Istituto Zooprofilattico Sperimentale del Mezzogiorno
Campania | Calabria

PFAS tra Ambiente e Salute:
aspetti analitici e studi di monitoraggio
Portici, 20 marzo 2024

CoRN ANALISI E STUDIO DI CORRELAZIONE TRA AMBIENTE, ANIMALE E UOMO

Aggiornamenti su produzione, utilizzo e ciclo di vita dei PFAS. Focus su fluoropolimeri e gas fluorurati

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ISTITVTO SVPERIORE DI SANITA

Istituto Superiore di Sanità

Fonti bibliografiche:

OECD Global Forum on the Environment dedicated to Per- and Polyfluoroalkyl Substances
https://www.oecd.org/chemicalsafety/oecdglobalforumontheenvironmentdedicatedtoper-andpolyfluoroalkylsubstances.htm

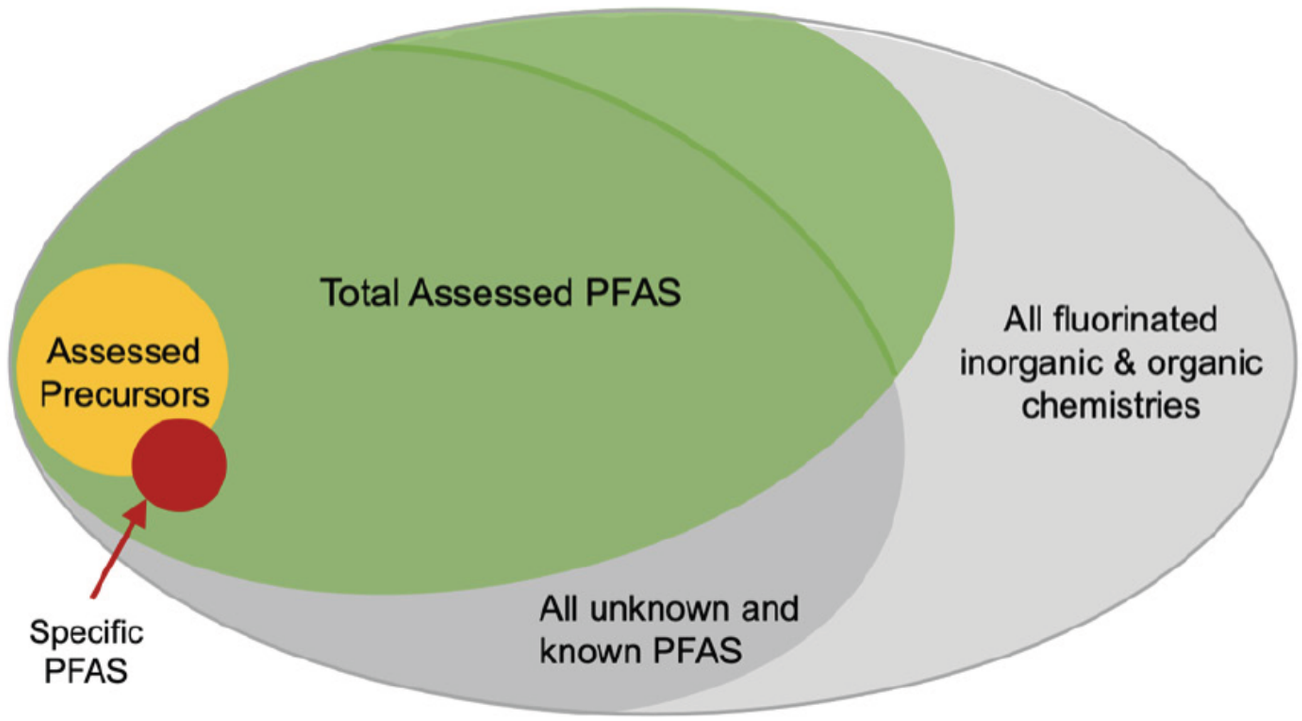
Synthesis Report on Understanding Perfluoropolyethers (PFPEs) and Their Life Cycle (in progress)

