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I composti perfluoroalchilici: l'evoluzione dello stato della conoscenza scientifica

Assoreca
Associazione tra le Società di Consulenza e di Servizi per l'Ambiente, l'Energia, la Sicurezza e la Responsabilità Sociale

CONFINDUSTRIA PER LA SOSTENIBILITÀ

ADERENTE A
CONFINDUSTRIA SERVIZI INNOVATIVI E TECNOLOGICI

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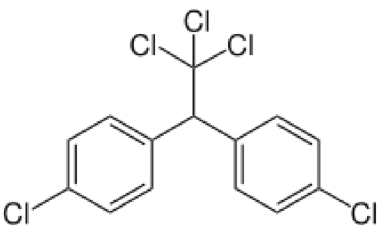
CHE COSA SONO I PFAS? UN PASSO INDIETRO…

A PARTIRE DA ANNI 40’-50’: CRESCITA ESPONENZIALE DEI BULK CHEMICALS DI ORIGINE PETROLCHIMICA. Tra questi molti **composti organici alogenati**



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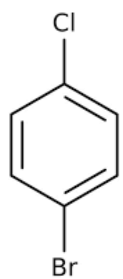

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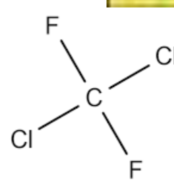

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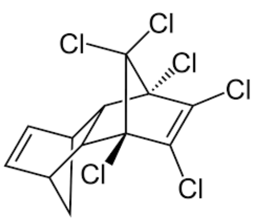

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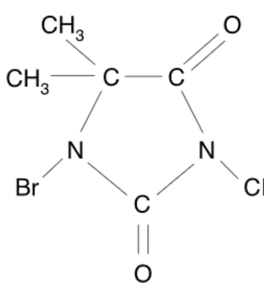

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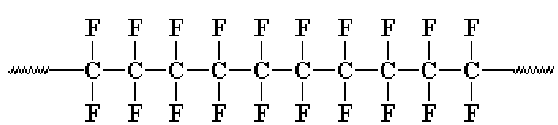
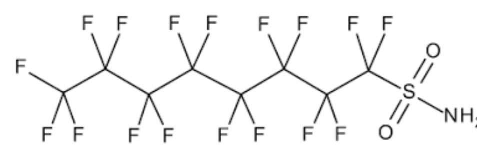


TEFLON

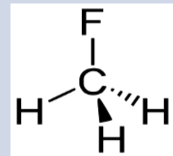
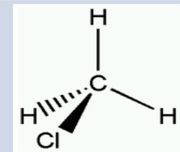
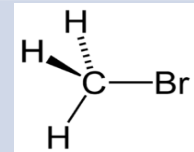
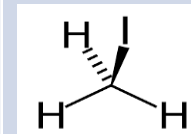


PERFLUOROOTTAN SULFONAMIDE

CHE COSA SONO I PFAS? CARATTERISTICHE CHIMICO-FISICHE

- Il legame C-F è **altamente polarizzato** ($C^{\partial+}$–$F^{\partial-}$) e da ciò deriva una inusuale attrazione elettrostatica tra $F^{\partial-}$ e $C^{\partial+}$. Questo effetto di polarizzazione fa sì che il fluoro si comporti da debole donatore dei 3 doppietti elettronici liberi.
- I legami più corti nella chimica organica tendono ad essere quelli più difficili da scindere. La lunghezza di legame dipende dal raggio degli atomi legati. Il legame **C-F è il più corto dei legami carbonio-alogeno**, e più corto del legame singolo C-N e C-O

Forza di legame e lunghezza del legame carbonio-alogeno

				
Lunghezza legame (A)	1.39	1.78	1.93	2.14
Forza di legame (kJ/mol)	472	350	293	239

- STABILITA' CHIMICA
- INERZIA CHIMICA

$\delta+$ $\delta-$
C—F

CHE COSA SONO I PFAS? CARATTERISTICHE CHIMICO-FISICHE

CONSEGUENZA:

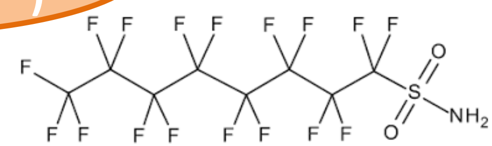
- **Stabilità termica e chimica → recalcitranza alla degradazione!**
- Inoltre a differenza degli altri organoalogenati, nelle sostanze perfluroalchiliche TUTTI gli atomi di H sono sostituiti da atomi di F nella catena alchilica, il che contribuisce a rendere la molecola ancora più stabile, e quindi inerte.
- Nelle sostanze polifluoroalchiliche, la % di sostituzione è comunque elevatissima

INERZIA CHIMICA = INNOCUI PER L'UOMO
= NON DESTAVANO PREOCCUPAZIONE

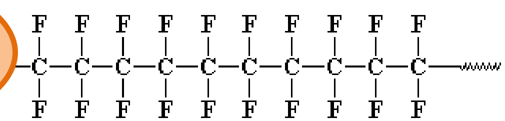
CARATTERISTICHE TECNICHE: OLEOREPELLENZA, IDROREPELLENZA, INERTI CHIMICAMENTE

QUANTITATIVI DI PRODUZIONE < RISPETTO AGLI ALTRI COMPOSTI ORGANOALOGENATI (NE BASTA POCO PER CONFERIRE AGLI OGGETTI CARATTERISTICHE DI IDRO-OLEOREPELLENZA)

PFOSF (SCOTCHGARD ®)



PTFE (TEFLON ®)



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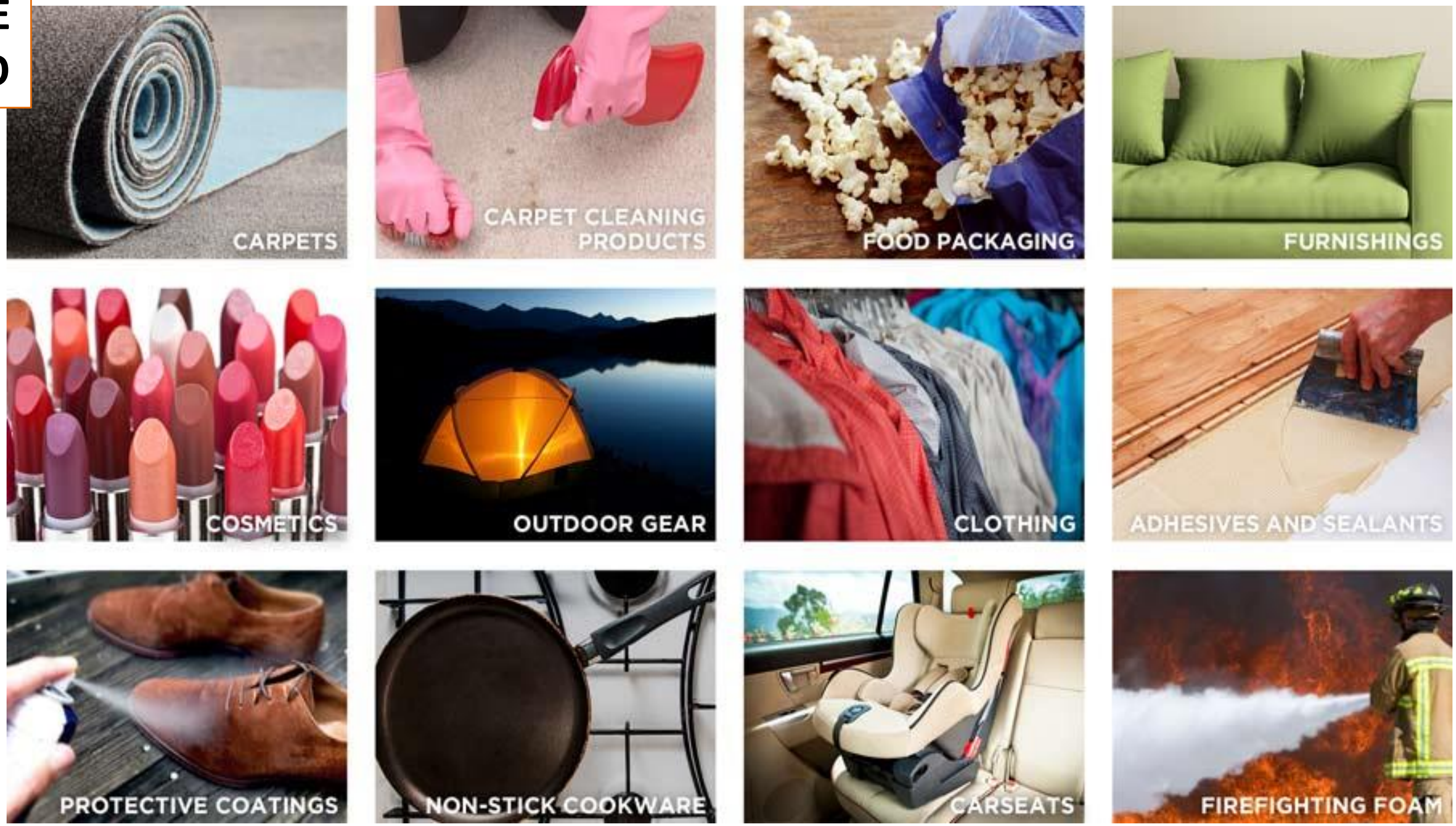
ESEMPI DI PRODUZIONE (TONNELLAGGIO) DI ALCUNI PFAS (1958-2002)

	1958 - 2002 [t]
PFOS	
1. Emissions from production (to water and soil)*	714 - 716
2. Emissions from use and disposal (to water)	267 - 2677
3. Emissions from degradation of *x*FOSA/Es**	5 - 337
4. Emissions from degradation of POSF**	160 - 491
Total	1146 - 4221
xFOSA/Es	
1. Emissions from production (to air, water, and soil)	557 - 689
2. Emissions from use and disposal (to air and excluding Sulfluramid)***	175 - 6950
3. Emissions from application of Sulfluramid (to air and soil)	114 - 141
Total	846 - 7780
POSF	
1. Emissions from production (to air and soil)*	652 - 653

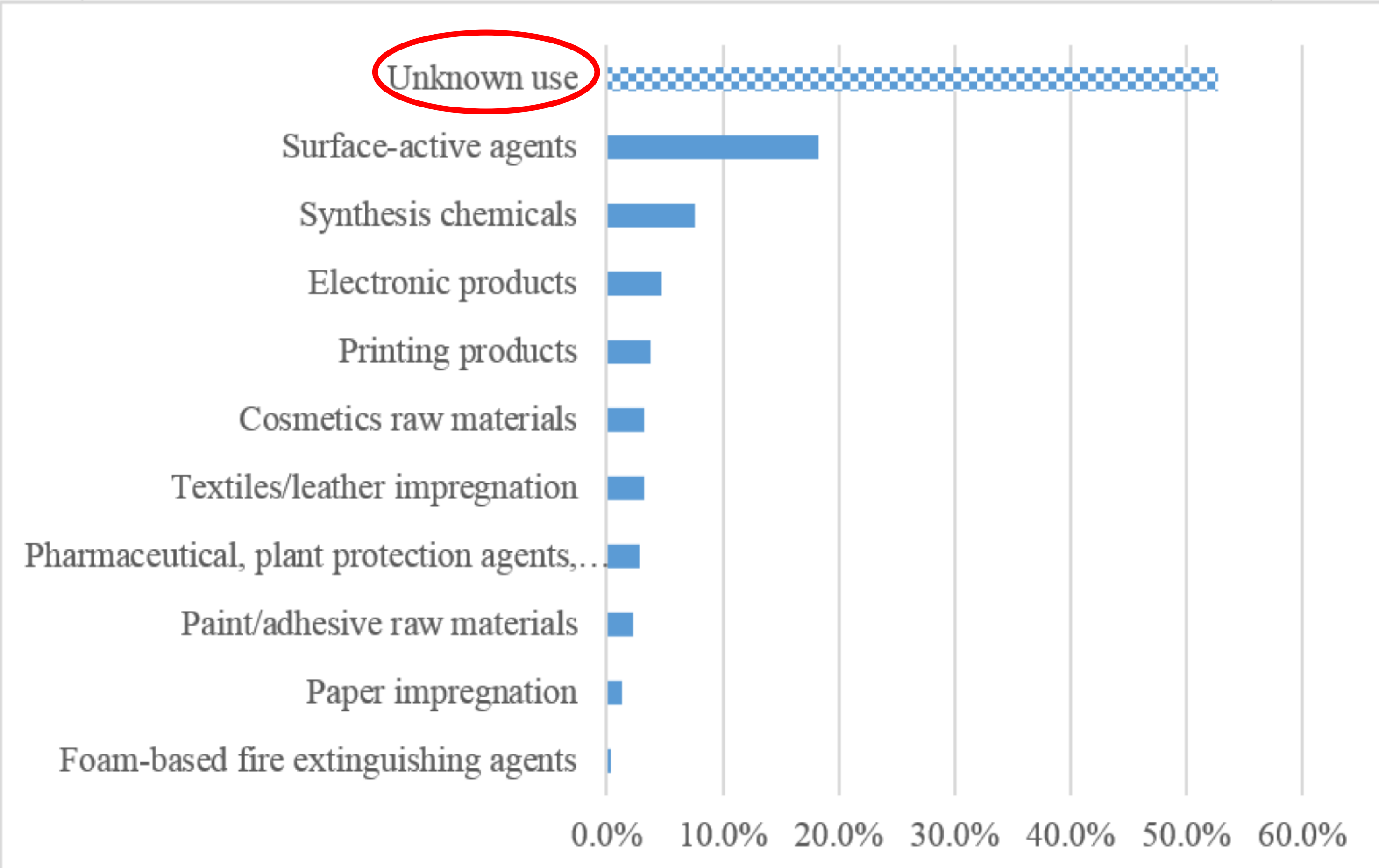
	1958–2002 [t]
PFHxS	
1. Emissions from Production*	86–86
2. Emissions from Use and Disposal	6–307
3. Emissions from Degradation of *x*FHxSA/Es**	1–410
4. Emissions from Degradation of PHxSF**	20–61
Total	113–864
PFDS	
1. Emissions from Production*	4–5
2. Emissions from Use and Disposal	33–358
3. Emissions from Degradation of *x*FDSA/Es**	0–3
4. Emissions from Degradation of PDSF**	1–4
Total	38–370
PHxSF	
1. Emissions from Production*	78–78
PDSF	
1. Emissions from Production*	4–4

USI CONOSCIUTI DEI PFAS

RAPIDA DIFFUSIONE E SUCCESSO



USI SCONOSCIUTI DEI PFAS



The main limitation in uncovering information on end uses of PFAS is the fact that it is often not generally available. In addition a difficulty generally encountered by purchasers of PFAS- based products is the fact that the product name is often retained even if the chemical composition is changed over time (Swedish Chemicals Agency 2014)

KEMI, 2015. *Occurrence and use of highly fluorinated substances and alternatives*

DALL'INIZIO DEGLI ANNI 2000 INIZIA NEI PAESI ECONOMICAMENTE AVANZATI UNA ESTESA AZIONE DI REGOLAMENTAZIONE DEI PFAS, ANCHE SU BASE VOLONTARIA

2002

USEPA PUBLISHES SNUR (U.S) TO RESTRICT THE PROD. OF PFOS AND RELATED SUBSTANCES

2006

PFOA STEWARDSHIP PROGRAM (USEPA and 8 major companies)

2008

EFSA SETS TDIs FOR PFOS AND PFOA (150 and 1500 ng/Kg/d)

2009

- PFOS AND RELATED POSF-based chemicals LISTED AS POPs (STOCKHOLM CONVENTION → restriction of production and use)
- USEPA Drinking water health adv. PFOA/PFOS (400 ng/l and 200 ng/l)

2010

Reg. 757/2010 → restriction on PFOS and PFOS-related substances use in products

2013

- Dir. 2013/39/EU → PFOS included in priority substances list for superficial Waters
- ECHA→ PFOA/APFO and C11-C14 PFCA labelled as VHC substances under REACH given the vPvB nature;
- DIR. 649/2012 Obligation for PFOS and PFOS- derivatives to notification procedure.

Assoreca

COSA E' SUCCESSO?

