

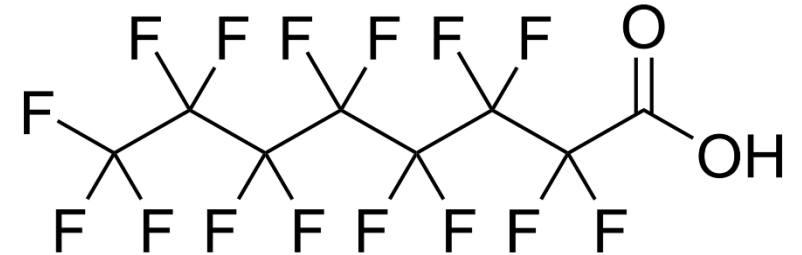
PFAS ASPETTI ANALITICI

DR E.AGUSSON

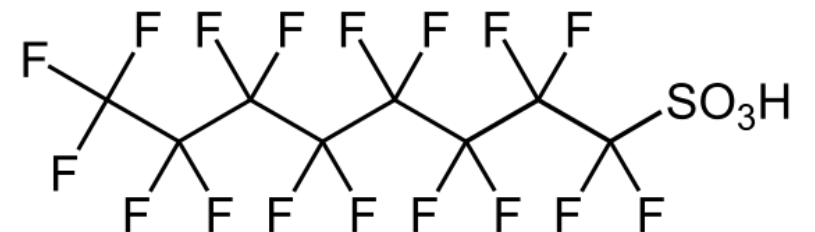
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PFAS = sostanze perfluoroalchiliche

Acido ottanoico → Acido perfluorottanoico
PFOA



Acido ottansolfonico → Acido perfluorottansolfonico
PFOS



According to the currently most accepted terminology (Buck et al., 2011), per- and polyfluoroalkyl substances (PFASs) are a family of anthropogenic chemicals that “contain one 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on which all the H substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety $(C_nF_{2n+1}-)$.”

(fonte: OECD ENV/JM/MONO(2018)7)

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DUE VIE DI SINTESI

ELETTROFLUORURAZIONE

TELOMERIZZAZIONE

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Che impieghi hanno i PFAS?

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Table 4-1. Potential major manufacturing sources of PFAS releases to the environment

Sector	Example Uses	References
Textiles & Leather	Factory- or consumer-applied coating to repel water, oil, and stains. Applications include protective clothing and outerwear, umbrellas, tents, sails, architectural materials, carpets, and upholstery.	Rao and Baker 1994; Hekster, Laane, and de Voogt 2003; Brooke, Footitt, and Nwaogu 2004; Poulsen et al. 2005; Prevedouros et al. 2006; Walters and Santillo 2006; Trudel et al. 2008; Guo et al. 2009; USEPA 2009a; Ahrens 2011; Buck et al. 2011; UNEP 2011; Herzke, Olsson, and Posner 2012; Patagonia 2015; Kotthoff et al. 2015; ATSDR 2015
Paper Products	Surface coatings to repel grease and moisture. Uses include non-food paper packaging (for example, cardboard, carbonless forms, masking papers) and food-contact materials (for example, pizza boxes, fast food wrappers, microwave popcorn bags, baking papers, pet food bags).	Rao and Baker 1994; Kissa 2001; Hekster, Laane, and de Voogt 2003; Poulsen et al. 2005; Trudel et al. 2008; Buck et al. 2011; UNEP 2011; Kotthoff et al. 2015; Schaidler et al. 2017
Metal Plating & Etching	Corrosion prevention, mechanical wear reduction, aesthetic enhancement, surfactant, wetting agent/fume suppressant for chrome, copper, nickel and tin electroplating, and post-plating cleaner.	USEPA 1996; USEPA 1998; Kissa 2001; Prevedouros et al. 2006; USEPA 2009b; UNEP 2011; OSHA 2013; KEMI 2015; Danish EPA 2015
Wire Manufacturing	Coating and insulation.	Kissa 2001; van der Putte et al. 2010; ASTSWMO 2015
Industrial Surfactants, Resins, Molds, Plastics	Manufacture of plastics and fluoropolymers, rubber, and compression mold release coatings; plumbing fluxing agents; fluoroplastic coatings, composite resins, and flame retardant for polycarbonate.	Kissa 2001; Renner 2001; Poulsen et al. 2005; Fricke and Lahl 2005; Prevedouros et al. 2006; Skutlarek, Exner, and Farber 2006; van der Putte et al. 2010; Buck et al. 2011; Herzke, Olsson, and Posner 2012; Kotthoff et al. 2015; Miteni 2016; Chemours 2017
Photolithography, Semiconductor Industry	Photoresists, top anti-reflective coatings, bottom anti-reflective coatings, and etchants, with other uses including surfactants, wetting agents, and photo-acid generation.	SIA 2008; Choi et al. 2005; Rolland et al. 2004; Brooke, Footitt, and Nwaogu 2004; van der Putte et al. 2010; UNEP 2011; Herzke, Olsson, and Posner 2012