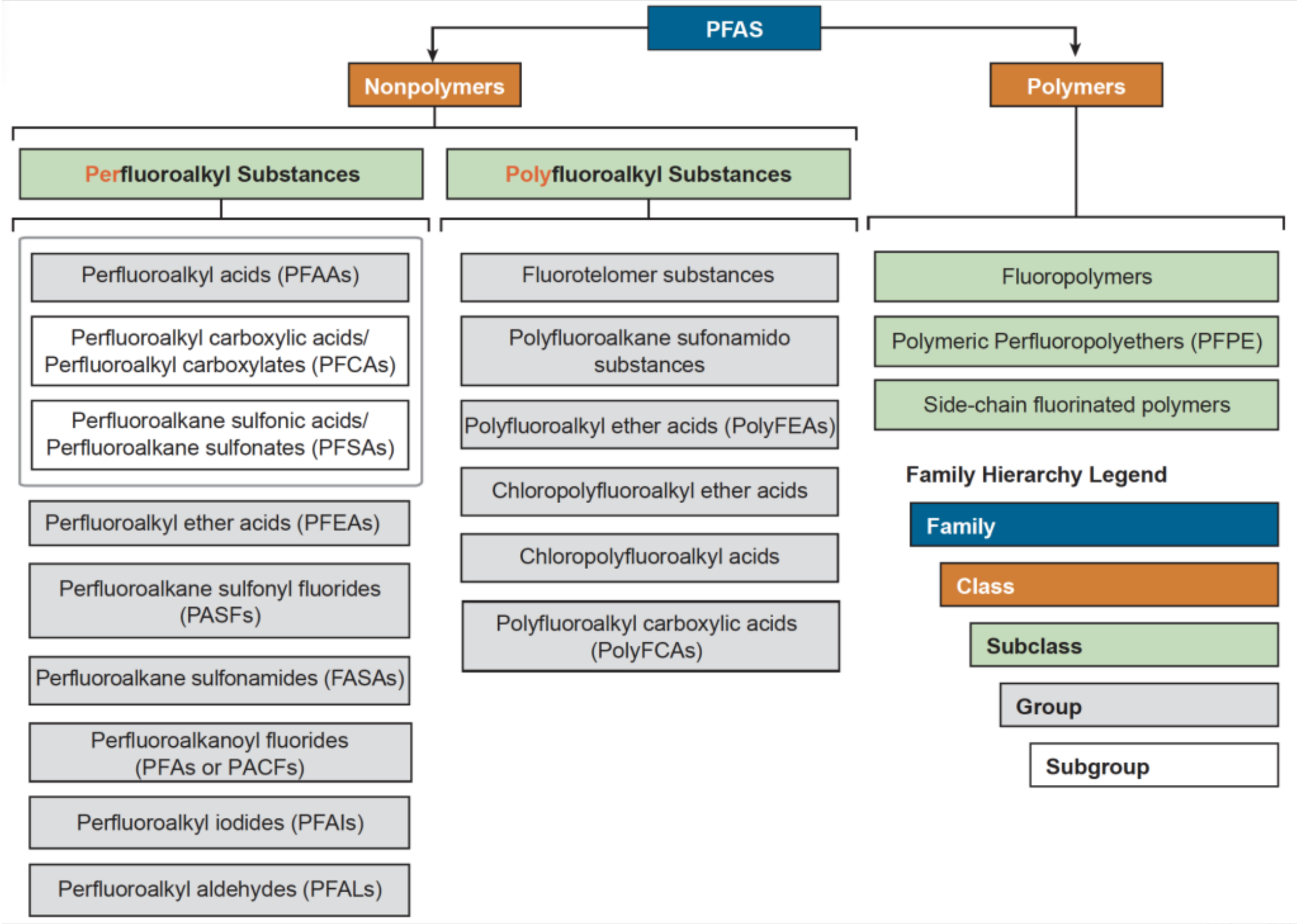
OECD (2022), Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle, OECD Series on Risk Management, No. 73, Environment, Health and Safety, Environment Directorate, OECD.

ECHA Annex to the ANNEX XV RESTRICTION REPORT

I (Fluoro)polimeri rappresentano un’area grigia sia nella classificazione che nei regolamenti della Unione Europea poichè non sono al momento inquadrati nel Regolamento REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals).

Tuttavia, nell’ambito della revisione di tale Regolamento, è prevista la registrazione obbligatoria dei polimeri, inclusi quelli fluorurati




PFAS
Nonpolymers
Polymers
Perfluoroalkyl Substances
Polyfluoroalkyl Substances
Perfluoroalkyl acids (PFAAs)
Perfluoroalkyl carboxylic acids/ Perfluoroalkyl carboxylates (PFCAs)
Perfluoroalkane sulfonic acids/ Perfluoroalkane sulfonates (PFSAs)
Perfluoroalkyl ether acids (PFEAs)
Perfluoroalkane sulfonyl fluorides (PASFs)
Perfluoroalkane sulfonamides (FASAs)
Perfluoroalkanoyl fluorides (PFAs or PACFs)
Perfluoroalkyl iodides (PFAIs)
Perfluoroalkyl aldehydes (PFALs)
Fluorotelomer substances
Polyfluoroalkane sufonamido substances
Polyfluoroalkyl ether acids (PolyFEAs)
Chloropolyfluoroalkyl ether acids
Chloropolyfluoroalkyl acids
Polyfluoroalkyl carboxylic acids (PolyFCAs)
Fluoropolymers
Polymeric Perfluoropolyethers (PFPE)
Side-chain fluorinated polymers
Family Hierarchy Legend
Family
Class
Subclass
Group
Subgroup

Fluoropolymers with significant production volumes

polytetrafluoroethylene (PTFE),

polyvinylidene fluoride (PVDF),

fluorinated ethylene propylene (FEP),

Fluorine Kautschuk materials (FKMs) or fuoroelastomers,

ethylene tetrafluoroethylene (ETFE),

ethylene chlorotrifluoroethylene (ECTFE),

perfluoropolyethers (PFPEs),

perfluoroalkoxyalkanes (PFA),

copolymers of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride (THV).