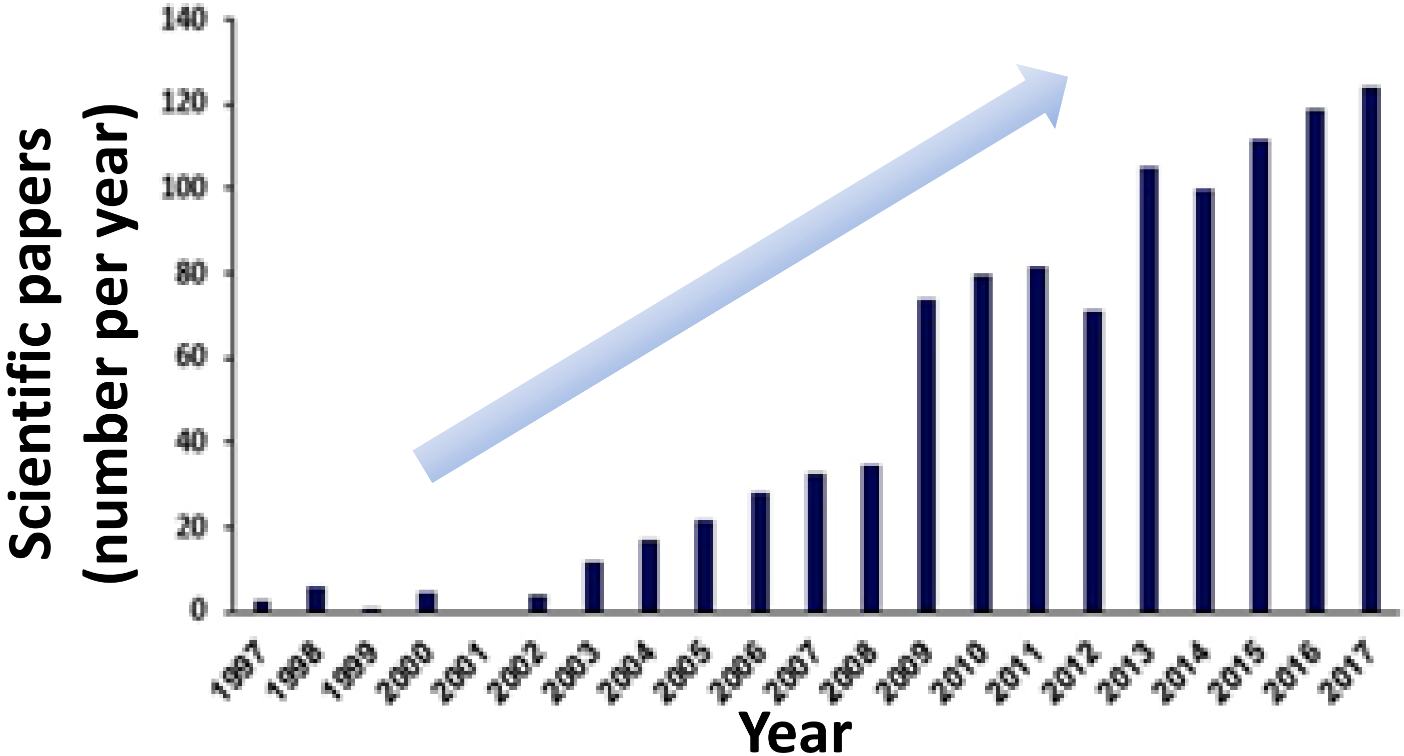
IL SUPERAMENTO DEL LIMITE TECNOLOGICO-ANALITICO

"It was only after **LC/MS** instrumentation became commonly available in the **mid- to late-1990s** that it became possible to measure PFAS in the low **ng/mL (ppb) range,** allowing for the first time the accurate evaluation of background levels of PFASs in biological and environmental matrices. **Early work in this area was difficult due to the relatively low concentrations found in most matrices**, a lack of pure authentic **standards** and appropriate internal standards"

(Lindstrom et al., 2011. *Polyfluorinated Compounds: Past, Present, and Future*)

Meanwhile, ecotoxicology estabilished itself as a self-standing science, as the general awareness of anthropogenic pressure on the environment kept growing

DAGLI ANNI '90 IL NUMERO DI INDAGINI SCIENTIFICHE SULLA PRESENZA DI QUESTE SOSTANZE NEL SIERO DEL SANGUE UMANO, NELLE ACQUE SUPERFICIALI E SOTTERRANEE E NEI TESSUTI DI PESCI, UCCELLI E MAMMIFERI MARINI INIZIA AD AUMENTARE NOTEVOLMENTE



Numero di pubblicazioni scientifiche per anno riscontrate nel database "ISI Web of Science" inserendo le keywords "perfluorinated" ed "environmental" al 23.10.2017

DIFFUSIONE UBIQUITARIA IN AMBIENTE, IN PARTICOLARE NELLE ACQUE NATURALI

Starting from late ’90s, PFAS are **found ubiquitously in shallow waters all over the world (rivers, lakes, oceans)** (Lindstrom et al., 2011):

- Highest concentrations detected in areas nearby direct industrial emission sources impacting shallow waters(**~ 1- 1000 ng/L**)
- Concentrations in oceans ~ 3 orders of magnitude lower **(~ 10-100 pg/L**)

⇩

PFAS are permanently introduced in aquatic ecosystems (Ahrens et al., 2014)

A NEVERENDING STORY

Tale classe di molecole non rimane confinata nell'antroposfera, ma entra in diversi modi nell'ambiente naturale; le proprietà chimico-fisiche di questa classe di sostanze le rende però estremamente recalcitranti alla degradazione (tecnologicamente mediata ma soprattutto naturale)

"[PFAS ARE POTENTIALLY] AN INTRACTABLE, NEVER-ENDING CHEMICALS MANAGEMENT ISSUE"

(Wang et al., *A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFAS)* , 2017)

COSA SONO I PFAS?
CARATTERISTICHE CHIMICHE

COMINCIAMO DALL'INIZIO…

EMERGING SUBSTANCES

A substance that has been detected in the environment, but which is currently not included in routine monitoring programmes and whose fate, behaviour and (eco)toxicological effects are not well understood.
Examples from the **LIST OF EMERGING SUBSTANCES:** flame retardants, pharmaceuticals and personal care products, biocides, polar pesticides and their degradation products and various proven or suspected endocrine disrupting compounds (EDCs).

EMERGING POLLUTANTS

A substance currently not included in routine environmental monitoring programmes and which may be candidate for future legislation **due to its adverse effects and/or persistency** (research on their (eco)toxicity, potential health effects) and public perception and on monitoring data regarding their occurrence in the various environmental compartments.

PFAS are emerging pollutants!

COMINCIAMO DALL'INIZIO…

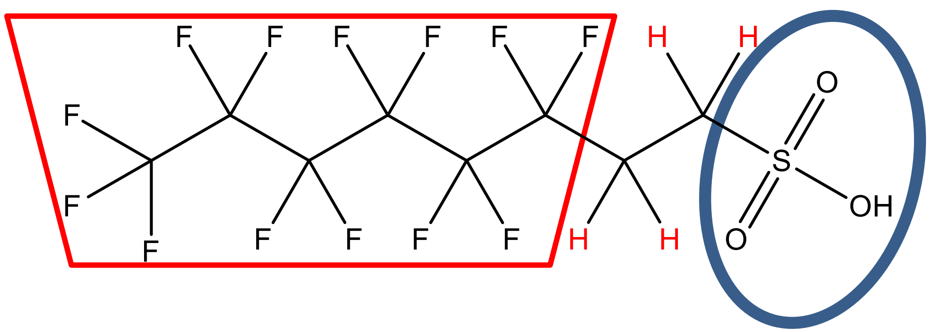
- **"FLUORINATED SUBSTANCES":** substances that contain at least 1 F atom, with vastly different physical, chemical, and biological properties (Banks et al. 1994). Synonyms include **"fluorochemicals"** and **"fluorinated chemicals."**
- A subset of fluorinated substances is the highly fluorinated aliphatic substances that contain 1 or more C atoms on which all the H substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety C_nF_{2n+1}–. These compounds are referred to as **"PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES" = PFAS (also referred to as PFAS)**

IN BREVE:

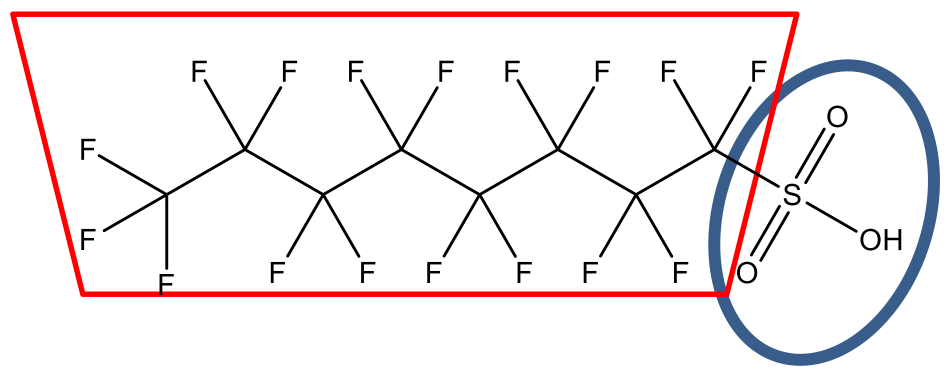
… una famiglia di **> 3000 sostanze** chimiche prodotte sin dagli anni ‘40 del secolo scorso (**fino a 4730** secondo l’ultimo rapport dell’OCSE (OECD) 2018)

GRUPPO FUNZIONALE TERMINALE (ES. CARBOSSILCO, SOLFONICO, SULFONAMIDICO, FOSFONICO, ALCOLICO), IDROFILICO, ED UNA O PIÙ CATENE ALIFATICHE POLIFLUOROURATA (ES. FTOH) O PERFLUORURATA (ES. PFOS , PFOA) → **ANFIFILICITA’**

→ STRUTTURALMENTE **SIMILI AI TENSIOATTIVI**



6:2 Fluorotelomer sulfonate (6:2 FTSA)



Perfluoroctan Sulfonate (PFOS)

I PFAS [$CF_3(CF_2)_N$-R] COMPRENDONO:

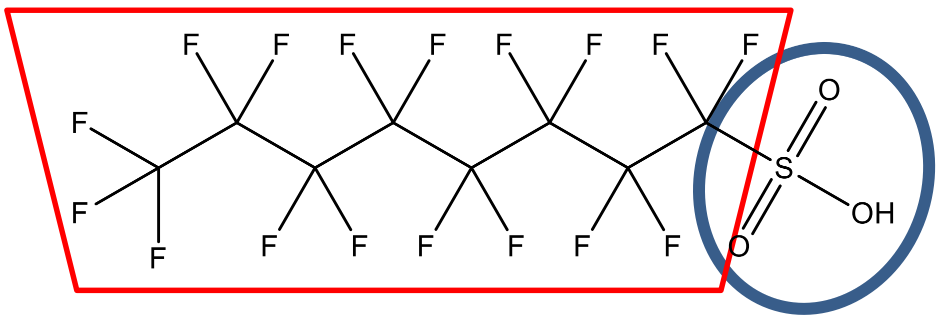
- PFASs
  - perfluoroalkyl acids (PFAAs)
    - perfluoroalkyl carboxylic acids (PFCAs)
    - perfluoroalkane sulfonic acids (PFSAs)
    - perfluoroalkyl phosphonic acids (PFPAs)
    - perfluoroalkyl phosphinic acids (PFPiAs)
    - per- and polyfluoroether carboxylic acids (PFECAs)
    - per- and polyfluoroether sulfonic acids (PFESAs)
  - PFAA precursors
    - PASF-based substances
    - Fluorotelomer-based substances
  - other polymers
    - fluoropolymers (FPs)
      - polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), fluorinated ethylene propylene (FEP), perfluoroalkoxyl polymer (PFA), polyvinyl fluoride (PVF), etc.
    - perfluoropolyethers (PFPEs)

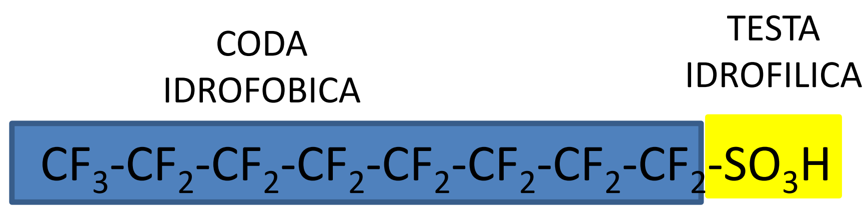
ACIDI PERFLUOROALCHILICI

- **Perfluoroalkyl substances/acids (PFAA)→** all of the H atoms attached to C atoms have been replaced by F atoms (except those H atoms whose substitution would modify the nature of any functional groups present), in such a manner that they contain the perfluoroalkyl moiety **C_nF_{2n+1}–R**. **Perfluoroalkyl substances are fully fluorinated (perfluoro-) alkane (carbon-chain) molecules**

- "**C_nF_{2n+1} –R**" defines the length of the perfluoroalkyl chain tail

e.g. PFOS (perfluorooctanesulfonic acid)





C_8F_9-SO_3H

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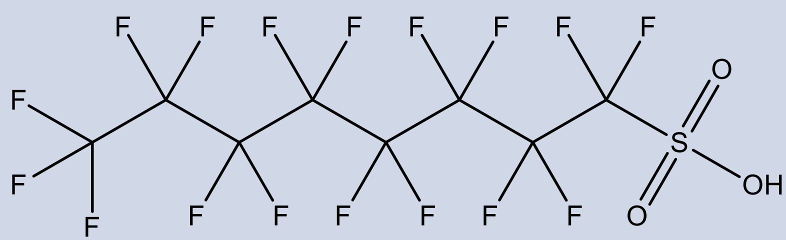
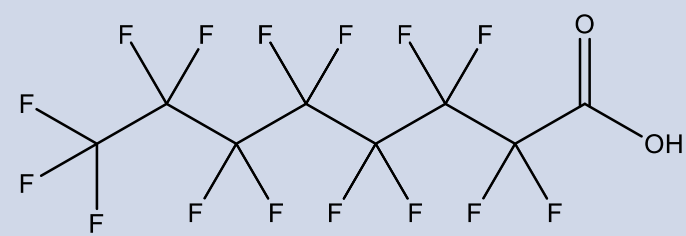
ACIDI PERFLUOROALCHILICI: PFOA E PFOS

- Perfluoroalkyl acids represent the **most studied class of PFAS**.
- primary PFAS for which health-based guidance values have been established. As a result, they tend to drive site investigation and remediation decisions, and so it is helpful to understand the naming conventions for this class.

Among PFAA, the most (in)famous ones are indeed PFOA and PFOS, the most studied PFAS and the fist to be detected in human blood.

