INSTITUTE OF
CHEMICAL TECHNOLOGY
PRAGUE

PFCs INTRODUCTION:
PRIORITIES AND STRATEGIES

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ORGANIC CONTAMINANTS

- Organohalogen contaminants
  - PCBs
  - OCPs
  - PCDDs/Fs
  - BFRs
  - **Perfluorinated compounds (PFCs)**
- Polycyclic aromatic hydrocarbons (PAHs)
- Pesticides
- „Musk“ compounds
- Phthalates
- Alkylphenols

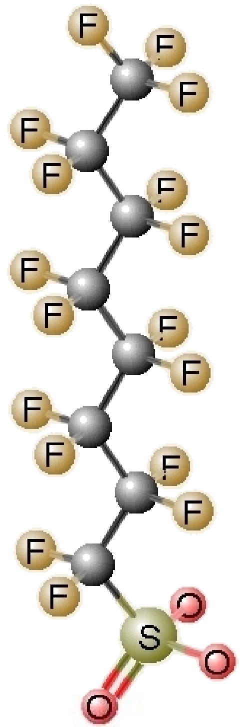
HISTORY OF THE DISCOVERY OF PFOS IN BIOTA

- 1968: Organofluorine reported in blood
- 1970s and 1980s: Monitoring studies of organofluorine
- 1976: PFOA tentatively identified
- 1990s: LC-MS/MS methodology developed
- 1997–1998: Widespread PFOS confirmed
- 2000: 3M announces phase out of production
- Present: Continued biomonitoring efforts

Perfluorooctyl sulfonates (PFOS): persistent manmade chemicals used extensively since the 1950's in protective coatings and surfactants.

PFCs CHARACTERISTICS

- A class of organofluorine compounds that have all hydrogens replaced by fluorine on a carbon chain – but also contain at least one different atom or functional group
- Usually 4 – 20 carbon atoms in the molecule
- The most abundant C8 compounds (derived from n-octane)



PERFLUORINATED CHEMICALS (PFCS)

- Applications:
  - Stain repellants, packaging materials, industrial surfactants, fire-fighting foams, etc.

Persistent, bioaccumulative, toxic

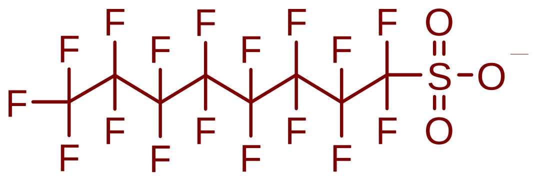
MAIN GROUPS OF PFCs

	Functional group	Example
Perfluorocarboxylic acids	$-COO^-$	Perfluorooctanoic acid (PFOA)
Perfluorosulphonates	$-SO_3^-$	Perfluorooctanesulfonic acid (PFOS)
Perfluorosulfonamides	$-SO_2NH_2$	Perfluorooctanesulfonamide (FOSA)
Telomeric alcohols	-OH	1H,1H,2H,2H-Perfluorodecanol (8:2 FTOH)

UBIQUITOUS PFCs

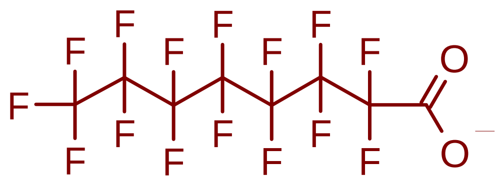
- In addition to industrial production, PFOS and PFOA can be formed by a degradation of fluorinated precursors