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Commercial and Consumer Products Containing PFAS:

- paper and packaging
- clothing and carpets
- outdoor textiles and sporting equipment
- ski and snowboard waxes
- non-stick cookware
- cleaning agents and fabric softeners
- polishes and waxes, and latex paints
- pesticides and herbicides
- hydraulic fluids
- windshield wipers
- paints, varnishes, dyes, and inks
- adhesives
- medical products
- personal care products (for example, shampoo, hair conditioners, sunscreen, cosmetics, toothpaste, dental floss)

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Quanti sono i PFAS?

OECD pubblica nel 2007 (e aggiorna nel maggio 2018)
: «Lists of PFOS, PFAS, PFOA, PFCA, Related Compounds and Chemicals
That May Degrade to PFCA»

In totale OECD stila una lista di **4730** sostanze riconducibili sotto la
denominazione della famiglia dei PFAS
(fonte: OECD ENV/JM/MONO(2018)7)

Nel documento si afferma che la lista è tuttavia INCOMPLETA

CAS_No	EC_No	Chemical_Name	Tonnage_Band	Registration_Type
85857-16-5	288-657-1	Trimethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane	10 - 100 tonnes per annum	Full
38565-52-5	254-004-4	(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)oxirane	Intermediate Use Only	Intermediate
80793-17-5	700-684-7	1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro octane	0 - 10 tonnes per annum	Full
2043-57-4	218-056-1	1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane	Intermediate Use Only	Intermediate
355-04-4	206-575-6	1,1,1,2,2,3,3,4,5,5,5-undecafluoro-4-(trifluoromethyl)pentane	0 - 10 tonnes per annum	Full
132182-92-4	459-520-5	1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-trifluoromethyl-pentane	Tonnage Data Confidential	NONS
756-13-8	436-710-6	1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone	0 - 10 tonnes per annum	Full
756-13-8	436-710-6	1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone	1000+ tonnes per annum	Full
34454-97-2	252-043-1	1,1,2,2,3,3,4,4,4-nonafluoro-N-(2-hydroxyethyl)-N-methylbutane-1-sulphonamide	10 - 100 tonnes per annum	Full
375-72-4	206-792-6	1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulphonyl fluoride	Intermediate Use Only	Intermediate
375-50-8	206-788-4	1,1,2,2,3,3,4,4-octafluoro-1,4-diiodobutane	Intermediate Use Only	Intermediate
335-27-3	206-386-9	1,1,2,2,3,3,4,5,5,6-decafluoro-4,6-bis(trifluoromethyl)cyclohexane	0 - 10 tonnes per annum	Full
15290-77-4	430-710-1	1,1,2,2,3,3,4-heptafluorocyclopentane	0 - 10 tonnes per annum	Full
15290-77-4	430-710-1	1,1,2,2,3,3,4-heptafluorocyclopentane	Tonnage Data Confidential	NONS
13846-22-5	237-579-6	1,1,2,2,3,3-hexafluoro-1,3-bis((trifluorovinyl)oxy)propane	Intermediate Use Only	Intermediate
874288-98-9	618-014-6	1,2-dichloro-1-[difluoro(trifluoromethoxy)methoxy]-1,2,2-trifluoroethane,	Intermediate Use Only	Intermediate
130841-23-5	415-580-4	1,4-dichloro-2-(1,1,2,3,3,3-hexafluoropropoxy)-5-nitrobenzene	Tonnage Data Confidential	NONS
130841-23-5	620-459-6	1,4-dichloro-2-(1,1,2,3,3,3-hexafluoropropoxy)-5-nitrobenzene	Intermediate Use Only	Intermediate
375-80-4	206-794-7	1,6-diiodoperfluorohexane	Intermediate Use Only	Intermediate
59493-72-0	407-400-8	1-[3-[4-((heptadecafluorononyl)oxy)-benzamido]propyl]-N,N,N-trimethylammonium iodide	Tonnage Data Confidential	NONS
382-28-5	206-841-1	2,2,3,3,5,5,6,6-octafluoro-4-(trifluoromethyl)morpholine	100 - 1000 tonnes per annum	Full
919005-14-4	700-835-7	2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]propanoic acid	Intermediate Use Only	Intermediate
42532-60-5	806-451-7	2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanenitrile	0 - 10 tonnes per annum	Full
382-26-3	609-534-4	2-[difluoro(methoxy)methyl]-1,1,1,3,3,3-hexafluoropropane	Intermediate Use Only	Intermediate
67584-55-8	266-733-5	2-[methyl((nonafluorobutyl)sulphonyl)amino]ethyl acrylate	100 - 1000 tonnes per annum	Full
756-12-7	690-995-3	2-Butanone, 1,1,1,2,4,4,4-heptafluoro-3-(trifluoromethyl)-	0 - 10 tonnes per annum	Full
88992-45-4	811-523-6	2-hydroxy-N,N,N-trimethyl-3-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thio]-1-propanimium chloride	0 - 10 tonnes per annum	Full
62880-93-7	811-522-0	2-methyl-2-[(1-oxo-3-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thio]propyl)amino]-1-propanesulfonic acid, sodium salt	0 - 10 tonnes per annum	Full
1228350-17-1	812-877-4	2-Propenoic acid, 2-methyl-, 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl ester	0 - 10 tonnes per annum	Full
85631-54-5	288-003-5	2-Propenoic acid, γ-w-perfluoro-C8-14-alkyl esters	0 - 10 tonnes per annum	Full
19430-93-4	243-053-7	3,3,4,4,5,5,6,6,6-nonafluorohexene	100 - 1000 tonnes per annum	Full
647-42-7	211-477-1	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol	Intermediate Use Only	Intermediate
34451-26-8	628-448-8	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane-1-thiol	0 - 10 tonnes per annum	Full
27619-89-2	248-576-4	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanesulphonyl chloride	Intermediate Use Only	Intermediate