PFOS, acido perfluorottansolfonico	PFOA, acido perfluoroottanoico
	

ACIDI PERFLUOROALCHILICI: 5 CLASSI

	CLASSE (Perfluoroalkyl-…)	CnF2n+1R, dove R è…	Esempi
PFAA	Carboxylic acids PFCAs	-COOH	Perfluorooctanoic acid (PFOA), $C_7F_{15}COOH$
	sulfonic acids PFSAs	$-SO_3H$	Perfluorooctane sulfonic acid (PFOS), C_8F17SO_3H
	Sulfinic acids PFSIAs	$-SO_2H$	Perfluorooctane sulfinic acid (PFOSI), $C_8F_{17}SO_2H$
	Phosphonic acids PFPAs	$-P(=O)(OH)_2$	Perfluorooctyl phosphonic acid (C8-PFPA), $C_8F_{17}P(=O)(OH)_2$
	Phosphinic acids PFPIAs	$-P(=O)(OH)(C_nF_{2n+1})$	Bis(perfluorooctyl) phosphinic acid (C8/C8-PFPIA), $C_8F_{17}P(=O)(OH)(C_8F_{17})$

DISSOCIAZIONE DEI PFAA IN ACQUA

Name	Acronym	Molecular Weight [g/mol]	Density[a] (20 - 25 °C) [g/ml]	Water Solubility (20 - 25 [g/L]							Kd (pH 7)	Dissociation Constant (pKa)
Perfluoroalkyl Carboxylates / Perfluoroalkyl Carboxylic Acids	**PFCAs**											
Perfluorobutanoic Acid	PFBA	214.04	1.65	Miscib								-0.2 to 0.7
Perfluoropentanoic Acid	PFPeA	264.05	1.70	112.								-0.06
Perfluorohexanoic Acid	PFHxA	314.05	1.72	21.7								-0.13
Perfluoroheptanoic Acid	PFHpA	364.06	1.79	4.2							4 - 1.1	-0.15
Perfluorooctanoic Acid	PFOA	414.07	1.80	3.4 - 9							0 - 3.4	-0.16 to 3.8
Perfluorononanoic Acid	PFNA	464.08	1.75	9.50							2.6 - 5.9	-0.17
Perfluorodecanoic Acid	PFDA	514.09	1.76	9.50							2.0 - 31	-0.17
Perfluoroundecanoic Acid	PFUnA	564.09	1.76	0.004						0	12 - 103	-0.17
Perfluorododecanoic Acid	PFDoA	614.10	1.77	0.000						--	24 - 269	-0.17 to 0.8
Perfluorotridecanoic Acid	PFTrdA	664.11	1.77	0.000						--	--	--
Perfluorotetradecanoic Acid	PFTeDA	714.12	1.78	0.0000						--	--	--
Perfluoropentadecanoic Acid	PFPeDA	764.12	--	--						--	--	--
Pentadecafluorooctanoic Acid Ammonium Salt (Ammonium Pentadecafluorooctanoate)	APFO	445.11	--	14.2						--	--	2.5
Perfluoroalkyl Sulfonates / Perfluoroalkyl Sulfonic Acids	**PFSAs**											
Perfluorobutane Sulfonate	PFBS	300.10	1.81	46.2 - 56.						1.00	--	-6.0 to -5.0
Perfluorohexane Sulfonate	PFHxS	400.11	--	2.3						1.78	0.6 - 3.2	-6.0 to -5.0
Perfluoroheptane Sulfonate	PFHpS	450.12	--	--						--	--	--
Perfluorooctane Sulfonate	PFOS	500.13	--	0.52 - 0.57	54	> 400	6.7	<2e-6 to 3e-4	6.43	2.5 - 3.1	0.1 - 97	-6.0 to -2.6
Perfluorodecane Sulfonate	PFDS	600.14	--	0.002			0.71	--	7.66	3.53	--	--

COSTANTI DI DISSOCIAZIONE DI ALCUNI PFAA (pKa) (CONCAWE report 2016)

PFBA	-0.2 to 0.7
PFPeA	-0.06
PFHxA	-0.13
PFOA	-0.16 to 3.8
PFNA	-0.17
PFBS	-6.0 to -5.0
PFHxS	-6.0 to -5.0
PFOS	-6.0 to -2.6

IN SOLUZIONE ACQUOSA SI DISSOCIANO FACILMENTE E SI TROVANO IN FORMA IONIZZATA

DISSOCIAZIONE DEI PFAA IN ACQUA: NOMENCLATURA

	GRUPPO	GRUPPO FUNZIONALE	ESEMPI
PFAA	Perfluoroalkyl carboxylic acids (PFCAs)	-COOH	Perfluoro**octanoic acid** (PFOA), $C_7F_{15}COOH$
	Perfluoroalkyl Carboxylates (PFCAs)	$-COO^-$	Perfluoro**octanoate** (PFOA), $C_7F_{15}COO^-$
	Perfluoroalkane sulfonic acids (PFSAs)	$-SO_3H$	Perfluorooctane **sulfonic acid** (PFOS), $C_8F_{17}SO_3H$
	Perfluoroalkane sulfonates (PFSAs)	$-SO3^-$	Perfluorooctane **sulfonate**, (PFOS), $C_8F_{17}SO_3^-$

PFAA LUNGHI, CORTI E ULTRA-CORTI

Ultra-short PFCA		Short-chain PFCA				Long-chain PFCA			
Trifluoroacetic acid	PeFPrA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA
Triflic Acid	PeFEtSA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS
Ultra-short PFSA		**Short-chain PFSA**		**Long-chain PFSA**					

PFAA are frequently referred to as "**long-chain**" or "**short-chain". Some authors have categorized the shortest ones as "ultra short-chained"** when they have 2-3 and 4-7 fully fluorinated C-atoms, respectively (Ateia et al., 2019[1]; Yeung et al., 2017)

According to the OECD (OECD 2011), "long-chain" refers to:

- PFCAs with eight carbons and greater (i.e., with **7** or more perfluorinated carbons)
- PFSAs with six carbons and greater (i.e., with **6** or more perfluorinated carbons).

PFAA LUNGHI, CORTI E ULTRA-CORTI

Ultra-short PFCA		Short-chain PFCA				Long-chain PFCA			
Trifluoroacetic acid	PeFPrA	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA
Trifl[illegible]									[illegible]nS
Ul[illegible]									

LUNGHEZZA DELLA CATENA MOLTO DIVERSA E GRUPPI FUNZIONALI MOLTO DIVERSI ALL'INTERNO DELLA STESSA CLASSE

↓

TENDENZIALMENTE PIU' E' CORTA LA CATENA PERFLUOROALCHILICA PIU' SONO IDROFILICI

PFAA ar[illegible] **ave categorized the shortest ones as "ultra short-chained"** when they have 2-3 and 4-7 fully fluorinated C-atoms, respectively (Ateia et al., 2019[1]; Yeung et al., 2017)

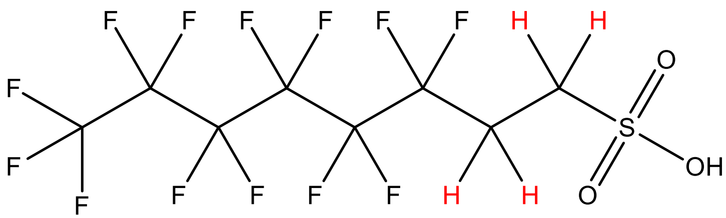
According to the OECD (OECD 2011), "long-chain" refers to:

- PFCAs with eight carbons and greater (i.e., with **7** or more perfluorinated carbons)
- PFSAs with six carbons and greater (i.e., with **6** or more perfluorinated carbons).

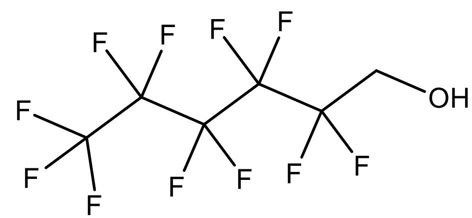
PRECURSORI DEI PFAA: LE SOSTANZE POLIFLUOROALCHILICHE

- **Polyfluoroalkyl substances** → aliphatic substances for which all H atoms attached to at least one (but not all) C atoms have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety **C_nF_{2n+1}–**

EXAMPLES:

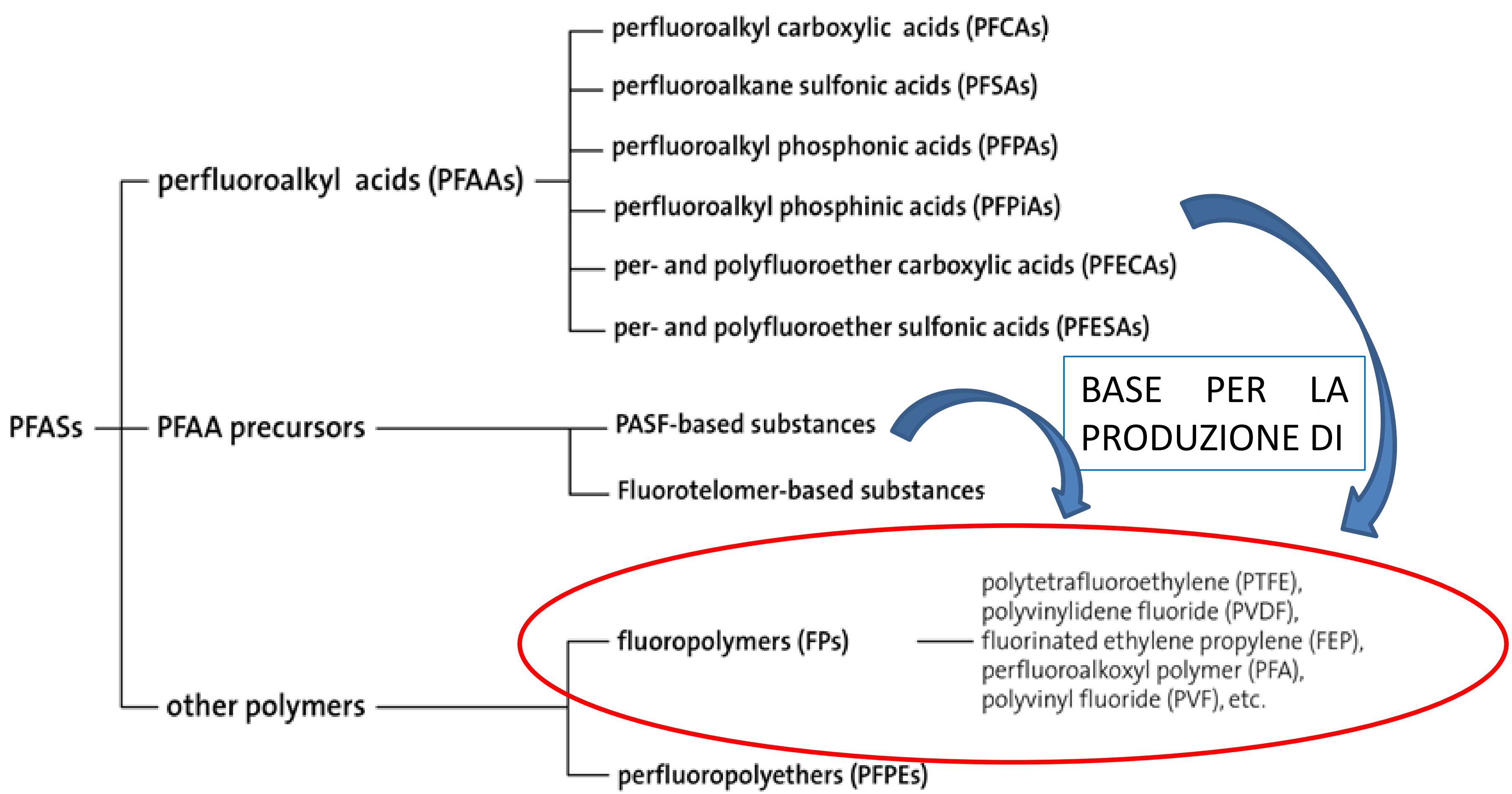


6:2 Fluorotelomer sulfonate (6:2 FTSA)



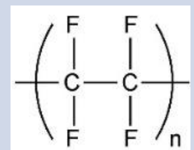
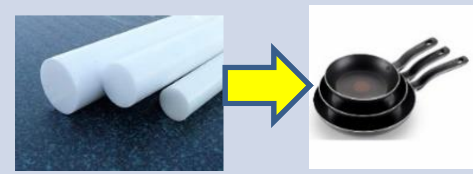
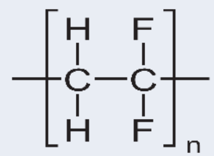
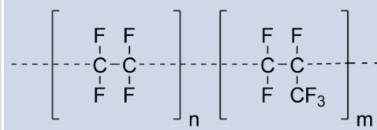
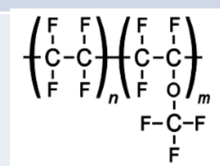
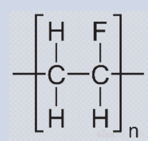
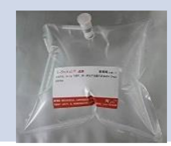
Fluorotelomer alcohol 5:1 (FTOH 5:1)

FLUOROPOLIMERI: SOSTANZE DI USO QUOTIDIANO



FLUOROPOLIMERI: SOSTANZE DI USO QUOTIDIANO

POSSONO DEGRADARSI PARZIALMENTE IN PFAS NON POLIMERICI (CIOE' IN PFAA), OPPURE RILASCIARE PFAA, INTRAPPOLATI NEL POLIMERO SOTTO FORMA DI IMPURITA'

Fluoropolymer name		Condensed formula	Materials
PTFE (Teflon®)	Poly tetrafluoro ethylene		
PVDF	Poly vinyldene fluoride		
FEP	Fluorinated ethylene propylene		
PFA	Perfluoro alkoxyl polymer		
PVF	Polyvinyl fluoride		

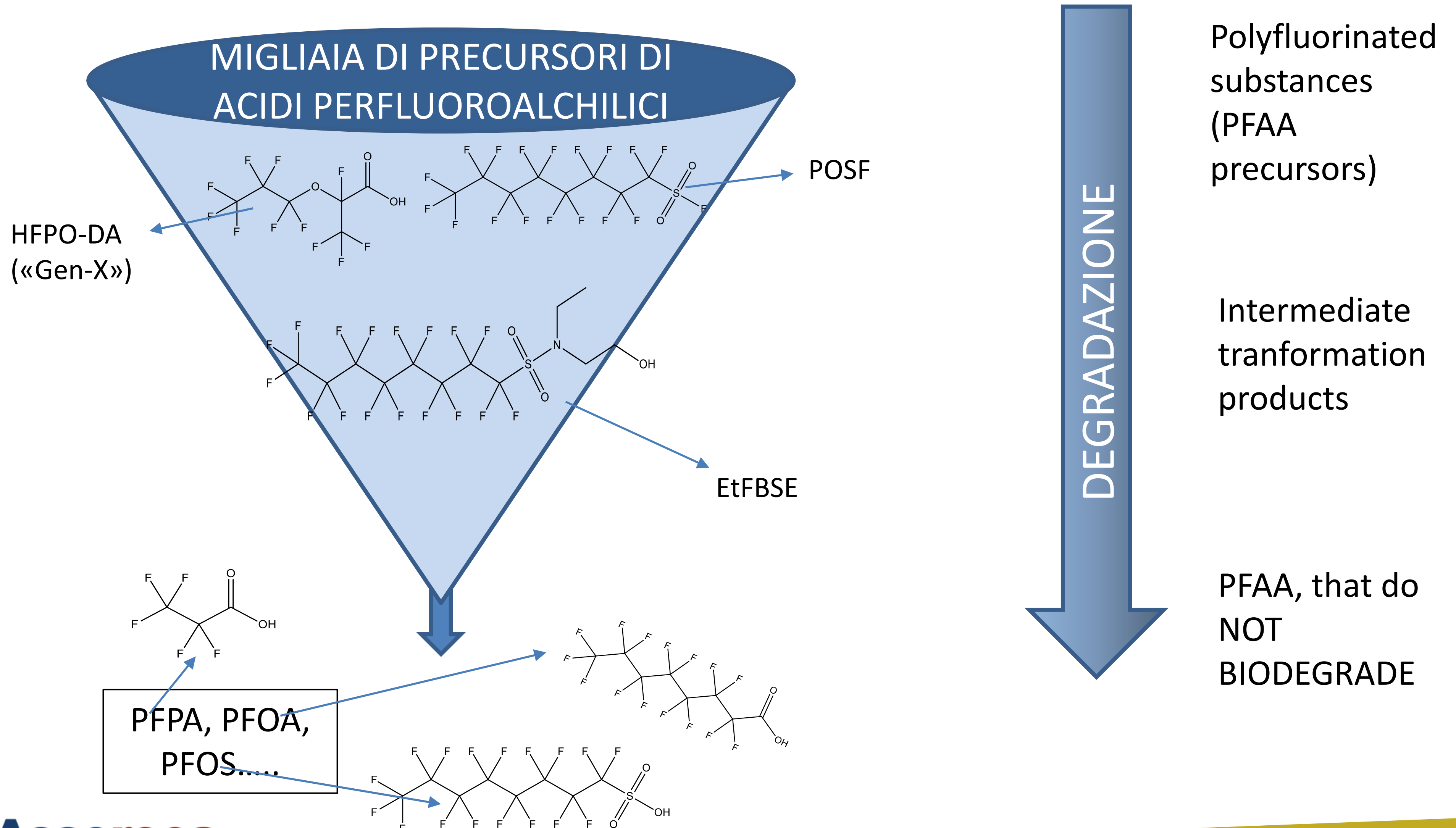
PIU' DI 3000 SOSTANZE… PERCHE' CI CONCENTRIAMO SUI PFAA?