PFOS = perfluorooctanesulfonic acid



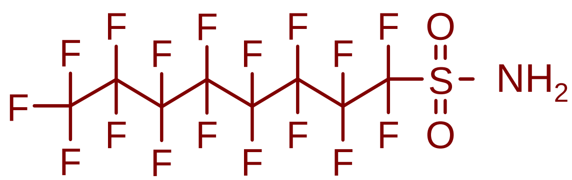
M_R 499 g/mol

PFOA = perfluorooctanoic acid



M_R 414 g/mol

FOSA = perfluorooctanesulfonamide

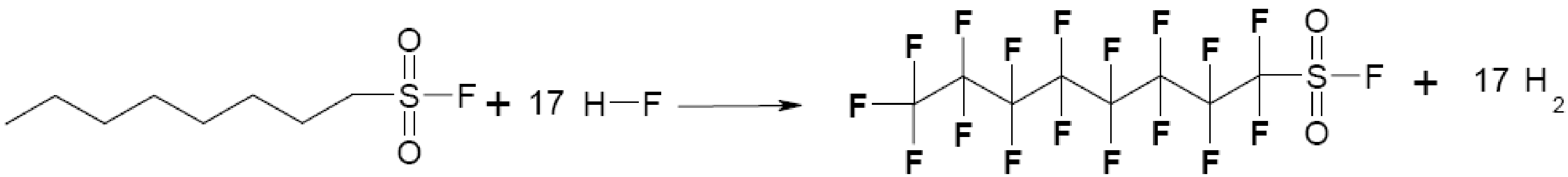


M_R 498 g/mol

PFCs SYNTHESIS

Electrochemical fluorination (ECF)

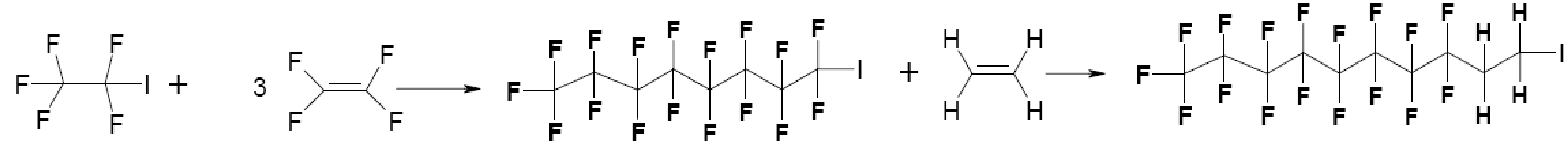
- The synthesis of PFOS uses perfluorooctanesulfonyl fluoride (POSF) as feedstock



1-Octane sulfonyl fluoride — Perfluoro-1-Octane sulfonyl fluoride (POSF)

Telomerization

- This production process yields straight chains, with hardly any impurities, but the products are not fully perfluorinated. The ethylene group is characteristic for this production process.

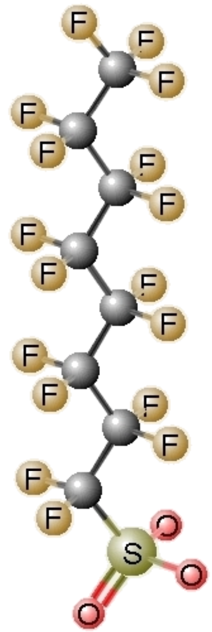


Iodopentafluorethane — Tetrafluoroethylene — Perfluorooctyl iodide — Ethylene — 1H,1H,2H,2H-Perfluorodecyl Iodide

GENERAL PROPERTIES OF PFOS

$\overset{\delta+}{C}$ — $\overset{\delta-}{F}$

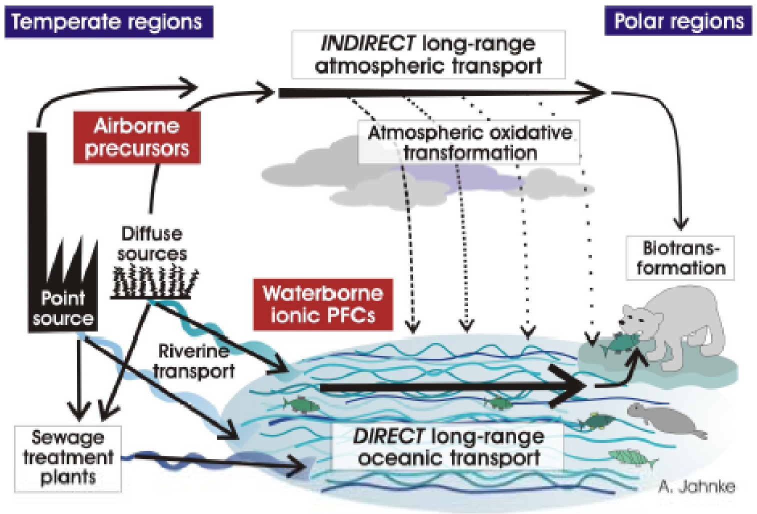
- Specific physico-chemical properties
  - Acidic
  - Rigid
  - Low solubility in water and in oil/fat
  - Low vapour pressure but sublimation
  - Ion-pair formation
  - Non-reactive