CAS_No	EC_No	Chemical_Name	Tonnage_Band	Registration_Type
96383-55-0	801-260-5	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-chloropropenoic acid ester	0 - 10 tonnes per annum	Full
17527-29-6	241-527-8	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate	100 - 1000 tonnes per annum	Full
2144-53-8	218-407-9	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate	100 - 1000 tonnes per annum	Full
1800-91-5	217-288-0	3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodeca-1,9-diene	0 - 10 tonnes per annum	Full
203929-12-8	941-221-0	3,3,4,4,5,5,6,6-octafluoro-6-iodohex-1-ene	Intermediate Use Only	Intermediate
297730-93-9	435-790-1	3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-(trifluoromethyl)-hexane	10+ tonnes per annum	Full
80806-68-4	670-981-3	4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononan-1-ol	Intermediate Use Only	Intermediate
36097-07-1	811-734-3	4-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfanyl]butane-1-thiol	0 - 10 tonnes per annum	Full
68391-08-2	269-927-8	Alcohols, C8-14, γ-ω-perfluoro	Intermediate Use Only	Intermediate
90622-71-2	292-474-2	Alkyl iodides, C6-18, perfluoro	Intermediate Use Only	Intermediate
85995-91-1	289-100-5	Alkyl iodides, C8-14, γ-ω-perfluoro	Intermediate Use Only	Intermediate
62037-80-3	700-242-3	ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate	10 - 100 tonnes per annum	Full
908020-52-0	700-323-3	ammonium difluoro[1,1,2,2-tetrafluoro-2-(pentafluoroethoxy)ethoxy]acetate	10 - 100 tonnes per annum	Full
52299-25-9	700-183-3	bis(nonafluorobutyl)phosphinic acid	0 - 10 tonnes per annum	Full
34455-29-3	252-046-8	Carboxymethyl-dimethyl-3-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulphonyl]amino]propyl]ammonium hydroxide	100 - 1000 tonnes per annum	Full
73609-36-6	277-551-0	Dichloromethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane	0 - 10 tonnes per annum	Full
73609-36-6	277-551-0	Dichloromethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane	Intermediate Use Only	Intermediate
220133-51-7	452-310-4	Dimethylphenylsulphonium 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanedisulphonate	Tonnage Data Confidential	NONS
307-35-7	206-200-6	Heptafluorooctanesulphonyl fluoride	Intermediate Use Only	Intermediate
161075-00-9	500-537-5	Hexafluoropropene, oxidized, oligomers, reduced, fluorinated	10 - 100 tonnes per annum	Full
19190-61-5	700-677-9	Methyl 2,2,3,3,4,4-hexafluoro-4-(trifluoroethoxy)butanoate	0 - 10 tonnes per annum	Full
958445-54-0	640-001-9	methyl 2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]propanoate	Intermediate Use Only	Intermediate
25628-08-4	700-536-1	N,N,N,-triethylethanaminium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate	0 - 10 tonnes per annum	Full
371771-07-2	609-338-9	N-(2-methylsulfinyl-1,1-dimethyl-ethyl)-N'-(2-methyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]phenyl)phthalamide	Intermediate Use Only	Intermediate