- Perfluorinated PFAS historically were referred to as perfluorinated compounds but are now more commonly termed **PFAA** (perfluoroalkyl acids)
- Polyfluoroalkyl substances are often referred to as **precursors to the PFAA**

↓

1) Polyfluoroalkyl substances tend to degrade in the environment to form PFAA, wich may comprise perfluoroalkyl sulfonic acids (PFSAs), such as PFOS and PFOA.
2) They are also the first subtances that have been detected in environmental and epidemiological studies

“[PFAS] always form PFAA, which are extremely persistent” (Ross et al., 2018)



NORMATIVA

Di conseguenza, la normativa a livello italiano, europeo e mondiale (almeno per quanto riguarda i Paesi economicamente avanzati e in particolare quelli dell'Unione Europea) si è concentrata sugli acidi perfluoroalchilici, in particolare PFOA e PFOS

LIMITI ACQUE POTABILI ITALIA

Sostanza	Limiti (ng/L)
PFOS e isomeri ramificati	30
∑PFOA+ PFOS	500
Altri PFASs *	500

LIMITI ACQUE POTABILI VENETO

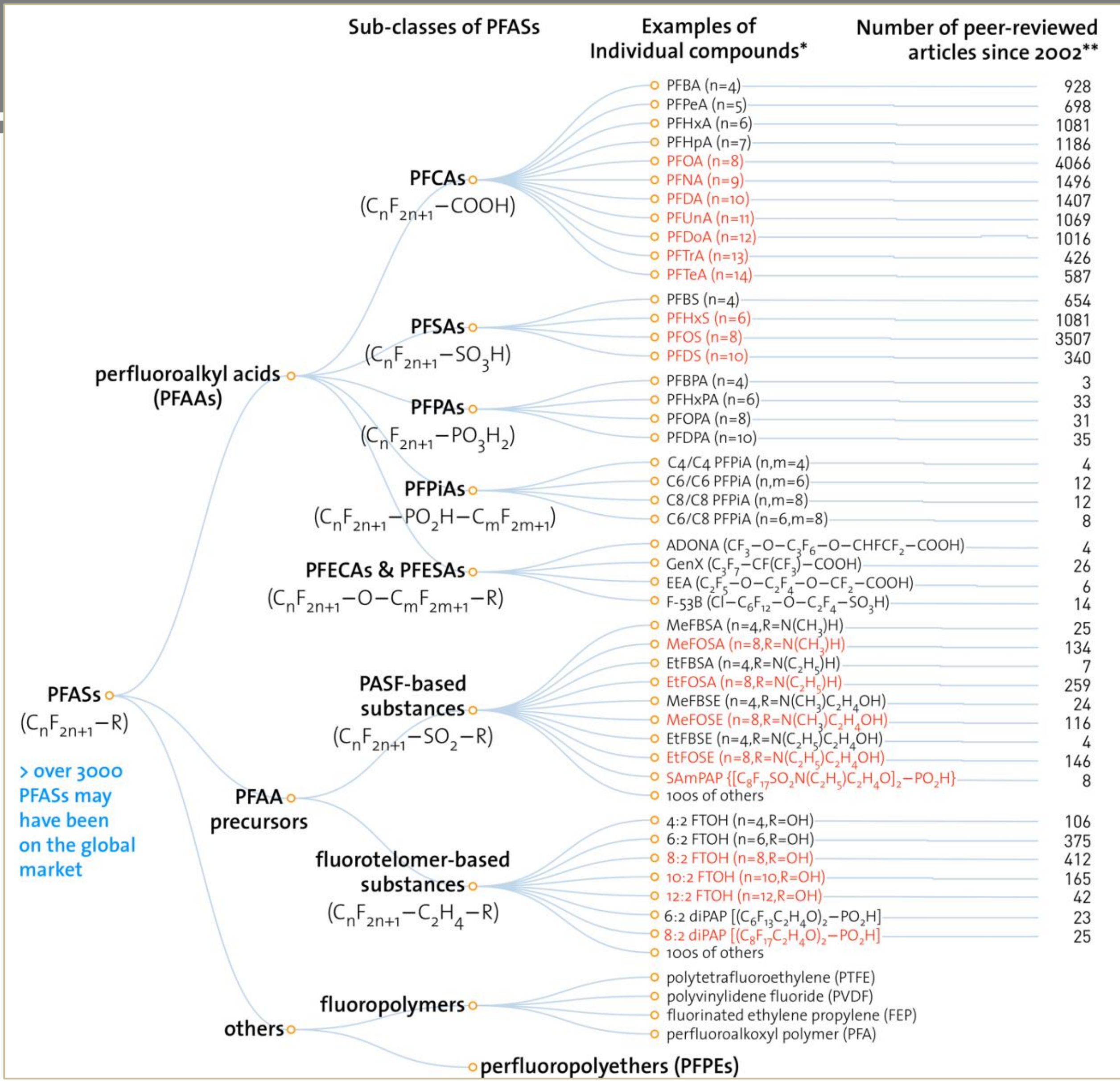
Sostanza	Limiti (ng/L)
PFOS e isomeri ramificati	30
∑PFOA + PFOS	90
Altri PFASs *	300

*somma di PFBA, PFPeA, PFBS, PFHxA, PFHxS, PFHpA,PFNA, PFDeA, PFUnA, PFDoA

NORMATIVA

LIMITI ACQUE SUPERFICIALI (STANDARD DI QUALITA' AMBIENTALE): ITALIA ED EUROPA

SOSTANZA	Standard di qualità ambientale (valore medio annuo) (ng/L)		Standard di qualità ambientale (concentrazione massima ammissibile) (ng/L)		Standard di qualità ambientale (µg/g)
	acque superficiali interne (fiumi e laghi)	altre acque di superficie	acque superficiali interne (fiumi e laghi)	altre acque di superficie	Biota (pesci)
PFOS	0.65	0.13	36000	7200	9,1
PFBA	7000	1400	-	-	-
PFPeA	3000	600	-	-	-
PFHxA	1000	200	-	-	-
PFOA	100	20	-	-	-
PFBS	3000	600	-	-	-



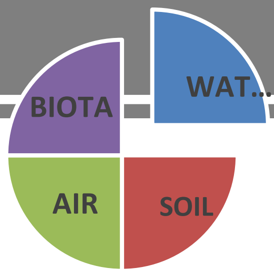
*PFAS in red are those that have been restricted under global/national/regional regulatory or voluntary frameworks, with or without specific exemptions (OECD, 2015)

** retrieved on SciFinder at Nov. 1, 2016

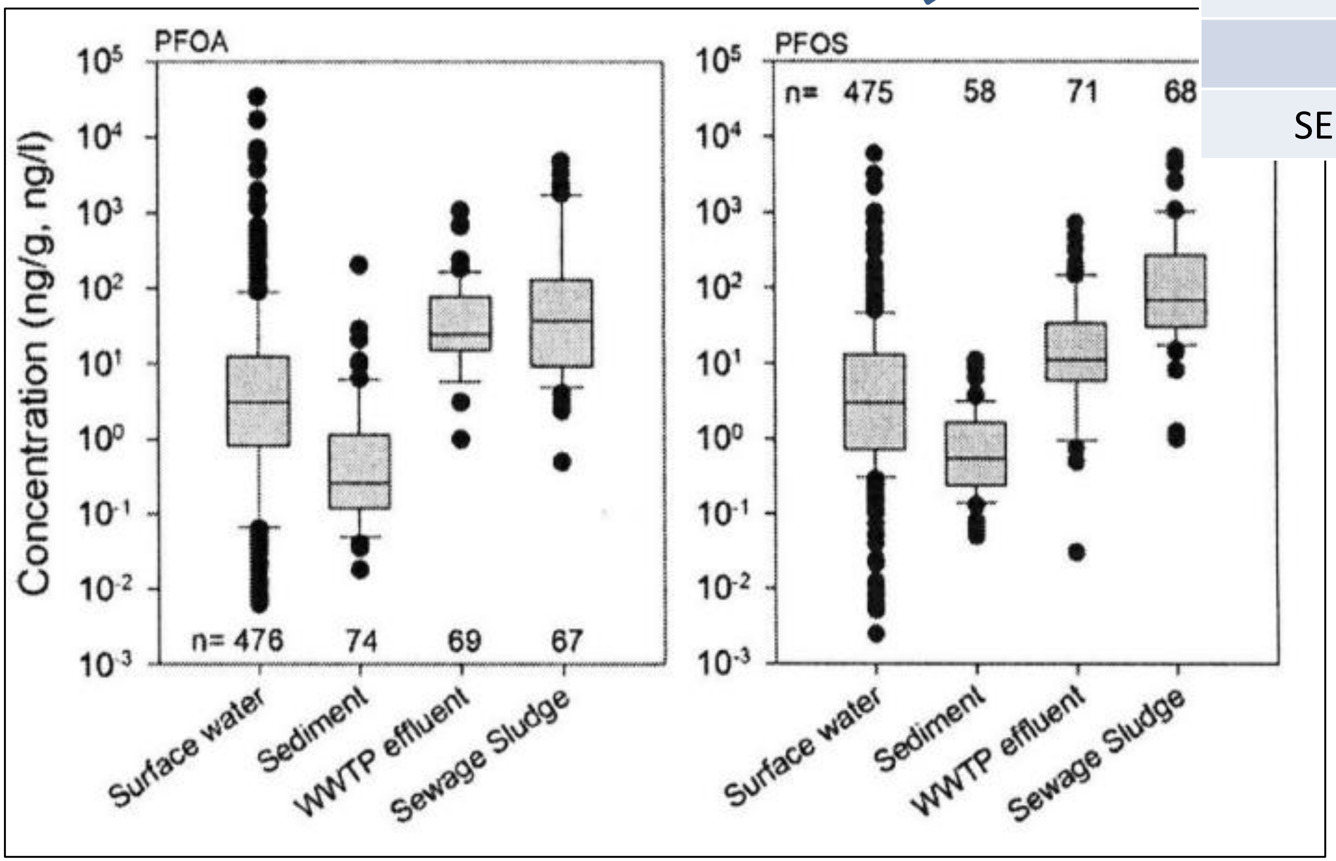
Wang et al., 2017. *A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFAS)?*

PRESENZA IN AMBIENTE

ACQUE SUPERFICIALI



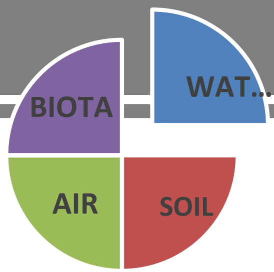
CONC.MEDIA (ng/L)	PFOA	PFOS
ACQUA SUPERF.	5	5
EFFLUENTE IMP. TRATT.	40	20
FANGHI	60	80
SEDIMENTO (ng/g)	0,4	0,7



Zareitalabad et al. (2013). *Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater - A review on concentrations and distribution coefficients*

Samples taken in USA, Italy, Germany, The Netherlands, Sri Lanka, Canada, China, Japan, Kenya and Brazil.

ACQUE POTABILI



Kaboré et al., 2018. *Worldwide drinking water occurrence and levels of newly-identified perfluoroalkyl and polyfluoroalkyl substances*

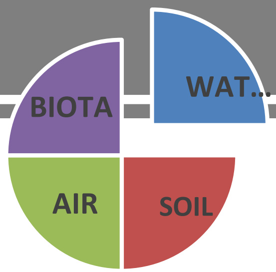
29 target and 104 suspect-target PFAS were screened in drinking water samples (n = 97) from Canada and other countries (Burkina Faso, Chile, Ivory Coast, France, Japan, Mexico, Norway, and the USA) in 2015–2016. PFCAs, PFSAs and perfluoroalkyl acid precursors were recurrently detected (concentration range: **<LOD to 39 ng/L**).

PFAS class	Mean (ng/L) bottled water	Mean (ng/L) tap water
∑PFCAs	0.62	4.1
∑PFSAs	0.50	1.6
∑TOT 29 PFAS	1.1	7.1

Gao et al., 2019. *Levels, spatial distribution and isomer profiles of perfluoroalkyl acids in soil, groundwater and tap water around a PFSA manufactory in China (Hubei province)*

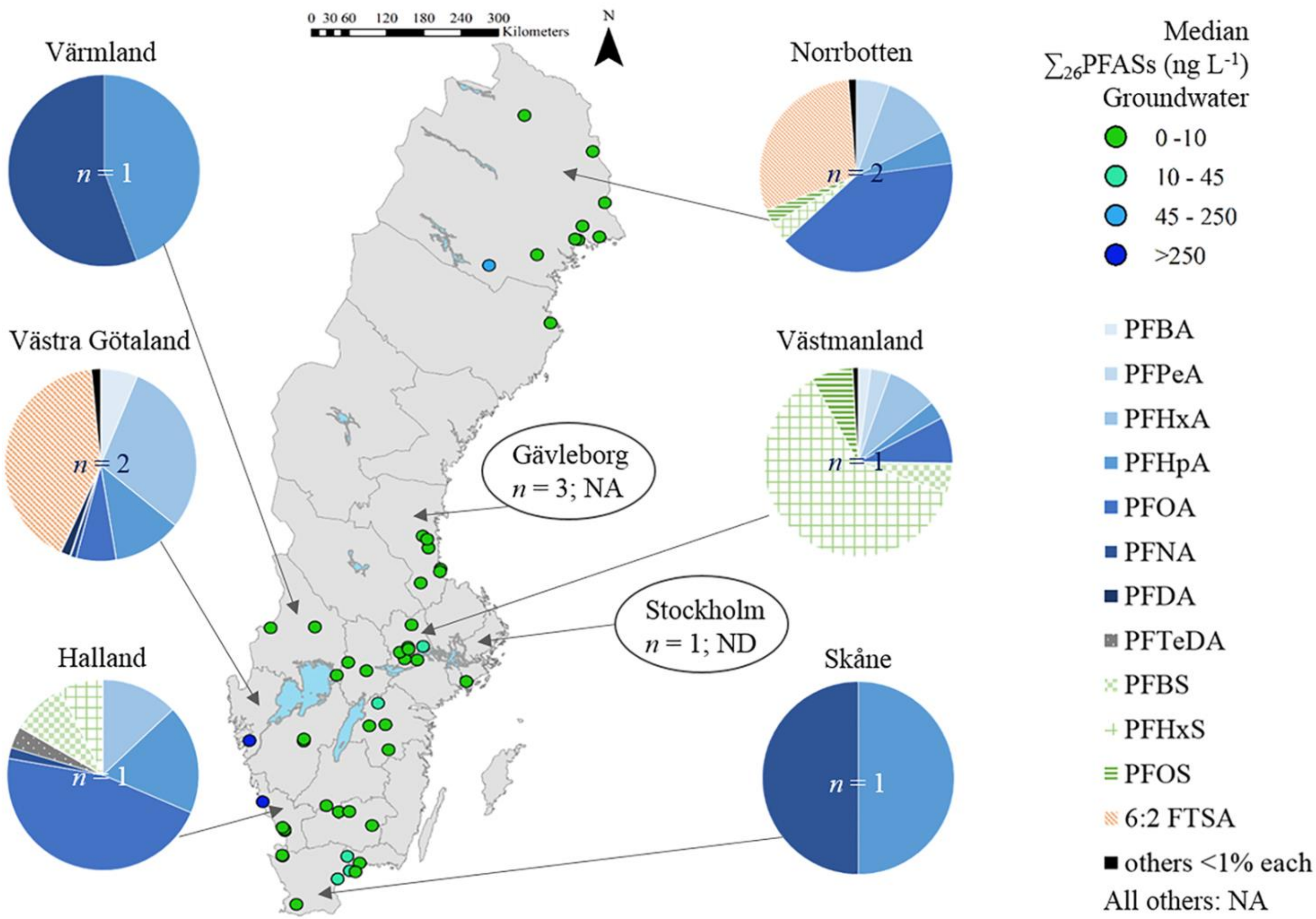
Total PFAS in tap water samples were in the range of **11.8-59.7 ng/L** with a mean and median concentration of 23.2 ng/L and 14.9 ng/L, respectively

ACQUE SOTTERRANEE



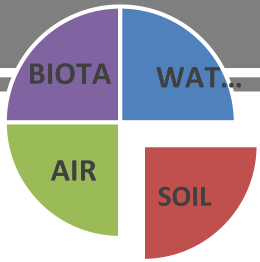
Gobelius et al., 2018. *Per- and Polyfluoroalkyl Substances in Swedish Groundwater and Surface Water: Implications for Environmental Quality Standards and Drinking Water Guidelines*

Groundwater sampling locations in Sweden and median PFAS composition profiles



Assoreca

SUOLO



Rankin et al., 2016. *A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence*

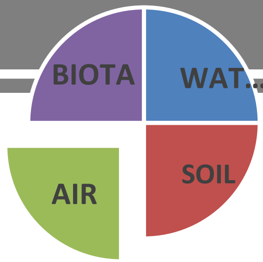
32 PFAS in surface soils determined at 62 locations (North America n = 33, Europe n = 10,Asian = 6, Africa n = 5, Australia n = 4, South America n = 3 and Antarctica n = 1).

Perfluoroalkyl carboxylates were observed in all samples with total concentrations ranging from **29 to 14,300 pg/g** (dry weight), while perfluoroalkane sulfonates were detected in all samples but one, ranging from **<LOQ-3270 pg/g**, confirming the global distribution of PFAS in terrestrial settings.