- Resistant to degradation by natural processes such as metabolism, hydrolysis, photolysis, or biodegradation making it persistent indefinitely in the environment

PFCs IN THE ENVIRONMENT

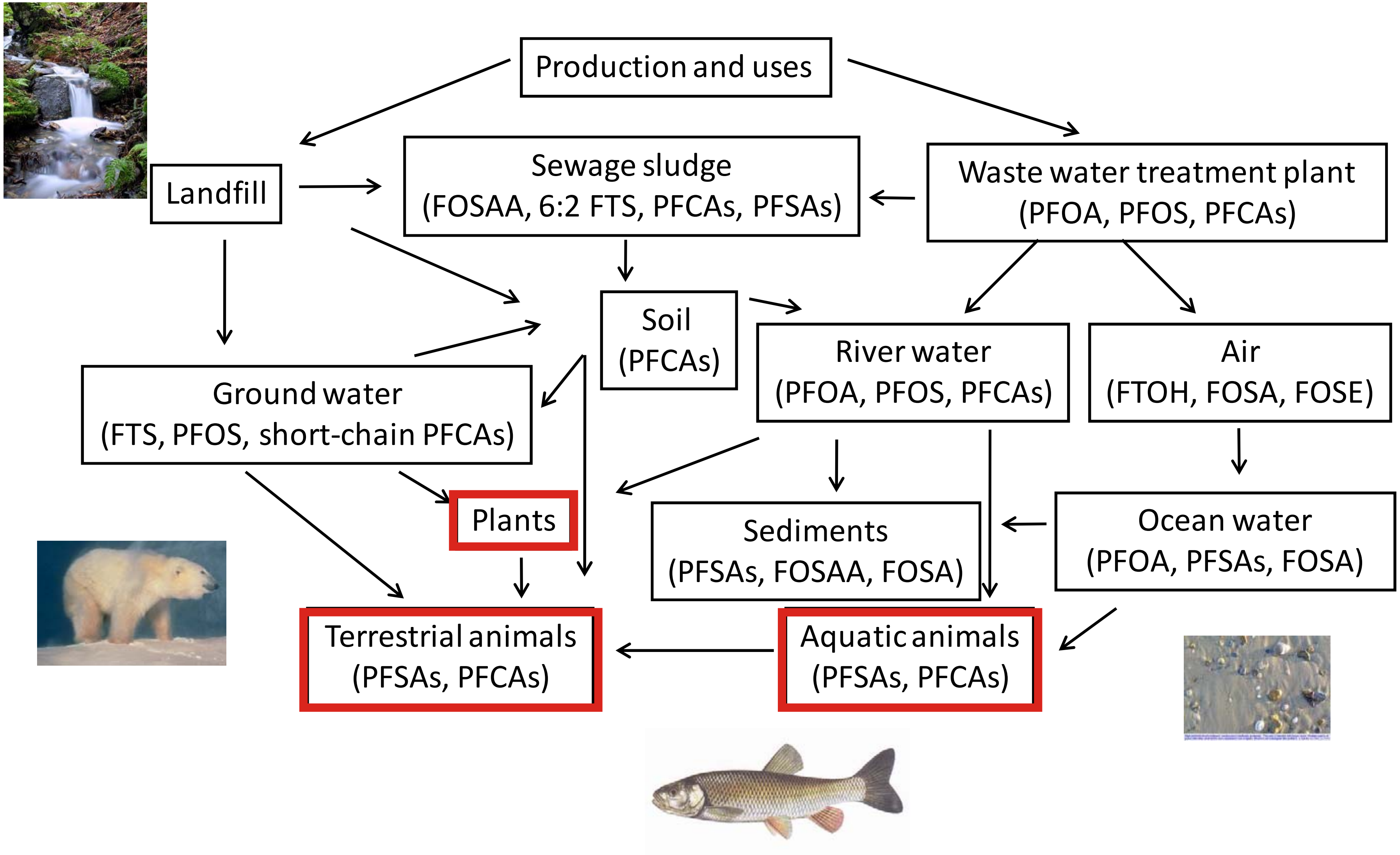
- Can release into the environment:
  - Directly from industrial sites
  - Waste dumps
  - Fire service practicing areas
  - Waste water treatment plants