103055-07-8	410-690-9	N-[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoropropoxy)-phenyl-aminocarbonyl]-2,6-difluorobenzamide	Tonnage Data Confidential	NONS
34455-22-6	608-993-8	N-[3-(dimethylamino)propyl]-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octane-1-sulfonamide	Intermediate Use Only	Intermediate
76-19-7	200-941-9	Octafluoropropane	10 - 100 tonnes per annum	Full
1190931-27-1	682-238-0	Reaction mass of Ammonium difluoro{[(4S,5R)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate, Ammonium difluoro{[(4R,5S)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate, Ammonium difluoro{[(4S,5S)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate and Ammonium difluoro{[(4R,5R)2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate	10 - 100 tonnes per annum	Full
1190931-41-9	682-239-6	Reaction mass of difluoro{[(4S,5R)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetic acid, difluoro{[(4R,5S)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetic acid, difluoro{[(4S,5S)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetic acid and difluoro {[(4R,5R)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetic acid	Intermediate Use Only	Intermediate
1190931-39-5	682-240-1	Reaction mass of potassium difluoro{[(4S,5R)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate, potassium difluoro{[(4R,5S)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate, potassium difluoro{[(4S,5S)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate and potassium difluoro{[(4R,5R)-2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate	Intermediate Use Only	Intermediate
102061-82-5	422-100-7	sodium 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanedisulfinate	Tonnage Data Confidential	NONS
220689-12-3	444-440-5	tetrabutyl-phosphonium nonafluoro-butane-1-sulfonate	1+ tonnes per annum	Full
220689-12-3	444-440-5	tetrabutyl-phosphonium nonafluoro-butane-1-sulfonate	Tonnage Data Confidential	NONS
56773-42-3	260-375-3	Tetraethylammonium heptafluorooctanesulphonate	0 - 10 tonnes per annum	Full
26650-09-9	607-977-8	Thiocyanic acid, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester	Intermediate Use Only	Intermediate
1189052-95-6	700-812-1	tridecafluorooctyl-phosphonic acid sodium salt (1:1)	0 - 10 tonnes per annum	Full
101947-16-4	435-230-4	Triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptafluorodecyl)silane	Tonnage Data Confidential	NONS
1187-93-5	214-703-7	Trifluoro(trifluoromethoxy)ethylene	100 - 1000 tonnes per annum	Full
428-59-1	207-050-4	Trifluoro(trifluoromethyl)oxirane	100 - 1000 tonnes per annum	Full
332350-93-3	442-960-7	triphenyl(phenylmethyl)phosphonium 1,1,2,2,3,3,4,4,4-nonafluoro-N-methyl-1-butanedisulfonamide (1:1)	Tonnage Data Confidential	NONS
144317-44-2	478-340-8	Triphenylsulfoniumperfluoro-1-butanedisulfonate	Tonnage Data Confidential	NONS
338-83-0	206-420-2	Perfluamine	100 - 1000 tonnes per annum	Full
306-94-5	206-192-4	Perfluafene	0 - 10 tonnes per annum	Full