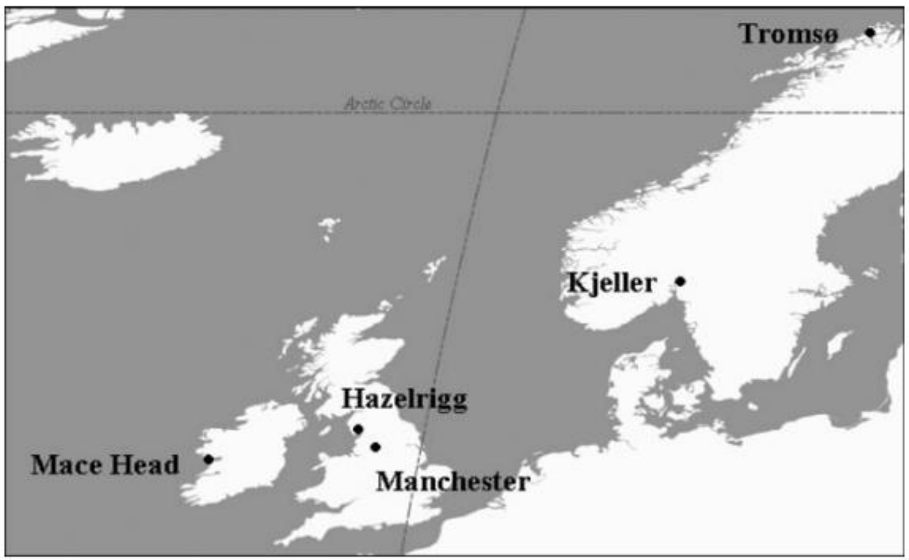
Gao et al., 2019 *Levels, spatial distribution and isomer profiles of perfluoroalkyl acids in soil, groundwater and tap water around a manufactory in China*

The total concentrations of PFAA in soil samples ranged **from 1.30 ng/g dw to 914 ng/g dw**,.

ARIA

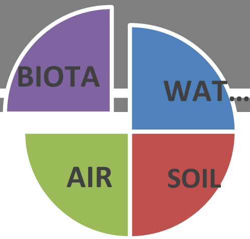


Barber et al., 2007. *Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe*

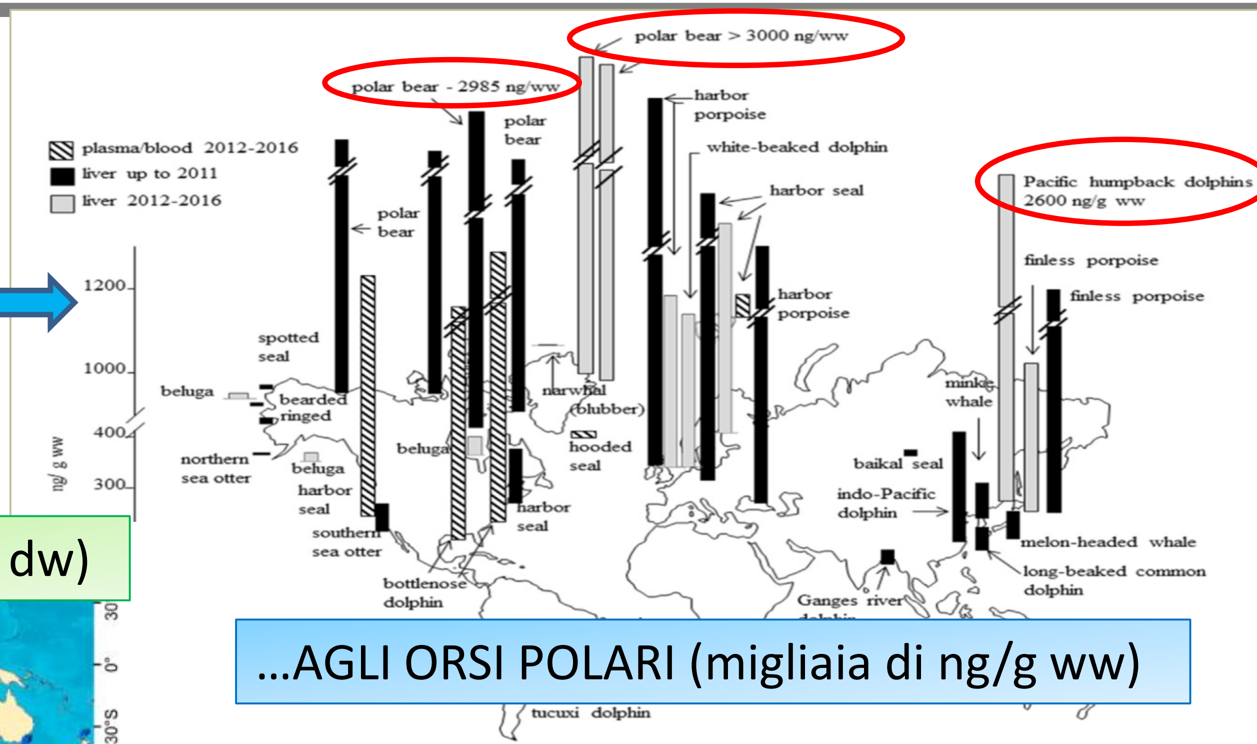


- Neutral precursors to PFAS screened along with fluorobutane sulfonamides/ethanols, as well ionic PFAS, including PFCAs and PFSAs.
- Air samples were collected from several **field sites in Europe**
- **PFOA** was often the predominant analyte found in the particulate phase at concentrations ranging from 1–818 pg/m^3, and **8:2 fluorotelomer alcohol (FTOH) and 6:2 FTOH** were the prevailing analytes found in the gas phase, at 5–243 pg m3 and 5–189 pg/m^3, respectively. **These three PFAS were ubiquitous in air samples**.

BIOTA

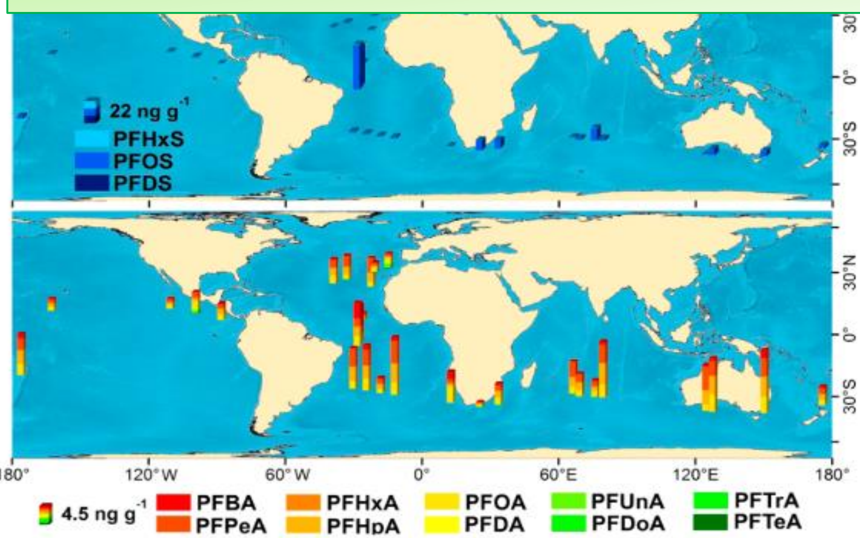


Fair, P.A. & Houde, M. 2018. Poly- and Perfluoroalkyl Substances in Marine Mammals (tipically **top predators**) → **biomagnification**



…AGLI ORSI POLARI (migliaia di ng/g ww)

DAL PLANKTON… (decine di ng/g dw)



Environmental Science & Technology

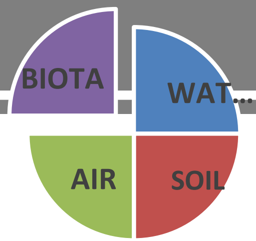
Article

pubs.acs.org/est

Accumulation of Perfluoroalkylated Substances in Oceanic Plankton

Paulo Casal,† Belén González-Gaya,†,‡ Yifeng Zhang,§ Anthony J. F. Reardon,§ Jonathan W. Martin,§ Begoña Jiménez,‡ and Jordi Dachs*,†

BIOTA



Autohors	Location	Types of organisms		PFAS analyzed	Concentrations (ng/g dw) (ng/g ww) Range	Mean
Hong et	West coast of South Korea	Fish		∑12PFAS	3.2-180	56
		Bivalve			5.1-47	
		Crab			2.6-53	
		Gastropod			2.1-200	
		Shrimp			3.4-135	
	Charleston Harbor and tributaries, S. Carolina (US)	Riverine and estuarine fishes		∑PFCA		8,3
				∑PFSA		15,4
				∑10PFAS		23,7
Fang et al., 2014	Taihu Lake, China	Lake fishes, 5 species	1	∑11PFAS		564.3
			2			328,7
			3			604
			4			959,7
			5			741

Early studies ('90) demonstrated the presence of PFAS in human blood, marine mammals, ocean going birds, animal species of remote areas (cetaceans, seals, polar bears..) (Lindstrom et al., 2011);

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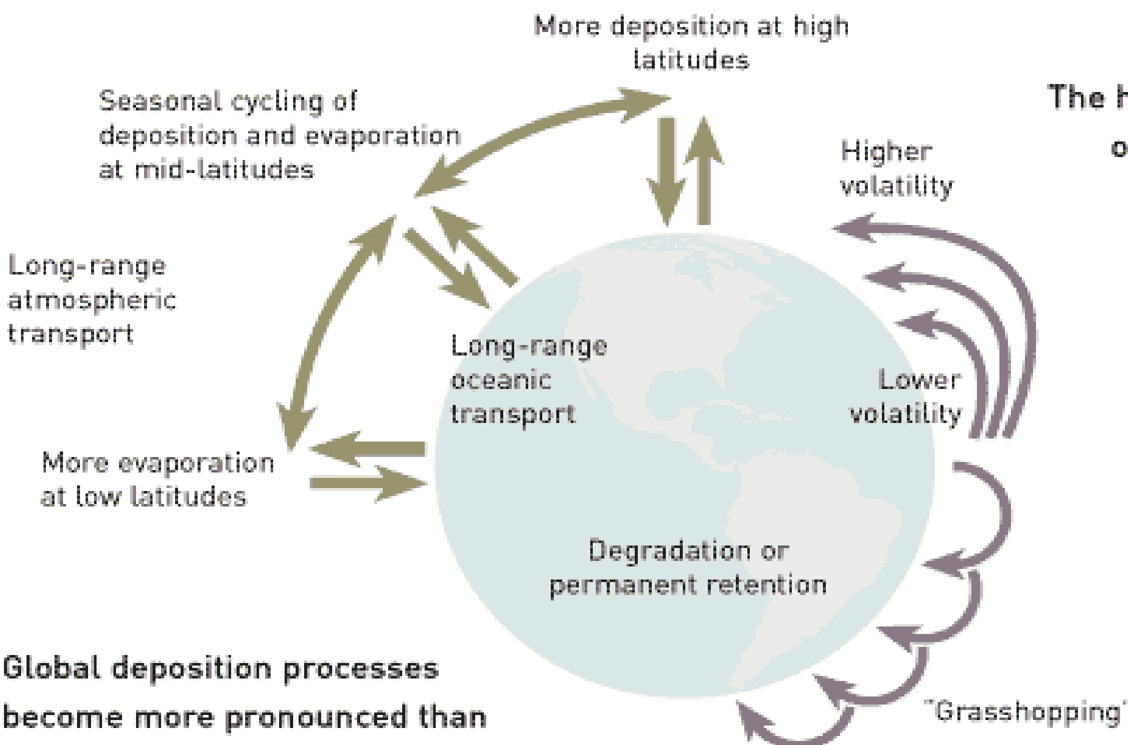
TRASPORTO A LUNGO RAGGIO

- PFAS end up in the environmental matrices
- The environmental fate (transport, partitioning, degradation) depends on their physical-chemical properties and environmental conditions
- Acknowledged as ubiquitous contaminants→ found all over the world
- Contribution of each route depends on the location



Global deposition processes become more pronounced than evaporation at high latitudes and lower temperatures.

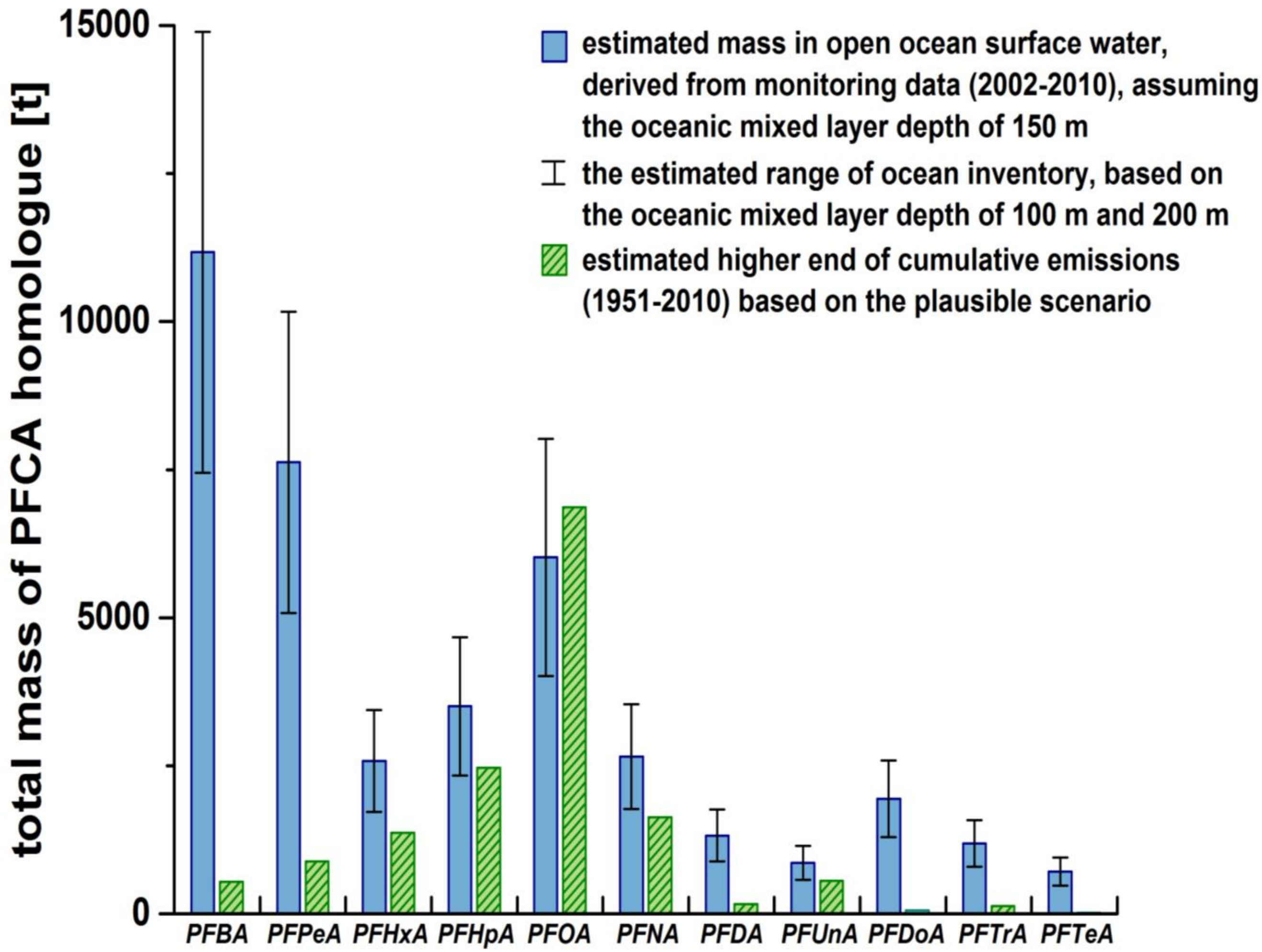
The higher the volatility of the chemical, the more likely it is to reach the poles.

Chemicals may travel to the poles in several steps, sometimes taking decades before degrading or being permanently retained.

Source: UNEP.