Prodotti

Film

Tubi

Fogli

Condutture

Membrane

Sigillanti

Isolanti

Additivi

Industria

Trasporti

Auto

Aerospaziale

Alimentare

Cosmetica

Farmaceutica

Elettrica/elettronica

Fili e cavi

Fotovoltaico

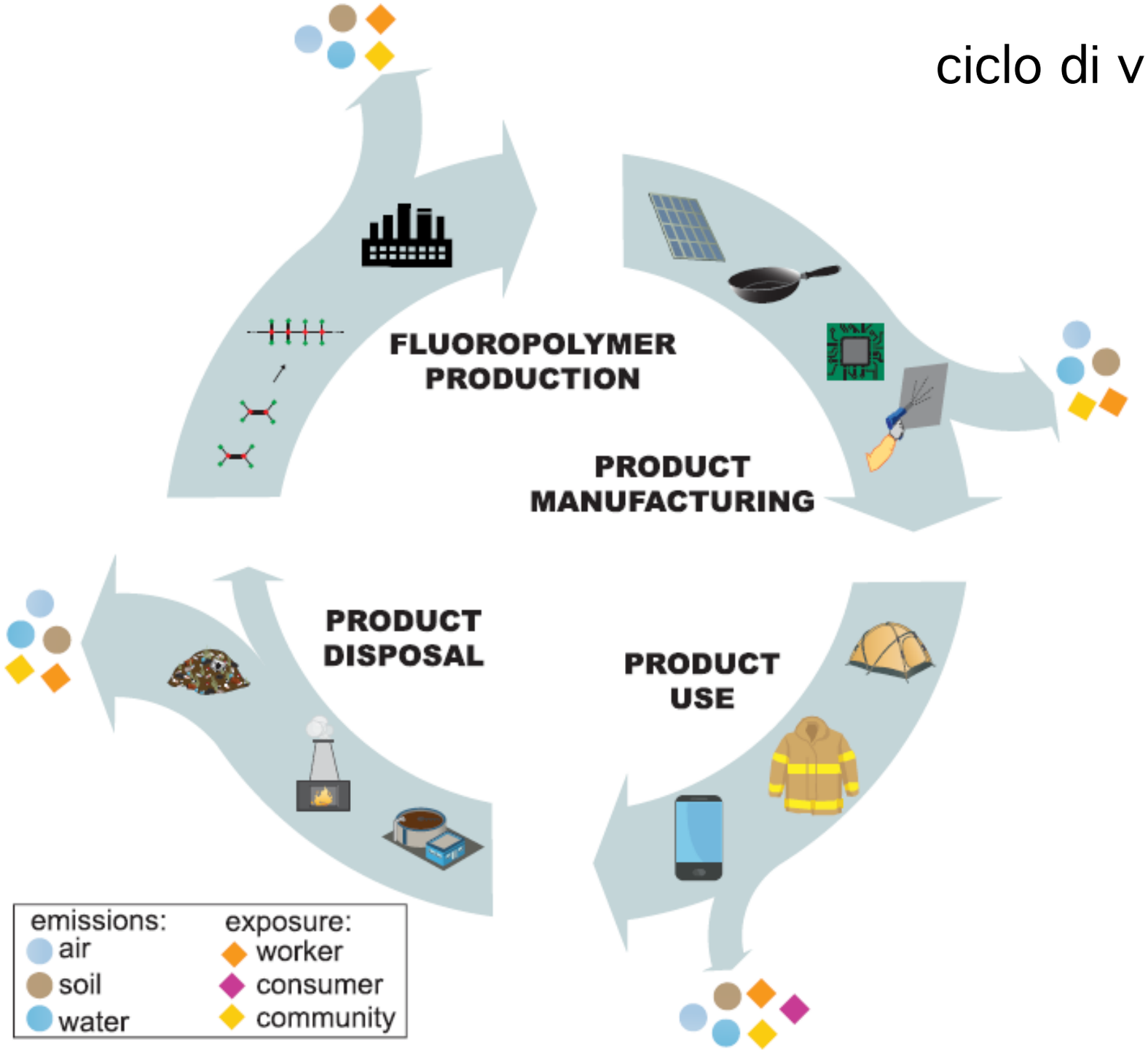
Batterie e generatori di energia

Edilizia

In base alle caratteristiche fisico-chimiche richieste, si sintetizzano mono- o co-polimeri partendo da una o più dei seguenti monomeri

tetrafluoroethylene (TFE),
trifluoroethylene (TrFE),
hexa-fluoropropylene (HFP),
hexafluoropropylene oxide (HFPO),
chlorotrifluoroethylene (CTFE),
vinylidene fluoride (VDF) e
vari perfluoroethers (e.g. perfluoropropylvinyl ether (PPVE)

ciclo di vita dei fluoropolimeri



Rainer Lohmann, et al., *Environmental Science & Technology* **2020** *54* (20), 12820-12828
DOI: 10.1021/acs.est.0c03244

Al momento i polimeri fluorurati non rientrano tra gli obblighi di registrazione Reach, in quanto ritenuti «inerti» e quindi di bassa preoccupazione.

