradation of acrylate and urethane SCFPs

Latest measurements of degradation half-lives of two acrylate SCFPs: several decades.



an example of fluorotelomer acrylate polymers



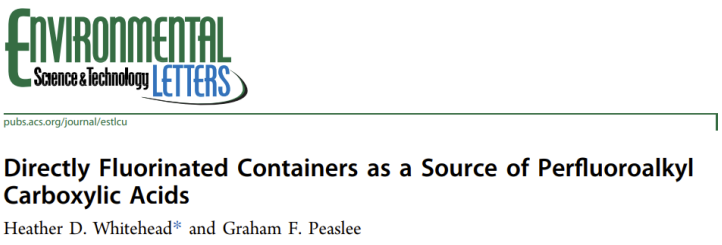
conceptual chemical composition of a fluorotelomer urethane polymer

Emissions of PFAAs and PFAA-precursors

- During the application of commercial formulations and the processing of treated materials into articles
  - 3M, 1999: 10–25% loss, in the case of fibre, textile and leather
- During the use and disposal of treated articles
- Target urethane SCFP compositions measured in lake sediment, soil samples, sludge from WWTPs and landfill leachates
  - They act as long-term sources of PFAAs to the environment
- The lifecycle of modern SCFPs would lead to emissions of PFBS and PFHxA (and their precursors) primarily
  - Negligible long-chain impurities (including POP PFAS)

Fluorinated high-density polyethylene (HDPE) containers

- Special category (not strictly fluorinated polymers)
  - Direct fluorination of plastic with fluorine-inert gas mixture to replace hydrogens with a thin layer of fluorine on the plastic surface
- Leaching experiments showed that PFCAs (including PFOA, PFNA, PFDA, PFUnDA) can leach from containers into food
- US EPA is currently investigating



Conclusions - Fluoropolymers

- Fluoropolymers produced in relatively high quantities
  - 320,000 tonnes in 2018 (industrial uses dominate)
- Industry pressure to separate them from other PFAS based on generalized claims of them being PLC
  - claim that it is challenging to find alternatives for some industrial uses
- Concerns remain:
  - Chinese emissions of PFOA, HFPO-TA
  - Companies continue to emit PFAS processing aids in Europe, US, etc.
    - but emissions controlled more and more
    - non-fluorinated processing aids being phased in
  - lack of information on other PFAS emissions during manufacture
  - end of life emissions?

Conclusions – SCFPs

- A wide range of SCFPs have been produced and used in many different applications (<10 000s tonnes/y)
- Many non-polymeric PFAS are present in SCFPs, sometimes up to % levels
- During the life cycle of SCFPs and related products, substantial amounts of SCFPs and associated non-polymeric PFAS are released (including POP PFAS)
- Degradation of SCFPs to form non-polymeric PFAS, including PFCAs and/or PFSAs, occurs in the environment and biota
  - SCFPs are acting as long-term significant sources to the global burden of non-polymeric PFAS
  - including POP PFAS stored in soils/landfills

Stockholm University

Thank you for your attention!

Acknowledgement: Thanks to Rainer Lohmann, Zhanyun Wang, and Roland Weber for sharing slides, and to IPCP for inviting me!

IPCP
International Panel on Chemical Pollution