TRASPORTO A LUNGO RAGGIO

- As the vat majority of PFAS is non-volatile, and given that the main transport pathway is the water…
- …PFAA will gradually become well-mixed in the oceans and deep **oceans will be the ultimate sink**

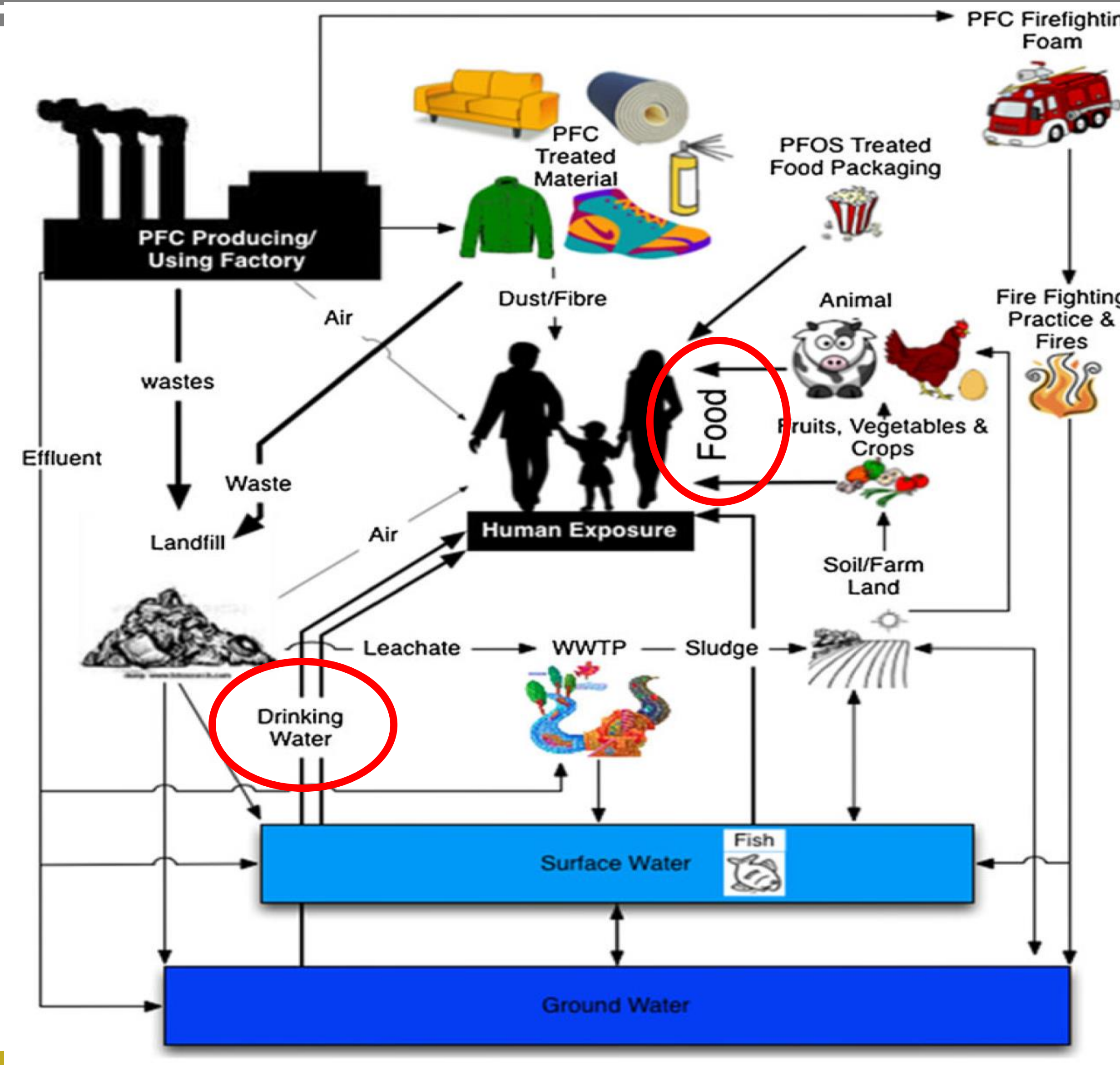


Assoreca

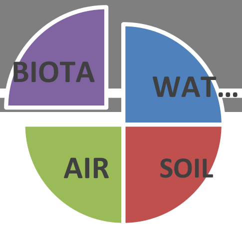
ESPOSIZIONE UMANA AI PFAS

ESPOSIZIONE UMANA AI PFAS

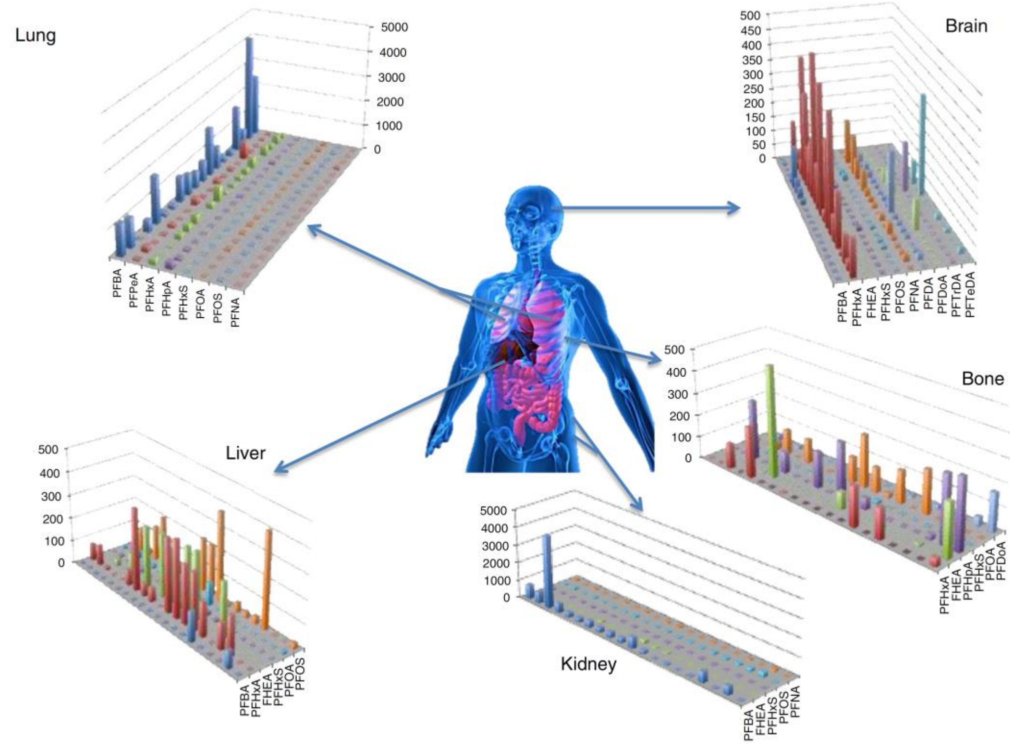
Human exposure to PFAS is mainly by **ingestion of contaminated food or water**. These compounds are not metabolized and bind to **proteins** (not to fats)



ESPOSIZIONE UMANA AI PFAS



- PFAS have been identified for the first time in the human body at the **end of 1970s→** 3M Company found PFOS in the blood serum of their employees
- Researches found the presence of 21 types of PFAS in **brain, liver, lungs and kidney** of deceased subjects that had been living in Tarragona (Catalonia, Spain). PFAS presence was confirmed for all tissue. The detection of PFBA and PFHxA confirms bioaccumulation of short-chain PFAA in human tissues. (Pérez et al., 2011)
- The ionic state of PFAA prevents them from accumulating in adipose tissues and induces rather a **proteinophilic behavior**, especially with plasma albumin (Jones et al., 2003, Chen and Guo, 2009)

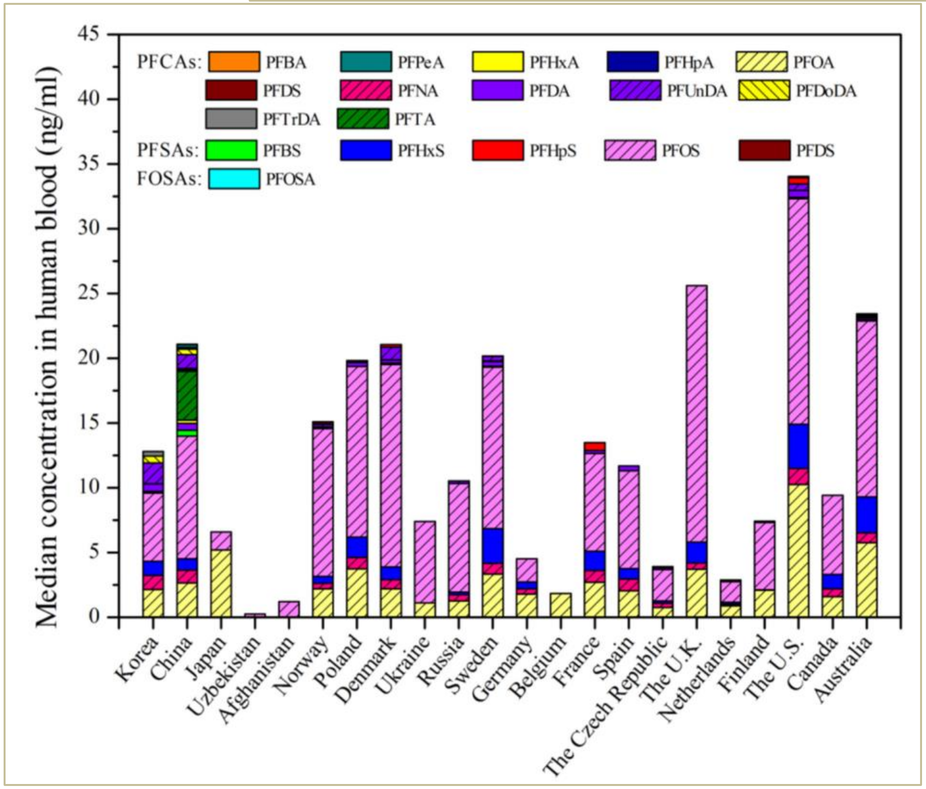


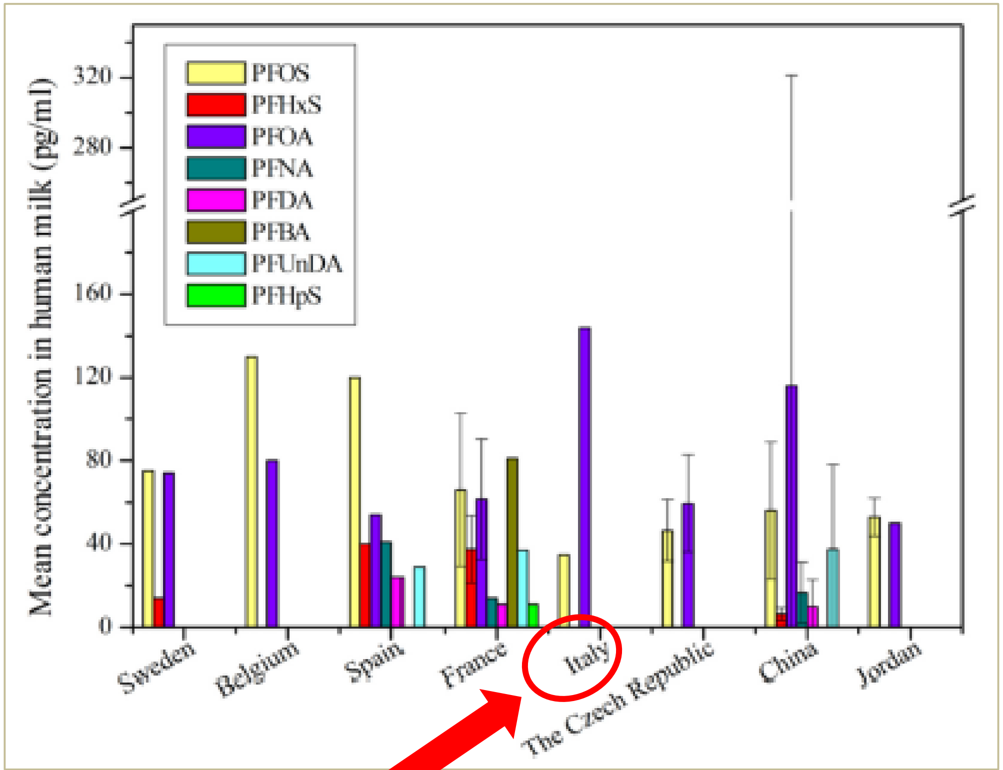
Perez et al., 2013

ESPOSIZIONE UMANA AI PFAS

BIOTA WAT... AIR SOIL

Jian et al., 2018. *A short review on human exposure to and tissue distribution of per- and polyfluoroalkyl substances (PFAS)*





Median: ~1 to 35 ng/ml (1000-35000 ng/L)

PFOA: averagely up to ~ 150 pg/ml (~150 ng/L) in Italy

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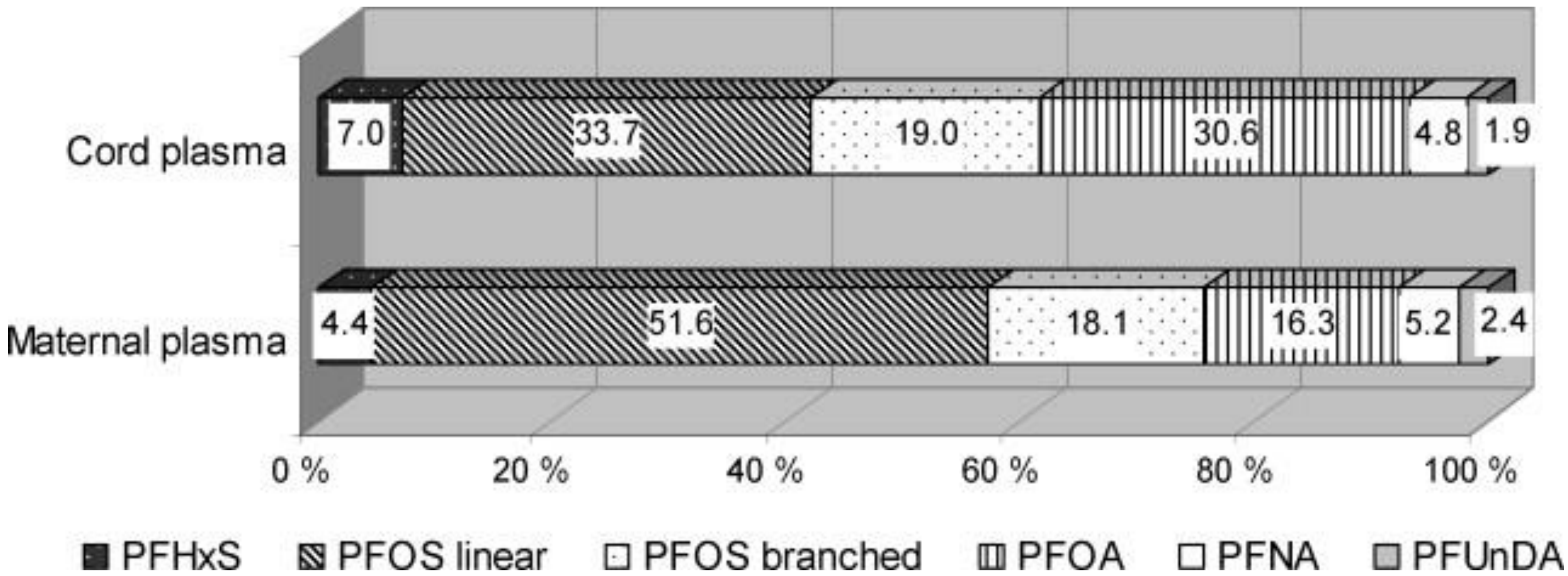
I PFAS POSSONO ATTRAVERSARE LA PLACENTA



Distribution of various PFCs in cord or maternal plasma (percent mean mass fraction of individual compound)

Gutzkow et al., 2011. Placental transfer of perfluorinated compounds is selective--a Norwegian Mother and Child sub-cohort study.

IN SINTESI: TOSSICITÀ LEGATA AI PFAS PER L'UOMO

Might be associated with testicular, kidney, prostate, and ovarian **cancers**, and **non-Hodgkin lymphoma** (Vieira et al., 2013)

Long half-lives in humans (PFOS and PFOA ~ 5.4 and 3.8 years; PFHxS ~8.5 years in humans. (Lindstrom et al., 2011)

HUMAN

increased affinity for **protein. They do not tend to accumulate in fat tissue** (Jones et al., 2003; Luebker et al., 2002; Vanden Heuvel et al., 1992; Weiss et al., 2009).

Detected in **human serum, cord blood, breast milk and several different tissues** (Domingo et al., 2012a; Ericson et al., 2007; Fromme et al., 2010; Haug et al., 2009a,b; Llorca et al., 2010).