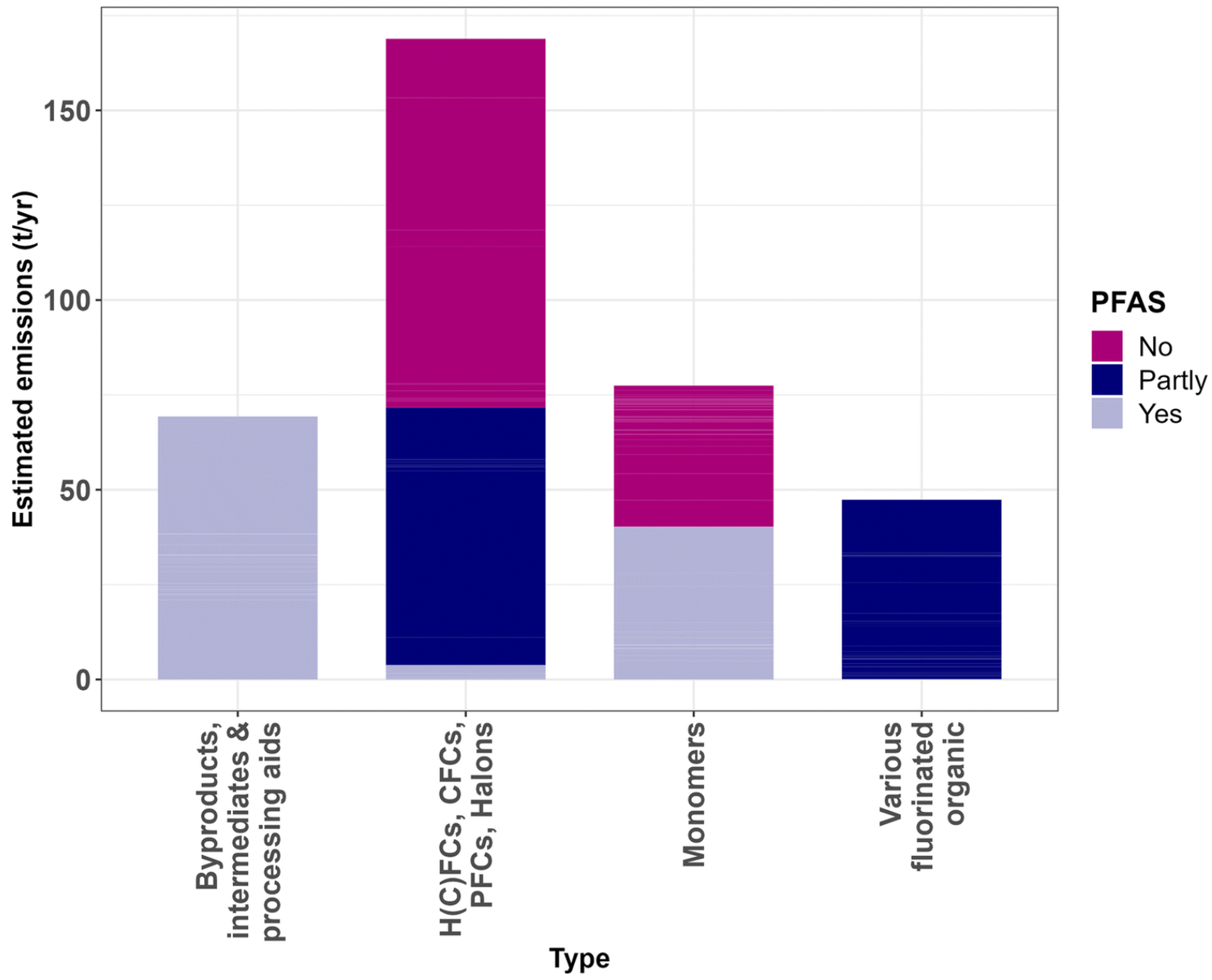
La nuova proposta di Restrizione sui PFAS, tuttavia li include, considerando il loro ciclo di vita:

Reattivi utilizzati nella sintesi
Prodotti a parziale polimerizzazione, sottoprodotti, intermedi di sintesi (Surfattanti fluorurati quali adiuvanti di sintesi (PFOA, Gen X, Adona, C6O4, ADV, >>> verso alternative non fluorurate.

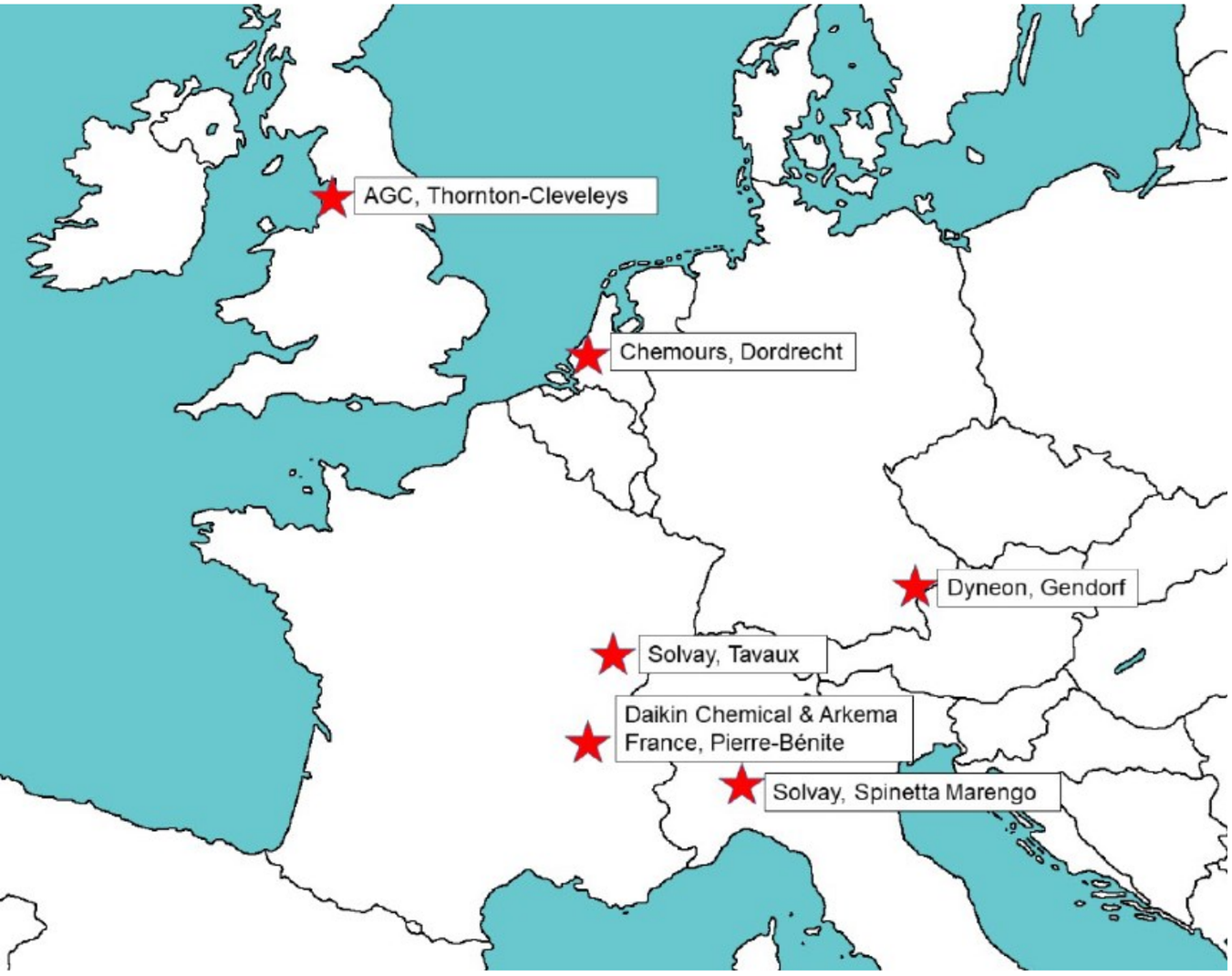
Prodotti rilasciati nell'ambiente dal loro utilizzo, degradazione/distruzione:

Termodistruzione a + 850 °C >>>HF
Processi di ossidazione acque reflue >>> PFAS a catena corta >>>TFA,….