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PFOS – Evoluzione Classificazione

- Per 40 anni è valso il principio che l'assenza di dati significasse prodotto sicuro.
- Nei primi anni 90 gli studi ecotossicologici hanno evidenziato pesanti effetti sull'ambiente e sull'uomo.
-
- Direttiva 2006/122 porta a delle restrizioni per il PFOS.
- Regolamento 1907/2006 (Reach) sancisce che se non vi sono dati il prodotto non può essere commercializzato, ed il PFOS viene inserito nell'Allegato XVII (Reg.552/2009).
- Regolamento 757/2010, il PFOS viene classificato POP's (Inquinante organico persistente).
- Direttiva 2013/39/UE il PFOS viene considerato sostanza prioritaria per le acque.

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Oggi il PFOS secondo il Regolamento 1272/2008 CLP è classificato:

Harmonised classification - Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation)

General Information

Index Number	EC / List no.	CAS Number	International Chemical Identification
607-624-00-8	217-179-8	1763-23-1	perfluorooctane sulfonic acid heptadecafluorooctane-1-sulfonic acid

ATP Inserted / Updated: ATP01

CLP Classification (Table 3)

Classification		Labelling			Specific Concentration limits, M-Factors, Acute Toxicity Estimates (ATE)	Notes
Hazard Class and Category Code(s)	Hazard Statement Code(s)	Hazard Statement Code(s)	Supplementary Hazard Statement Code(s)	Pictograms, Signal Word Code(s)		
Acute Tox. 4 *	H302	H302		GHS09 GHS08 GHS07 Dgr		
Acute Tox. 4 *	H332	H332				
Carc. 2	H351	H351				
Lact.	H362	H362				
STOT RE 1	H372 **	H372 **				
Aquatic Chronic 2	H411	H411				
Repr. 1B	H360D ***	H360D ***				

Signal Words	Pictograms		
Danger			
	Environment	Health hazard	Exclamation mark

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POP's

Regolamento Commissione Ue 1342/2014/Ue

Inquinanti organici persistenti - Modifica degli allegati IV e V del regolamento 850/2004/Ce

Sostanza		Valore limite di concentrazione di cui all'articolo 7, paragrafo 4, lettera a)
PFOS	Acido perfluorottano sulfonato e suoi derivati (PFOS) (C ₈ F ₁₇ SO ₂ X) (X = OH, sale metallico (O-M ⁺), alogenuro, ammidi, e altri derivati compresi i polimeri)	50 mg/kg

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PFAS liberi e no

Come si può procedere per analizzare tutte le sostanze derivate, comprese quelle che non rientrano tra le specie direttamente regolamentate?

PFAS liberi e no

I Laboratori all'estero propongono l'analisi del TOP (Total Oxidizable Precursors)

Acque, terreni, sedimenti e biota sono trattate con persolfato e idrossido a caldo in modo da ottenere un'ossidazione che degrada i vari precursori polifluorurati per ottenere le molecole finali inerti quali PFOA e PFOS.

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PFAS liberi e no

PROPOSTA:

Digestione mediante ossidazione
con una miscela di perossidisolfato, acido borico e idrossido di sodio.
(come APAT CNR IRSA 4060)

In particolare è stata provata su campioni di percolato.

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- HPLC-MS/MS :
- metodo consolidato HPLC con SPE (accessibile con investimento contenuto)
- Il campione, prelevato in bottiglia di polipropilene e già stabilizzato al momento del campionamento con l'aggiunta di 1 grammo di reattivo Trizma[®] in modo da fornire una concentrazione di quest'ultimo pari a 5 g/l, viene filtrato se necessario, trasferito nella vial e quindi pre-concentrato come previsto da metodo EPA 537, mediante colonna SPE online direttamente collegata all'autocampionatore.
- Terminata la fase di estrazione gli analiti sono automaticamente iniettati nel LC/MS/MS tramite la valvola a sei vie.
- I campioni vengono processati come da paragrafo 11.7 del metodo EPA 537 Rev. 1.1 September 2009 – Determination of selected Perfluorinated Alkyl Acids in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS).
- L'analisi dei dati e i calcoli vengono eseguiti come esposto nel paragrafo 12 del metodo EPA 537 Rev. 1.1 September 2009 –