PERMANGONO MOLTI FATTORI DI INCERTEZZA

1. **Toxicity data essentially referred to PFCAs and PFSAs, mostly PFOA and PFOS (also PFHxS)** «Information about sources, environmental fate and toxicokinetics of PFOS and PFOA is largely available [….]. In contrast, data on most of the PFAS currently in use, continues to be very limited.»
2. Toxicokinetics of different PFCs **differ considerably** between animal species and even between different genders within a given species.
3. **Long half-lives in humans** → difficult to determine how changes in lifestyle, diet, or other exposure-related factors influence blood levels.
4. While half-life has generally been observed to increase in proportion to compound chain length, this is **not always true**

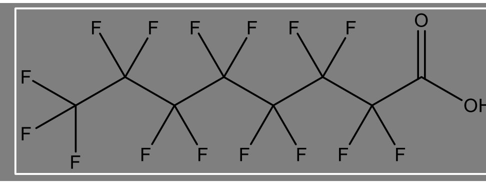
Lunghezza catena perfluorata	MOLECOLA	T di emivita (anni)
C8	PFOA	~3.8
C8	PFOS	~5.4
C6	PFHxS	~8.5

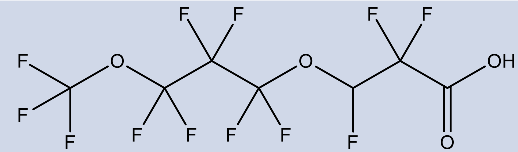
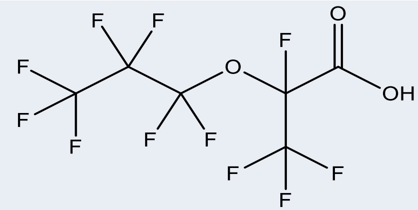
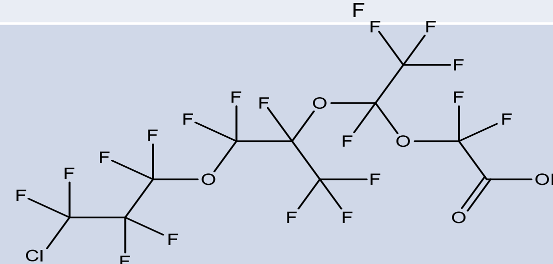
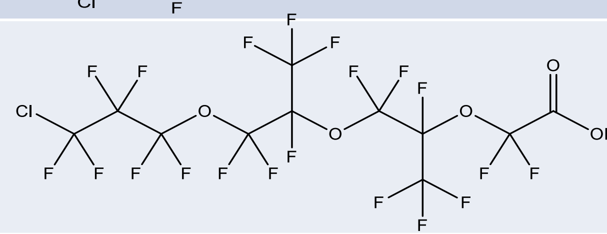
5. Investigations of potential health effects in workers occupationally exposed to these compounds have generally shown **inconsistent results**: because sample populations are small, historical exposure levels are uncertain, individuals often have had simultaneous exposures to other compounds, and they may have preexisting conditions that complicate evaluations.

LA RISPOSTA DEL MERCATO: I PFAS DI NUOVA PRODUZIONE

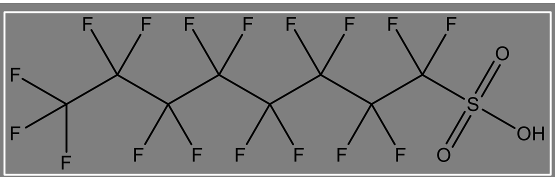
- Phase-out actions and use restrictions to reduce the environmental release of long-chain PFCAs, PFSAs and their precursors have been taken since 2000. In particular, long-chain poly- and perfluoroalkyl substances (PFAS) are being replaced with **shorter-chain homologues or other fluorinated or non-fluorinated alternative**
- The **scarcity of experimental data** prevents hazard and risk assessments for these substances
- Even though the fluorinated alternatives contain some structural differences, their physicochemical properties are **not significantly different from those of their predecessors** Furthermore, most of the alternatives are estimated to be similarly persistent and mobile in the environment as the long-chain PFAS. (Gomis et al., 2015).

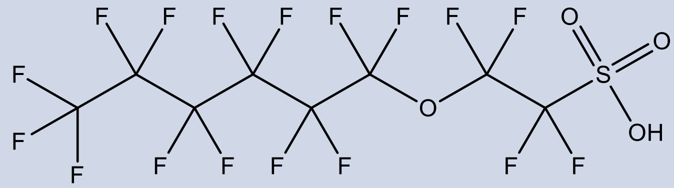
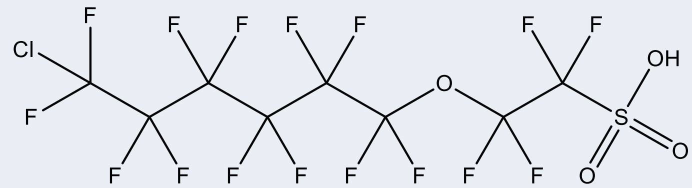
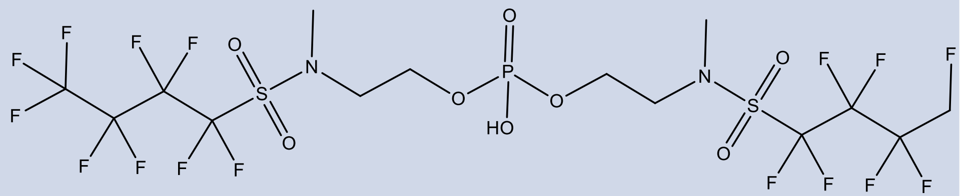
ESEMPI DI SOSTITUTI DEL PFOA



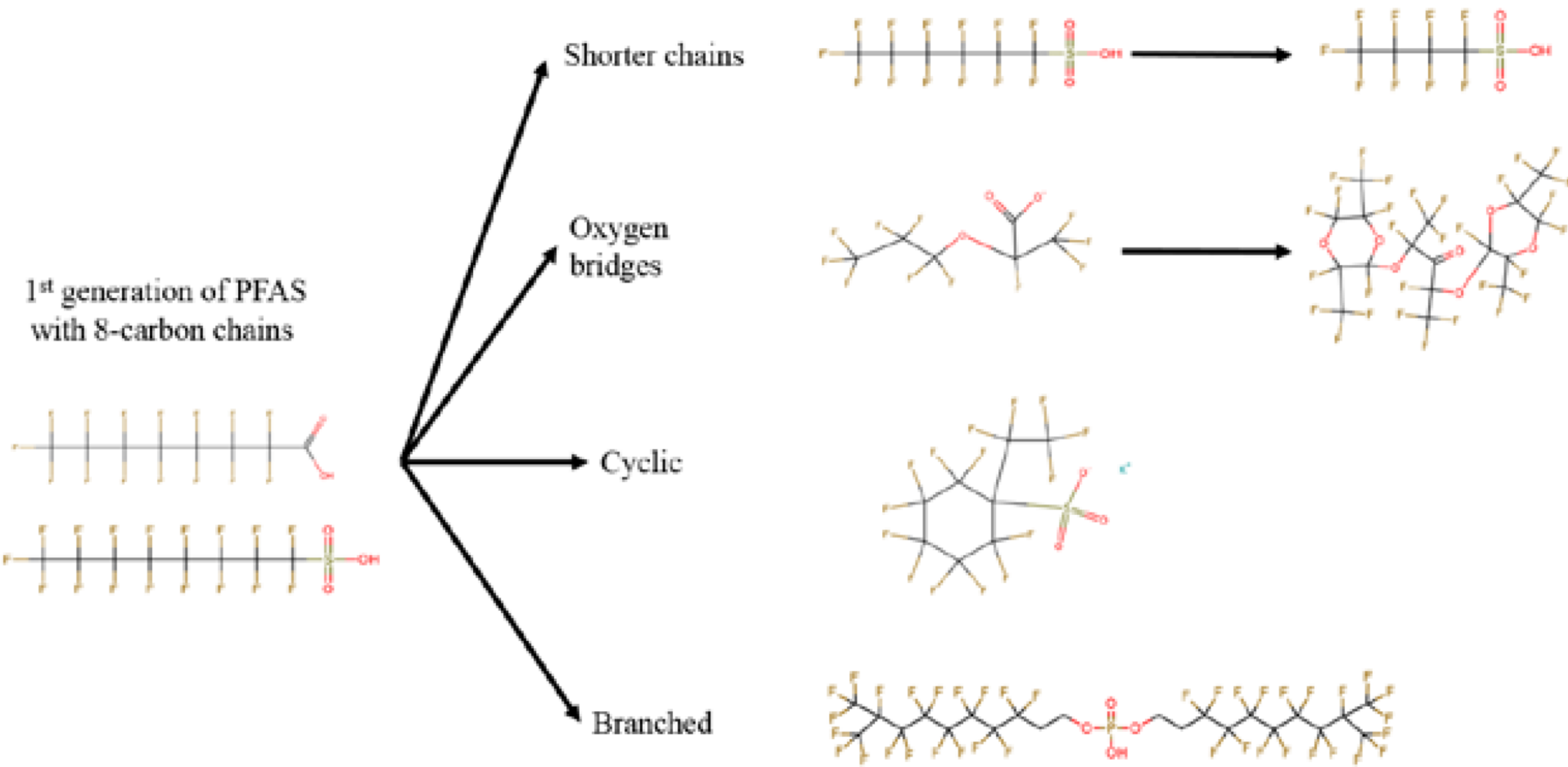
NOME COMMERCIALE	ABBREVIAZIONE	STRUTTURA
Adona	Adona	
GenX	GenX	
Unknown	PFTECA1	
Unknown	PFTECA2	

ESEMPI DI SOSTITUTI DEL PFOS



COMMERCIAL NAME	ABBREVIATION	STRUCTURE
F-53	F-53	
F-53B	F-53B	
Unknown	PFBSaPA (perfluorobutane sulfonamide w/phosphoric acid)	

PRINCIPALI CAMBIAMENTI CONFORMAZIONIALI DEI PFAS COMMERCIALIZZATI NEL MERCATO SECONDO LE RICERCHE DELL'AGENZIA CHIMICA SVEDESE

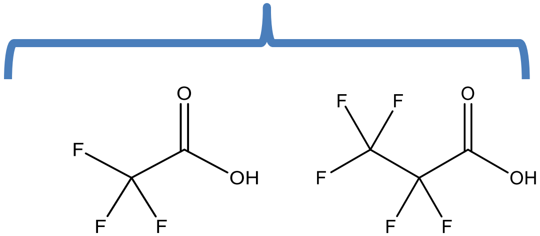


KEMI 2015. Occurrence and use of highly fluorinated substances and alternatives

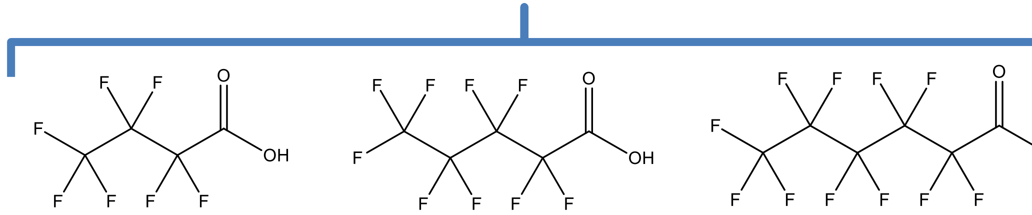
Assoreca

OMOLOGHI A CATENA PIU’ CORTA: COMPLICAZIONI

ULTRA-SHORT CHAIN PFCA



SHORT CHAIN PFCA



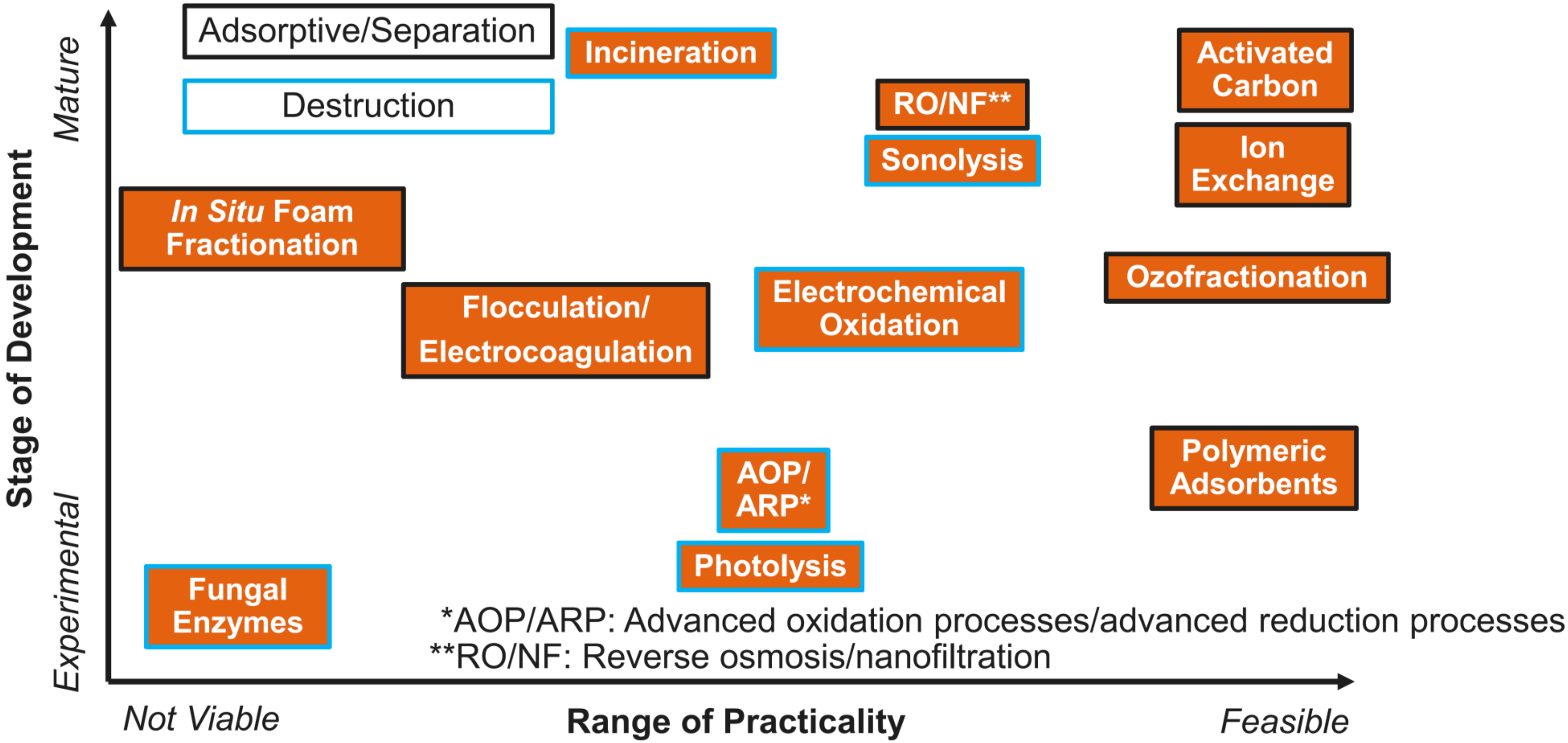
- Less bioaccumulative, not less persistent
- Even greater scarcitiy of information
- Weaker technical performance
- More hydrophylic → Harder to remove via typical WT technologies

C'E BISOGNO DI MAGGIORI CONOSCENZE PER VALUTARE LA PERICOLOSITA' DEI SOSTITUTI NEI CONFRONTI DELL'ESSERE UMANO E DEL BIOTA

To achieve a better understanding of environmental and toxicological behaviour of these substances, more informations are needed:

1) (bio)degradation experiments in relevant environmental media for individual substances;
2) pKa measurements of the acidic fluorinated alternatives
3) bioaccumulation experiments, including protein-binding experiments for the acidic fluorinated alternatives and K_{OW} experiments for the neutral ones:
4) toxicity tests to identify their mode-of-action and toxicity

PRINCIPALI TECNOLOGIE DI RIMOZIONE DEI PFAS DALLA MATRICE ACQUOSA



Ross et al., 2018. PFAS treatment technologies for water

Assoreca

EFFICIENZA DEI SISTEMI DI RIMOZIONE: TECNOLOGIA A MEMBRANE VS ADSORBIMENTO

I risultati di uno studio condotto in impianti full-scale di trattamento acque dimostrano l'indubbia efficienza del sistema ad osmosi inversa, che si mantiene inalterata al diminuire della lunghezza della catena perfluoroalchilica dei PFAA analizzati nello studio

ELSEVIER
Available online at www.sciencedirect.com
ScienceDirect
journal homepage: www.elsevier.com/locate/watres
WATER RESEARCH

Treatment of poly- and perfluoroalkyl substances in U.S. full-scale water treatment systems

Timothy D. Appleman [a], *Christopher P. Higgins* [a,*], *Oscar Quiñones* [b], *Brett J. Vanderford* [b], *Chad Kolstad* [c], *Janie C. Zeigler-Holady* [b], *Eric R.V. Dickenson* [a,b,**]