Si stima che nel mondo ci sia una produzione di circa 500.000 t/anno di Fluoropolimeri



Emissioni stimate di composti fluorurati in aria, da 4 impianti di produzione fluoropolimeri in Europa



Full chemical name	Formula	Synonyms	Users in EU
2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-(1,1,2,2,2-pentafluoroethoxy)ethoxy]acetic acid	$C_6HF_{11}O_4$	EEA, perfluoro-3,6-dioxaoctanoic acid, PFO2OA, SAA-1000*, Asahi's Product	AGC
2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoic acid	$C_6HF_{11}O_3$	Hexafluoropropylene oxide dimer acid (HFPO-DA), GenX*, FRD-903, FRD-902*	Chemours
2,2,3-Trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy)propanoic acid	$C_7H_2F_{12}O_4$	ADONA* 4,8-dioxa-3H-perfluorononanoica cid	Dyneon (3M)
2-(3-trifluoromethoxy-1,1,2,2,3,3-hexafluoropropoxy)-2,3,3,3-tetrafluoropropanoic acid	$C_7HF_{13}O_4$	MV31	Dyneon (3M)
(difluoro{[2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetic acid)	$C_6HF_9O_6$	cC6O4, F-DIOX acid, C6O4 cyclic	Solvay
3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctane-1-sulfonic acid	$C_8H_5F_{13}O_3S$	6:2 FTS, Capstone FS-17**, Capstone FS10	Chemours, Arkema
Undecafluorohexanoic acid	$C_6HF_{11}O_2$	PFHxA, C6	Daikin Chemical
1-Propene, 1,1,2,3,3,3-hexafluoro-,telomer with chlorotrifluoroethene, oxidized, reduced, hydrolyzed	$Cl(C_3F_6O)_n(C_2F_4O)_mCF_2COOH$	ADV*, Cl-PFPECAs, Fluorolink 7800 and 7850, Chloro-Galden, Solvay's product	Solvay
Pentadecafluorooctanoic acid	$C_8HF_{15}O_2$	PFOA, C8, APFO* FC-143*	All manufacturers (phased out)
Heptadecafluorononanoic acid Henicosafluoroundecanoic acid Pentacosafluorotridecanoic acid	$C_9HF_{17}O_2$ $C_{11}HF_{21}O_2$ $C_{13}HF_{25}O_2$	Surflon S-111*	Arkema (phased out)

	AGC	Chemours	Solvay SP
Substances on emission permit PFAS in **bold**	TFE, **HFP**, TrFE, HCFC-22, HFC-23, **HFC-125**, **EEA-NH_4**	TFE, **HFP**, VDF, **PFC-318**, **PFIB**, HCFC-22, HFC-23, H(C)FCs, **PMVE**, **PPVE**, **PEVE**, **HFC4310-mee**, **E1**, **Ether A/B**, **PFAC**, **HFPO-DA**, **6:2 FTS**, **C4-C14 PFCAs**, **PFBS**	TFE, **HFP**, VDF, **PFIB**, **PFC-318**, **PFOA***, HCFC-22, **PMVE**, **PPVE**, DIOFE, **DIOFB**, **DIOFH**, **inert particulate fluoropolymers**, **cC6O4****, **ADV****, **FSVE****

10.1039/D3EM00426K *Environ. Sci.: Processes Impacts*, 2024, **26**, 269-287

Table 1. Estimated annual emissions from the use phase for PFAS manufacture and major PFAS use sectors in 2020 (low, mid and high estimates)[a]. Emissions relate to new products on the market, unless stated otherwise. Mid points are used in impact assessment.

Application	PFAAs and PFAA precursors (t/y)			Fluorinated gases (t/y)			Polymeric PFASs (t/y)			Total PFASs (t/y)		
	low	mid	high	Low	mid	high	low	mid	high	low	mid	high
Manufacture	54	86	118	309	1 973	3 637	15	23	30	**378**	**2 082**	**3 785**
TULAC[b]	2 058	6 177	10 295				8 326	16 643	24 960	**10 384**	**22 820**	**35 255**
Food contact materials and packaging	123	491	858				99	100	100	**222**	**591**	**959**
Metal plating and manufacture of metal products[c]	0.5	6	11.4							**1**	**6**	**11**
Consumer mixtures										**23**	**23**	**23**
Cosmetics										**0.015**	**32**	**64**
Ski wax										**1**	**1**	**1**
Applications of fluorinated gases[d,e]				*38 806* 1 696	*38 806* 1 696	*38 806* 1 696				***38 806*** **1 696**	***38 806*** **1 696**	***38 806*** **1 696**
Medical devices	128	239	350	3 772	5 586	7 400	32	76	120	**3 932**	**5 901**	**7 870**
Transport[d]							*269* 35	*439* 58	*609* 80	***269*** **35**	***439*** **58**	***609*** **80**
Electronics and semiconductors	348	513	677	7	7	7	11	152	292	**366**	**671**	**976**
Energy sector	42	42	42				12	13	13	**53**	**55**	**56**
Construction products	88	152	216				1 364	2 338	3 311	**1 451**	**2 489**	**3 527**
Lubricants	0.11	0.6	1.1	29	46	62	123	174	225	**152**	**220**	**288**
Petroleum and mining[c]	0.3		2.3							**0**	**1**	**2**
TOTAL[f]	**2 842**	**7 707**	**12 571**	**42 923**	**46 418**	**49 912**	**10 251**	**19 958**	**29 660**	**56 038**	**74 137**	**92 232**
Total[g]	2 842	7 707	12 571	5 813	9 308	12 802	10 017	19 577	29 131	18 694	36 646	54 593