Fate in the environment

- Adsorption onto sediments
- Air or ocean stream long distance transfer of volatile PFCs
- Partial degradation

PFCs OCCURENCE - IN DIFFERENT PARTS OF THE ENVIRONMENT



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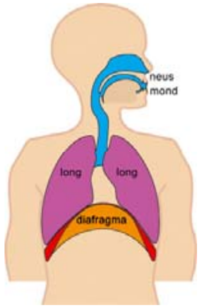
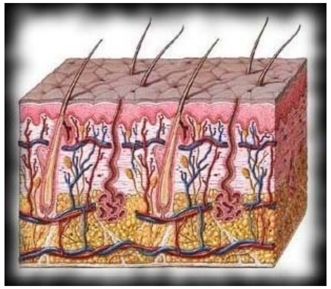
TOXICITY OF PFCs

- Human exposure by different ways – diet, dermal and inhalation



- Only limited data about toxity are available
- PFCs are especially toxic to developing fetuses and newborns.
- The developmental neurotoxic effects of PFCs are similar to those reported for PCBs and PBDEs.
- PFCS are endocrine disruptors and cause immune system damage

MONITORING AND RESTRICTIONS OF PFCs

- **2002** – 3M Company, the major PFOS producer phased out PFOS and some of its derivatives
- **2006** – EU has banned most uses of PFOS and related compounds from summer 2008 (*EU directive 2006/122/EG, 2008*)
- **2007** – EFSA recommended monitoring of PFCs (PFOS and PFOA) in the food chain
- **2008** – EFSA established the tolerable daily intake (TDI)

  PFOS - 150 µg/kg b.w.

  PFOA - 1.5 µg/kg b.w.
- **2009** – The 9 new POPs including PFOS and its salt, under the Stockholm Convention

efsa
European Food Safety Authority

Summary of opinion

Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts

Scientific Opinion of the Panel on Contaminants in the Food chain[1]

(Question N° EFSA-Q-2004-163)

Adopted on 21 February 2008

High exposure to PFOS and PFOA can have a harmful impact on health and can damage the liver, cause developmental and possibly reproductive problems. Certain laboratory experiments on rats have indicated some potential to promote cancer but it is not clear if these results have implications for human health.

Whilst a lack of consistent data precluded from the Panel from making a comprehensive risk assessment, experts considered there to be sufficient scientific data to establish a TDI for both PFOS and PFOA. For PFOS, the Panel established a TDI of 150 nanograms per kilogram of body weight per day and for PFOA 1.5 micrograms (1,500 nanograms) per kilogram of body weight per day.

The Panel concluded that the general population in Europe is unlikely to suffer negative health effects from PFOS and PFOA as the dietary exposure to these chemicals is below their respective TDIs, but noted that high consumers of fish might slightly exceed the TDI for PFOS. The Panel called for further research and data collection on PFOS/PFOA presence in foods and feeding stuffs in order to assess their relative contribution to human dietary exposure. Data on PFOS, PFOA and other perfluoroalkylated substances (PFAS) is needed, particularly in order to monitor exposure trends.

EFSA has published several opinions covering other environmental pollutants found in food, namely methyl mercury , dioxins, dioxin-like PCBs and non-dioxin like PCBs .

See also the scientific opinion on Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts

CURRENT EC RECOMMENDATION

L 68/22 EN Official Journal of the European Union 18.3.2010

RECOMMENDATIONS

COMMISSION RECOMMENDATION

of 17 March 2010

on the monitoring of perfluoroalkylated substances in food

(Text with EEA relevance)

(2010/161/EU)

. It is recommended that the Member States carry out the analysis of perfluoroalkylated substances in order to detect the presence of the compounds PFOS and PFOA and, if possible, their precursors such as perfluorooctane sulphonamide (PFOSA), N-ethyl perfluorooctane sulfonamidoethanol (NEtFOSE) and 8:2 fluorotelomer alcohol. The Member States should, if possible, include compounds similar to PFOS and PFOA but with different chain length (C4 – C15) and polyfluoroalkyl phosphate surfactants (PAPS) such as 8:2 diPAPS and 8:2 monoPAPS in order to estimate the relevance of their presence in food.