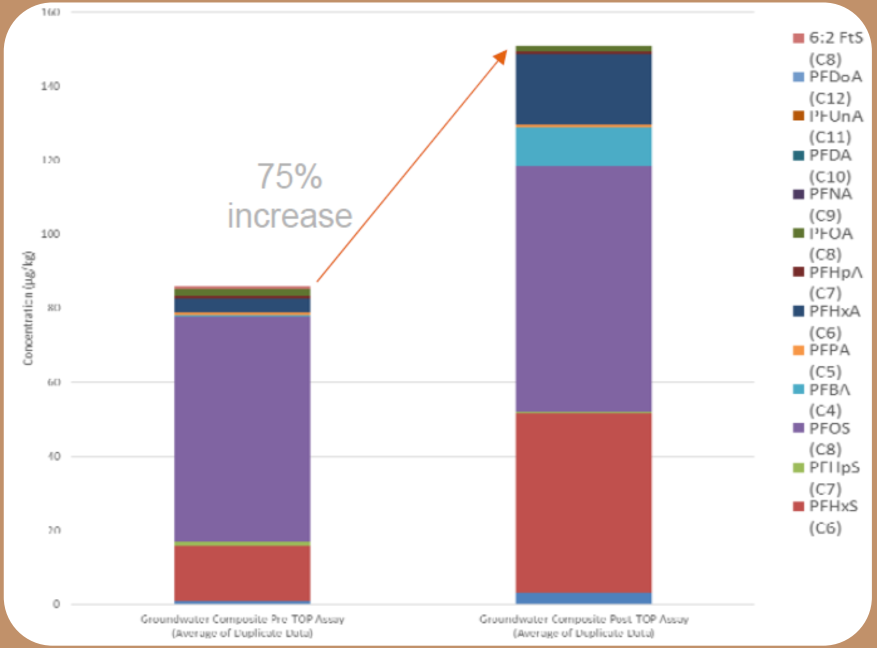
	RO		AIX		GAC
	09/02/2012	06/03/2012	30/05/2012	19/09/2012	25/4/2007-22/4/2008
PFBA	ND	>95 %	-9 %	0 %	-17 %
PFPeA	>99 %	>98 %	0 %	0 %	>22 %
PFHxA	>99 %	>99 %	14 %	-14 %	>68 %
PFHPa	>98 %	>95 %	54 %	38 %	ND
PFOA	>98 %	>98 %	76 %	73 %	>92 %
PFNA	>98 %	>95 %	ND	>67 %	ND
PFDA	>99 %	>99 %	ND	ND	ND
PFUnA	>77 %	>71 %	ND	ND	ND
PFDoA	>87 %	>84 %	ND	ND	ND
PFBS	>96 %	>94 %	83 %	80 %	ND
PFHxS	>96 %	>90 %	>97 %	>98 %	>41 %
PFOS	>96 %	>96 %	>90 %	>94 %	>95 %

T.D. Appleman et al. Water Research (2014)

I PFAS CHE NON VEDIAMO (CHE NON CERCHIAMO)

MORE THAN 3000 COMPOUNDS IN THE MARKET

TOTAL OXIDABLE PRECURSORS ASSAY (TOPA)



Arcadis report (2017)

70 ANNI DI PRODUZIONE E PIU' DI 20 ANNI DI STUDI…
PERCHE' SIAMO ANCORA QUI?

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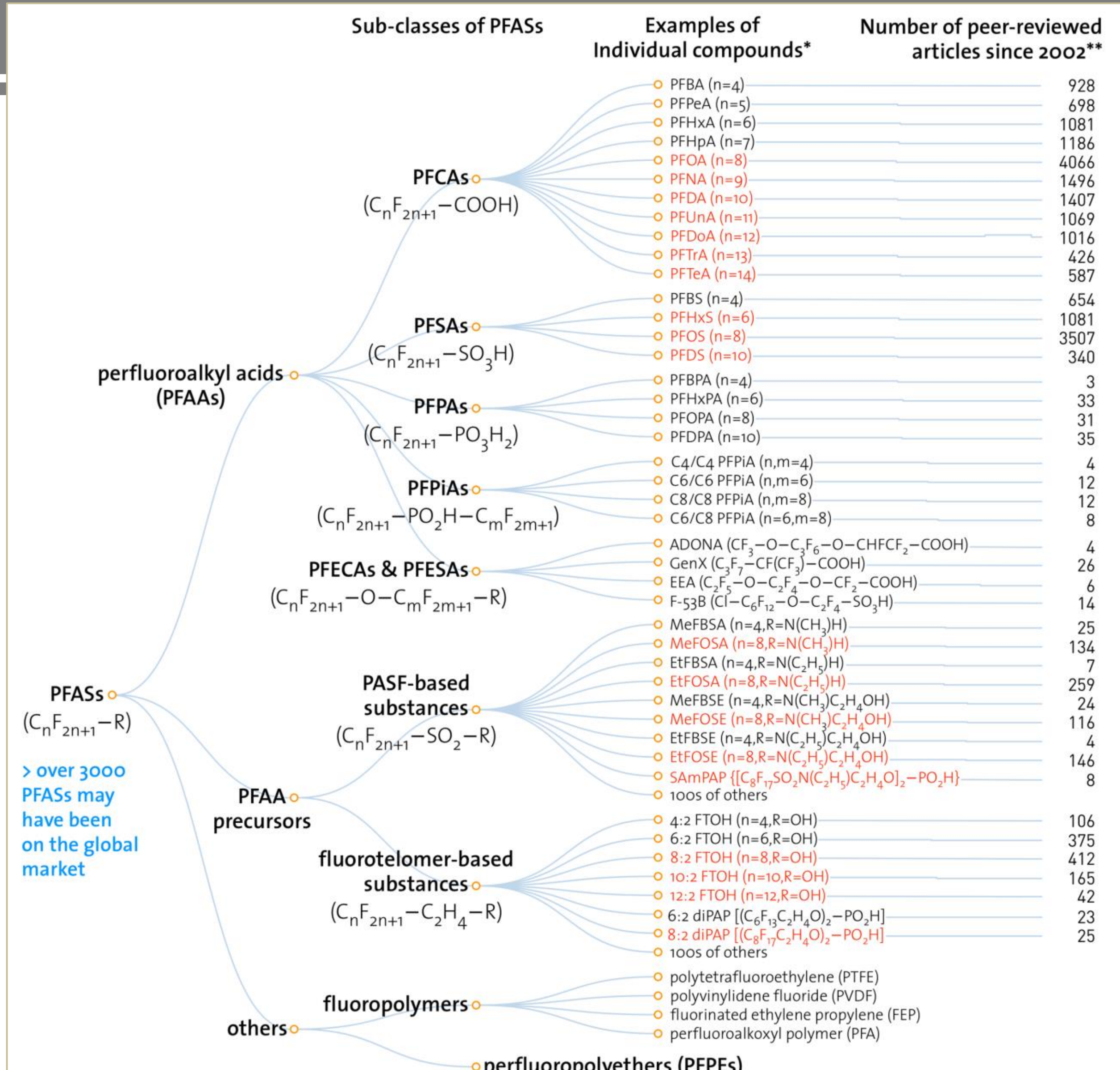
MOLTI PFAS TRASCURATI



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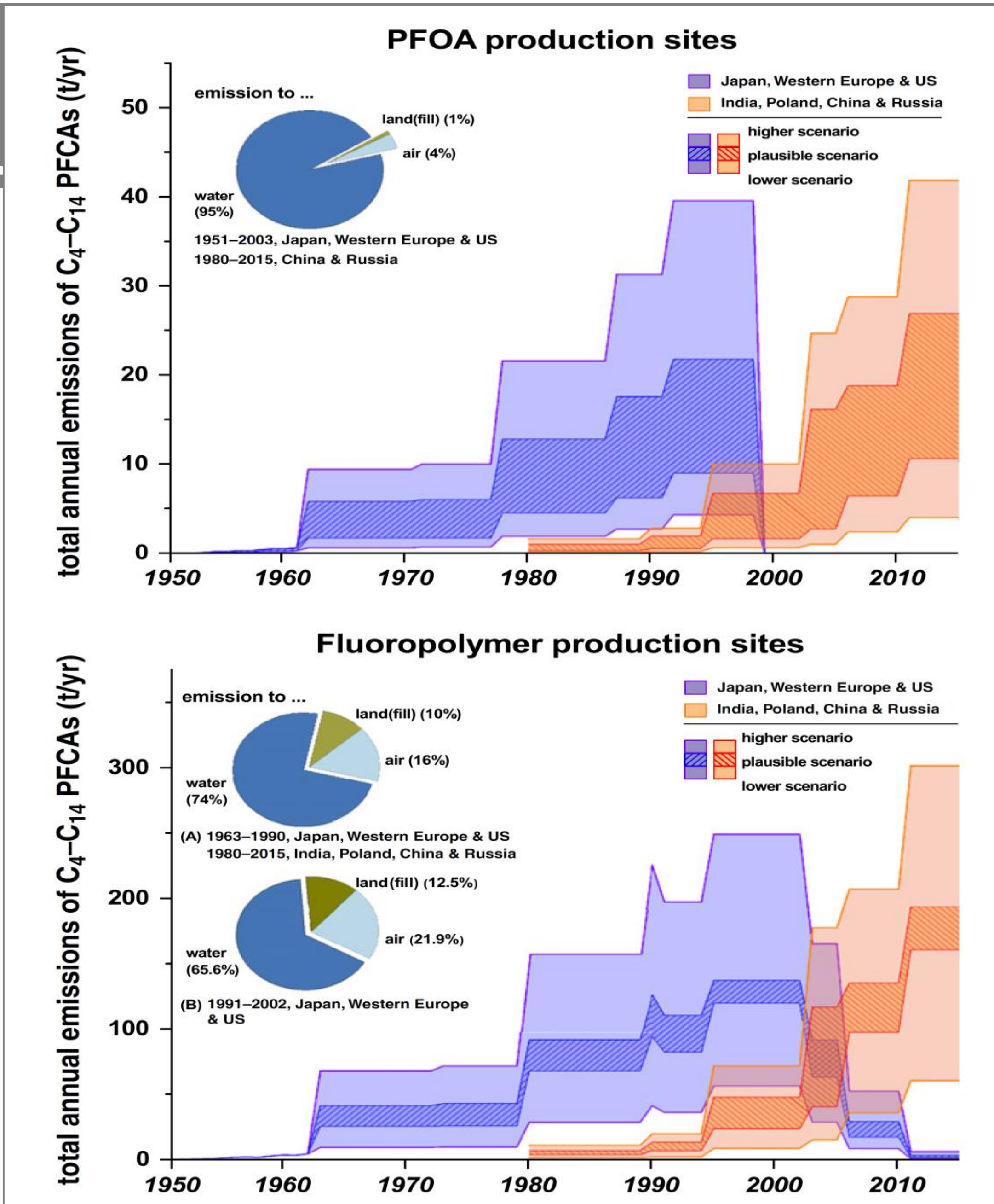
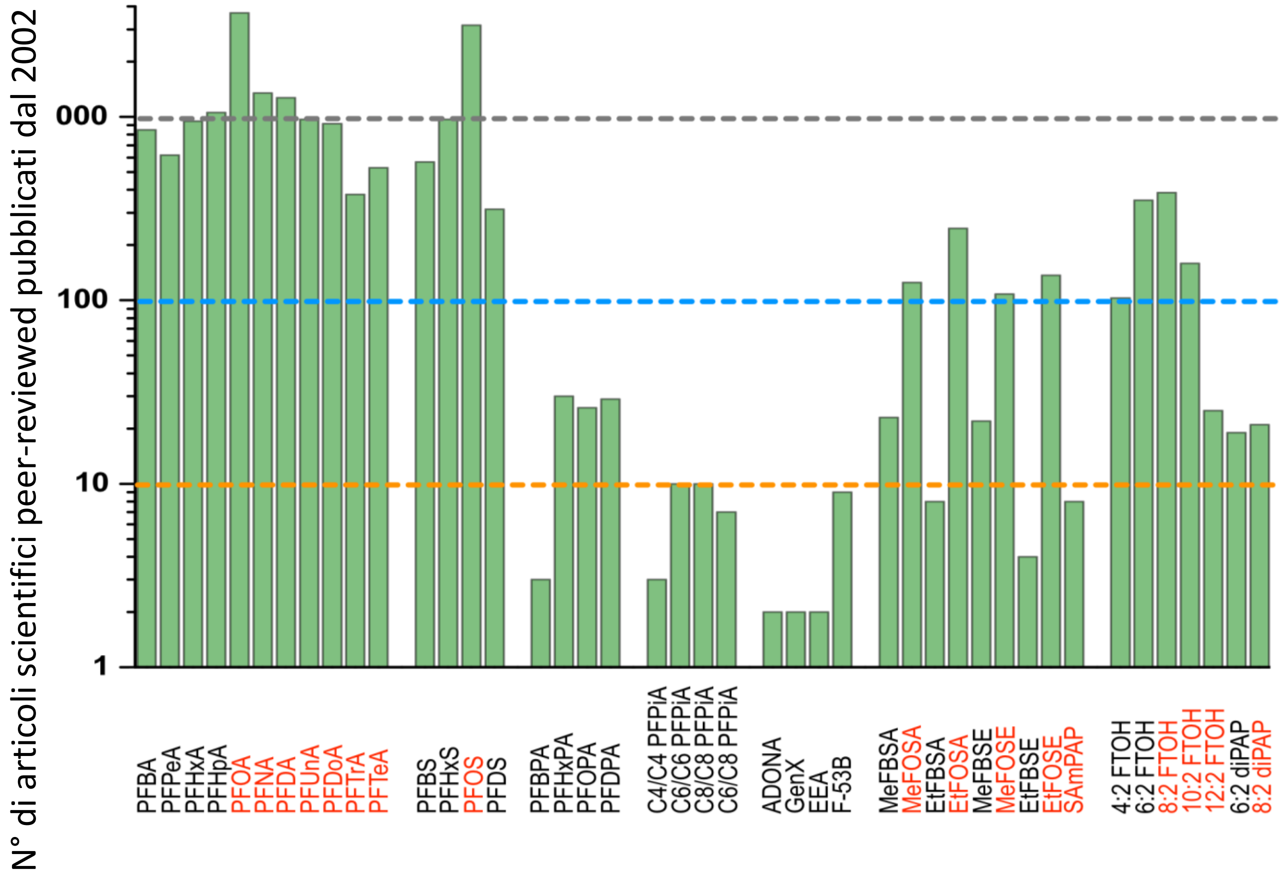
PRODUZIONE DI PFAS DI VECCHIA GENERAZIONE SI è SPOSTATA VERSO PAESI IN VIA DI SVILUPPO



Estimated annual releases of PFCAs from PFOA and fluoropolymer production sites (top) and fluoropolymer production sites (bottom) in the United States (US), Western Europe and Japan (purple) as well as in China, Russia, Poland and India (orange). The pie charts show fractions of emissions to different environmental media

Wang et al., 2014. Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: Production and emissions from quantifiable sources

INFORMAZIONI LIMITATE PER MOLTI PFAS



PFAS in red are those that have been restricted under national/regional global regulatory or voluntary frameworks, with or without specific exemptions (see OECD, 2015). The number of articles were retrieved from SciFinder® on Nov. 1, 2016

Wang et al., 2017. *A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFAS)?*

LA CONOSCENZA DELLE LORO PROPRIETA' PUO' CAMBIARE RAPIDAMENTE

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Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Comparing the toxic potency in vivo of long-chain perfluoroalkyl acids and fluorinated alternatives

Melissa I. Gomis[a], Robin Vestergren[a,b], Daniel Borg[c], Ian T. Cousins[a,*]

[a] Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, SE-10691 Stockholm, Sweden
[b] IVL Swedish Environmental Research Institute, SE-100 31 Stockholm, Sweden
[c] Swedish Chemicals Agency, 172 13 Sundbyberg, Sweden

«The toxicity ranking using modeled serum (GenX > PFOA > PFHxA > PFBA) and liver (GenX > PFOA≈PFHxA≈PFBA) concentrations indicated that some fluorinated alternatives have **similar or higher toxic potency** than their predecessors when correcting for differences in toxicokinetics.»

ALTRI PFAS IN ARRIVO?

- Using textile finishes as an example:

1950s: PFOA-based

1960s/70s: POSF-based + C_8–C_{20} fluorotelomer-based

2002: PBSF-based + C_8–C_{20} fluorotelomer-based

2015: PBSF-based + C_6 fluorotelomer-based

20XX: $(C_nF_{2n+1})CH_2(C_mF_{2m+1})C_2H_4$- &

$(C_nF_{2n+1})O(C_mF_{2m+1})C_2H_4$-?

→ A never - ending story?

COME CONCLUDERE QUESTA STORIA?

A similar concern for all PFAS including new replacements (particularly due to their **high P, mobility, similar mode(s)-of-action**)

→ We cannot continue to overlook the rest

→ Nor can we conduct research on, and regulate, them one at a time

→ Prioritisation is needed

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journal homepage: www.elsevier.com/locate/chemosphere

Helsingør Statement on poly- and perfluorinated alkyl substances (PFASs)

Martin Scheringer[a,*], Xenia Trier[b], Ian T. Cousins[c], Pim de Voogt[d], Tony Fletcher[e], Zhanyun Wang[a], Thomas F. Webster[f]

Perspectives | Brief Communication

The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs)

http://dx.doi.org/10.1289/ehp.1509934

A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)?

Zhanyun Wang†, Jamie C. DeWitt‡, Christopher P. Higgins§, and Ian T. Cousins*‖
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University Ca' Foscari Venice

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