a) In some cases a basis for providing a range is lacking. There the available estimate is applied throughout; b) TULAC = Textile, upholstery, leather, apparel and carpets; c) No data available for emission of polymeric PFASs; d) For these sectors the emissions relate to stock (presented in italics). For reference only, the emissions from tonnage brought new to market in 2020 are also given; e) Includes emissions of fluorinated gases in transport sector; f) Total based on emissions from best available data (stock if available, new to market if stock is not available); g) For reference only, also the total emissions from tonnage brought new to market in 2020 are presented.

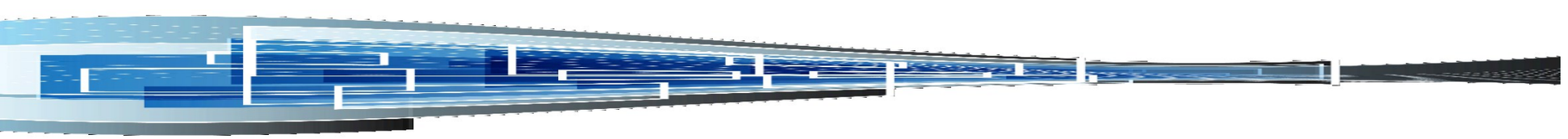
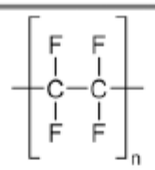
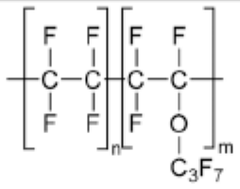
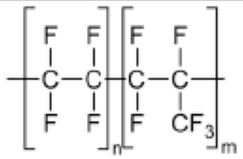
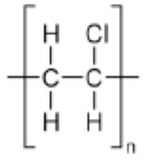
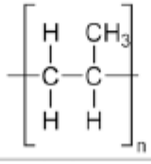
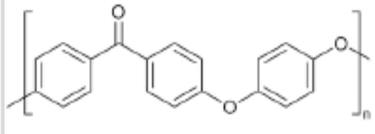


Table 3. Estimated annual tonnages for PFAS manufacture and major PFAS use sectors for 2020 (low, mid and high estimates)[a]. Tonnages are for PFAS used or placed on the market (as substance on their own, in mixtures or articles), unless stated otherwise. Mid points are used in impact assessment.

Application	PFAAs and PFAA precursors (t/y)			Fluorinated gases (t/y)			Polymeric PFASs (t/y)			Total PFASs (t/y)		
	low	mid	high	Low	mid	high	low	mid	high	low	mid	high
Manufacture	53 902	85 977	118 051	15 000	95 774	176 548	49 000	75 381	101 763	**117 902**	**257 132**	**396 362**
TULAC[b]	8 092	20 620	33 148				33 091	71 318	109 544	**41 183**	**91 938**	**142 692**
Food contact materials and packaging	3 267	6 305	9 342				15 330	17 880	20 430	**18 597**	**24 185**	**29 772**
Metal plating and manufacture of metal products	2	30	57				960	960	960	**962**	**990**	**1 017**
Consumer mixtures										**21**	**26**	**30**
Cosmetics										**0.028**	**32.1**	**64.2**
Ski wax										**1.6**	**1.6**	**1.6**
Applications of fluorinated gases[c,d]				*493 173* 30 671	*493 173* 30 671	*493 173* 30 671				***493 173*** **30 671**	***493 173*** **30 671**	***493 173*** **30 671**
Medical devices	1 279	2 387	3 495	20 160	33 080	46 000	3 233	7 633	12 032	**24 672**	**43 100**	**61 527**
Transport[c]							*97 216* 6 410	*159 712* 10 532	*222 208* 14 653	***97 216*** **6 410**	***159 712*** **10 532**	***222 208*** **14 653**
Electronics and semiconductors	841	1 195	1 549	140	140	140	1 560	3 088	4 615	**2 541**	**4 423**	**6 304**
Energy sector	293	294	294				2 592	2 756	2 920	**2 885**	**3 050**	**3 214**
Construction products	987	1 696	2 405				4 254	7 287	10 320	**5 241**	**8 983**	**12 725**
Lubricants	1	6	10	70	110	150	1 100	1 550	2 000	**1 171**	**1 666**	**2 160**
Petroleum and mining	4.4	7	9.5				3 500	5 500	7 500	**3 504**	**5 507**	**7 510**
TOTAL (excl. manufacture)[e]	**14 766**	**32 540**	**50 310**	**513 543**	**526 503**	**539 463**	**162 836**	**277 684**	**392 529**	**691 168**	**836 787**	**982 398**
Total[f]	14 766	32 540	50 310	51 041	64 001	76 961	72 030	128 504	184 974	137 860	225 105	312 341