4. Member States should carry out the analysis of perfluoroalkylated substances in accordance with Annex III to Regulation (EC) No 882/2004 of the European Parliament and of the Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules (1) by making use of a method of analysis that has been proven to generate reliable results. Ideally, the recovery rates should be in the 70-120 % range with limits of quantitation of 1 µg/kg.

5. It is recommended that the Member States provide on a regular basis to the EFSA the monitoring data expressed on whole weight basis with the information and in the

NEW POPs

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Stockholm Convention on persistent organic pollutants (POPs)

CONVENTION | PROGRAMMES | COUNTRIES | SECRETARIAT | PARTNERS

May 2009

New POPs

- Overview
- Decisions & Recommendations
- The 9 new POPs
- Training workshops
- Publications

COP4 Follow-up

- Information request (decision SC-4/19)

Submissions

- New POPs information (decision SC-4/19)

Programmes › New POPs › The 9 new POPs

The 9 new POPs under the Stockholm Convention

At its fourth meeting held from 4 to 8 May 2009, the Conference of the Parties (COP), by decisions SC-4/10 to SC-4/18, adopted amendments to Annexes A (elimination), B (restriction) and C (unintentional production) of the Stockholm Convention to list nine chemicals as persistent organic pollutants:

Click on the ⊞ sign for more information about the chemical

- Chlordecone
- Hexabromobiphenyl
- Hexabromodiphenyl ether and heptabromodiphenyl ether
- Alpha hexachlorocyclohexane
- Beta hexachlorocyclohexane
- Lindane
- Pentachlorobenzene (PeCB)
- Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F)
- Tetrabromodiphenyl ether and pentabromodiphenyl ether

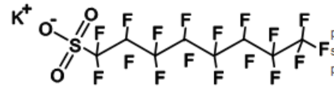
MOVE CLOSE

Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F)

Listed under Annex B with acceptable purposes and specific exemptions (decision SC-4/17)

Chemical identity and properties

PFOS is a fully fluorinated anion, which is commonly used as a salt or incorporated into larger polymers. PFOS and its closely related compounds, which may contain PFOS impurities or substances that can result in PFOS, are members of the large family of perfluoroalkyl sulfonate substances.



perfluorooctane sulfonic acid (CAS No: 1763-23-1) and its salts
perfluorooctane sulfonyl fluoride (CAS No: 307-35-7)

Use and production

PFOS is both intentionally produced and an unintended degradation product of related anthropogenic chemicals. The current intentional use of PFOS is widespread and includes: electric and electronic parts, fire fighting foam, photo imaging, hydraulic fluids and textiles. PFOS is still produced in several countries.

POPs characteristics of PFOS

PFOS is extremely persistent and has substantial bioaccumulating and biomagnifying properties, although it does not follow the classic pattern of other POPs by partitioning into fatty tissues but instead binds to proteins in the blood and the liver. It has a capacity to undergo long-range transport and also fulfills the toxicity criteria of the Stockholm Convention.

Replacement of PFOS

While alternatives to PFOS are available for some applications, this is not always the case in developing countries where existing alternatives may need to be phased in. For some applications like photo imaging, semi-conductor or aviation hydraulic fluids, technically feasible alternatives to PFOS are not available to date.

List of acceptable purposes and specific exemptions for production and use of PFOS, its salts and PFOS-F

EU DIRECTIVE 2006/122

L 372/32 | EN | Official Journal of the European Union | 27.12.2006

DIRECTIVE 2006/122/ECOF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 12 December 2006

amending for the 30th time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulfonates)

(Text with EEA relevance)

L 372/34 | EN | Official Journal of the European Union | 27.12.2006

ANNEX

The following point is added to Annex I to Directive 76/769/EEC:

'52. Perfluorooctane sulfonates (PFOS) $C_8F_{17}SO_2X$ (X = OH, Metal salt (O-M+), halide, amide, and other derivatives including polymers)	(1) May not be placed on the market or used as a substance or constituent of preparations in a concentration equal to or higher than 0,005 % by mass. (2) May not be placed on the market in semi-finished products or articles, or parts thereof, if the concentration of PFOS is equal to or higher than 0,1 % by mass calculated with reference to the mass of structurally or microstructurally distinct parts that contain PFOS or, for textiles or other coated materials, if the amount of PFOS is equal to or higher than 1 μg/m² of the coated material. (3) By way of derogation, paragraphs 1 and 2 shall not apply to the following items, nor to substances and preparations needed to

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