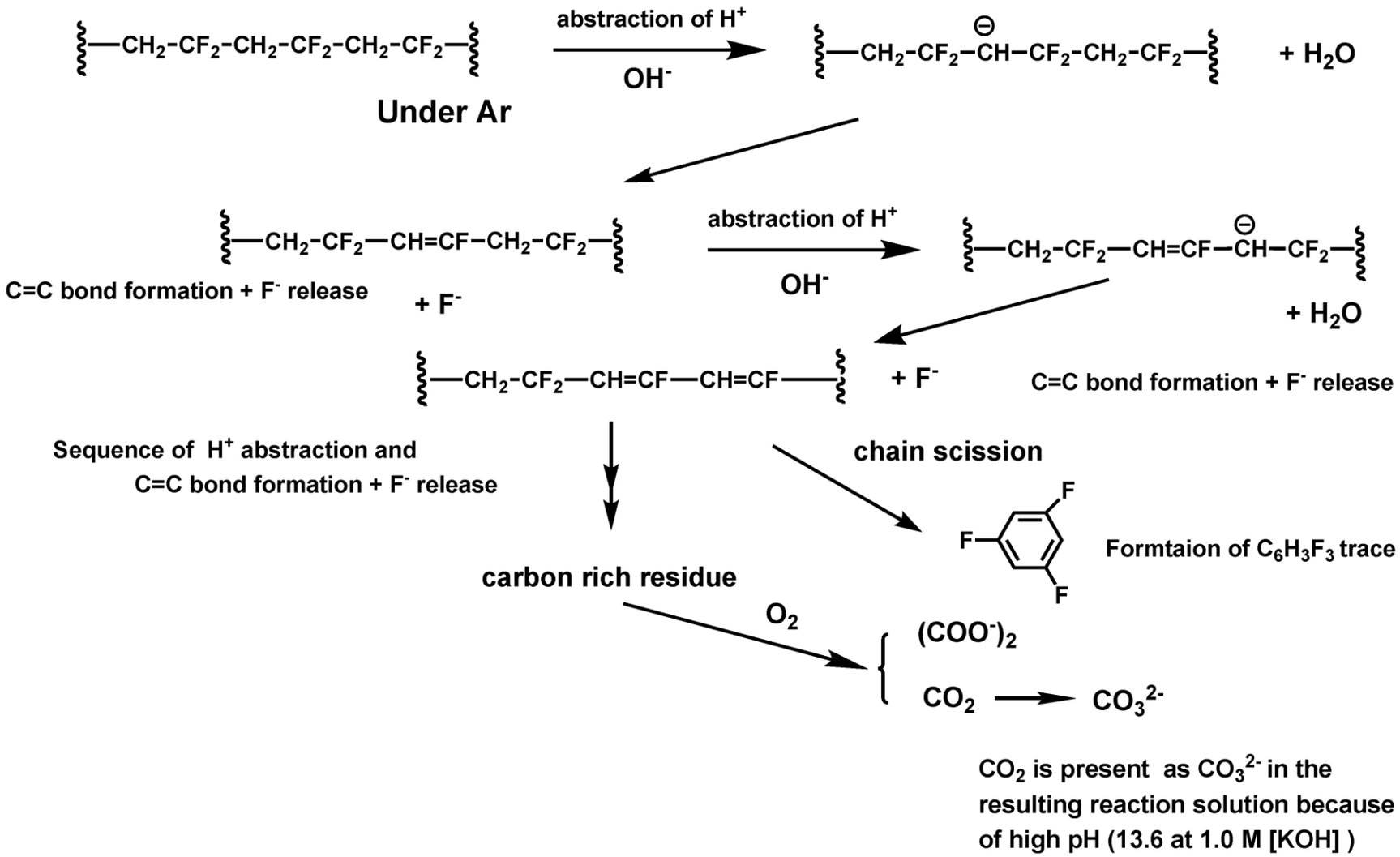
a) In some cases a basis for providing a range is lacking. There the available estimate is applied throughout; b) TULAC = Textile, upholstery, leather, apparel and carpets; c) For these sectors the tonnages relate to "technical stock volume" (presented in italics), representing an estimated 2020 PFAS volume in use in

Rilascio di PFAS a catena corta nell'acqua da fluoropolimeri presenti nell'apparecchiatura analitica HPLC

Polymer type	Monomer(s)	Structure	Leachate products identified
PTFE	Tetrafluoroethylene		TFA PFPrA **PFBA** PFHxA **PFOA**
PFA	Tetrafluoroethylene and perfluoroalkyl vinyl ethers (PAVEs): methyl (PMVE), ethyl (PEVE), or propyl (PPVE, drawn)		**TFA** **PFPrA** PFHxA **PFOA**
FEP	Tetrafluoroethylene and hexafluoropropylene		**TFA** PFPrA PFBA PFOA
PVC	Vinyl chloride		TFA PFBA PFOA
PP	Propene		TFA PFPrA
PEEK	Polyether ether ketone		TFA PFBA 4,4'-DFB Unknown aryl-F

Shira Joudan, Jeremy Gauthier, Scott A. Mabury, and Cora J. Young
Environmental Science & Technology Letters DOI: 10.1021/acs.estlett.3c00797

Degradazione di PDFV in presenza di acqua ossigenata



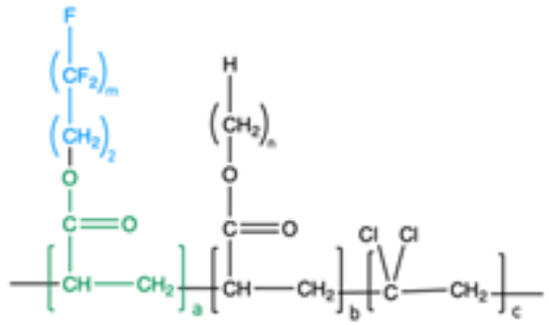
Reaction under Ar: Efficient F^- formation + carbon rich residue

Reaction under O_2: Efficient F^- formation + no residue

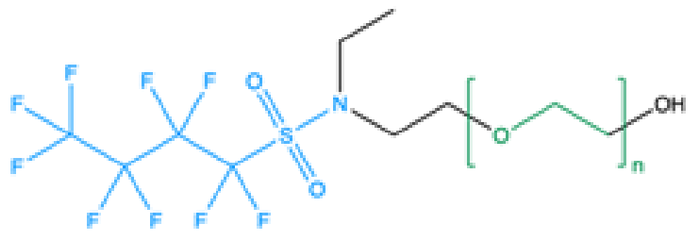
Hori, H.; Tanaka, H.; Watanabe, K.; Tsuge, T.; Sakamoto, T.; Manseri, A.; Ameduri, B. Hydrogen peroxide induced efficient mineralisation of poly(vinylidene fluoride) and related copolymers in subcritical water. Ind. Eng. Chem. Res. **2015**, 54, 8650–8658.

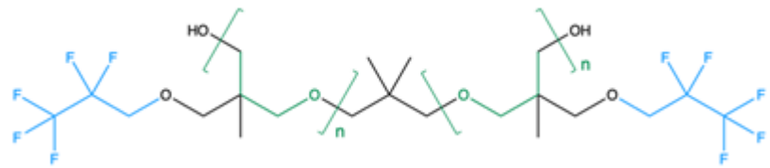
Categorizzazione dei Polimeri a catena fluorurata laterale (SCFP)

acrylates {e.g., [−CH2−CH(C(O)O**RF**)−]n},



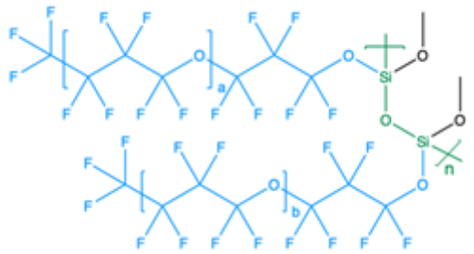
ethoxylates {e.g., [−O−CH2−CH2−]n},



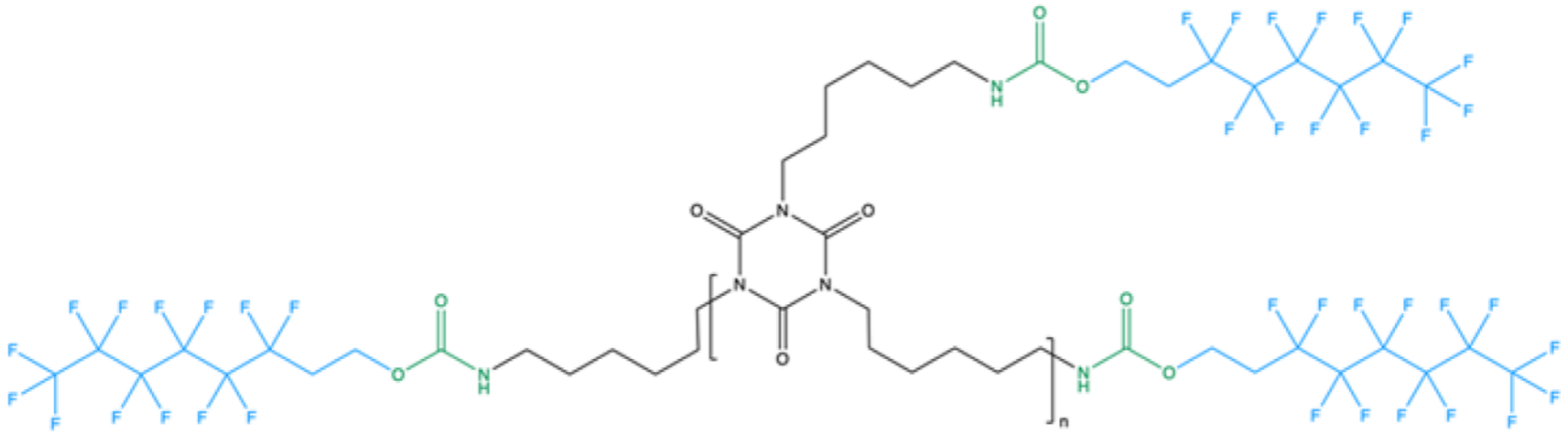


oxetanes {e.g., [−CH2−C(CH3)(CH2OCH2**RF**)−CH2−O−]n},

silicones {e.g., [−Si(CH2CH2**RF**)−O−Si(CH2CH2**RF**)−]n}



urethanes {e.g., [−NH−C(O)−O−]n},



L’industria tessile (TULAC) ha utilizzato abbondantemente nel passato polimeri a catena laterale fluorurata (Side Chain Fluoro-Polymers, SCFP). Le catene laterali di solito non sono polimeriche e costituiscono i precursori tra l’altro di PFAS carbossilati e sulfonati, rilasciati nell’ambiente e che vengono intercettati dal biota. Per i SCFP esistono le evidenze che rappresentino una importante sorgente di PFAS non polimerici, anche in base al ciclo di vita breve dei prodotti che li contengono.

Conclusioni

La Commissione Europea ha intenzione di istituire un nuovo registro delle Emissioni Industriali, che va ad integrare quello esistente E-PRTR (Environment Pollutant Release and Transfer Register).

Per gli impianti fluoropolimerici, non sempre i dati contenuti nelle AIA coincidono con i dati presenti nel E-PRTR.

ECHA andrà a definire le BREF per la produzione di fluoropolimeri.

La emissione di gas fluorurati va attenzionata per la loro degradazione in acido Trifluoroacetico (TFA), che con le precipitazioni rientra nel ciclo dell'acqua.

La Commissione Europea pubblicherà a breve le linee guida per il saggio TOP per la determinazione dei PFAS totali nell'acqua (limite a 500 ng/L) , tra cui è incluso il TFA