# Perfluoroalkylated acids and related compounds (PFAS) in the Swedish environment

Chemistry
Sources
Exposure

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# Preface

This report summarizes the results of several investigations conducted in Sweden during the years 2002-2005 concerning perfluoroalkylated substances (PFAS). The projects were mainly funded by the Swedish Environmental Protection Agency (S-EPA) within the environmental monitoring programs but for this compilation results from other investigations have also been included to provide a more complete overview of the present situation regarding the use of and pollution status for PFAS in Sweden. These investigations were funded by the Swedish Rescue Services Agency, the Regional County of Västra Götaland, Svenskt Vatten (VA-forsk grant nr.23:101 ) and the Nordic Council. This report also contains a compilation of literature data and information gathered from representatives of Swedish companies, authorities, and organisations. Patent information has been included and referenced in order to provide a more general picture of highly fluorinated organic compounds. It should be stressed however, that patent descriptions relate to the potential use and do not necessarily reflect the actual use. A list of information sources is given at the end of the report. The beginning of the report provides an outline of fluorinated organic compounds in general and is intended to provide a basis for the following detailed descriptions of the perfluoroalkyl substances (PFAS) that where selected by the S-EPA and Swedish Chemicals Inspectorate (KemI) for initial screening in the Swedish urban environment. The statements given in the report are the authors' solely and do not necessarily reflect the opinion of any of the governmental agencies supporting this work.

# Abstract

The perfluoroalkylated substances have gained increased attention among scientists and regulators during the last few years. In particular, perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and similar perfluorinated alkylated acids are regarded as the most stable end products of various perfluoroalkylated substances and have been shown to be extremely stable, bioconcentrate and biomagnify and have several toxicological effects. The industrial chemistry of perfluoroalkylated substances is extremely diverse and includes almost all chemical functionalities from simple pure alkanes to complex co-polymers. Major usage of perfluoroalkylated products is related to polymeric compounds and the dominant release to the environment is from primary and secondary production plants which are lacking in the Nordic countries. The occurrence of elevated concentrations of perfluoroalkylated acids in Sweden is strongly related to urbanized areas and the most likely path into the aquatic environment is through sewage water, although atmospheric input is also possible via more volatile precursor compounds. Up to 40 times elevated concentrations were found in biota from urban areas compared to unpolluted areas. Lake Mälaren and lower parts of the river Helge å are examples of aqueous environments clearly contaminated by PFOS. One of several potential point sources in Sweden has been screened for PFOS. A firefighting training site was found to release PFOS to the local aqueous environment (wetland) where µg/l concentrations where found.

Long chain (more than 8 C for sulfonates and 10 C or more for carboxylates) perfluoroalkylated acids are readily taken up by biota in aqueous environments and reach very high concentrations in predators at high trophic levels of aquatic food webs. Baltic guillemot egg showed an increasing trend in PFOS concentration from 20-30 ng/g by the end of sixties to more than 600 ng/g at present. Freshwater otter from various locations in Sweden showed concentrations similar to guillemot eggs and Baltic grey seal has extreme values up to ten times higher (21 µg/g sum of all acids 6-14 C, PFOS alone:11µg/g).

Human exposure, as described by Swedish human blood levels, appears to be similar to most other countries. No extreme values were encountered which would indicate occupational exposure. An excessive consumption of freshwater fish may contribute to an increased exposure, but this could not be clearly verified. Occupational settings where exposure to precursor compounds can take place are present in Sweden and should be included in future studies.

Industrial use of textile and leather impregnating formulations result in elevated concentrations of perfluorocarboylates in effluent water from sewage treatment plants. The relation between effluent and biota concentrations for an aquatic environment with this type of activity needs to be further described in particular for perfluoroalkyl carboxylates which are currently being discharged in Sweden.

Exposure routes and distribution behavior are yet not completely described for many PFAS, in particular their precursors. Environmental levels, human levels and human exposure data are lacking for a wide variety of PFAS discussed in this report

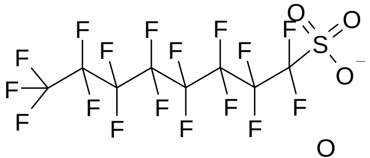
## Abbreviations

| | |
|---|---|
| DEA | Diethanolamine |
| ECF | Electrochemical fluorination |
| EtFOSA | N-ethylperfluorooctanesulfonamide |
| FOSE | Perfluorooctane sulfonamidoethanol |
| N-Et-FOSE | 2-(N-ethylperfluorooctanesulfonamido)-ethyl alcohol |
| N-Me-FOSE | 2-(N-methylperfluorooctanesulfonamido)-ethyl alcohol |
| N-MeFOSEA | N-methylperfluorooctanesulfonamidoethyl acrylate |
| PFAS | Perfluoroalkylated substances |
| PFCA | Perfluorocarboxylic acids |
| PFSA | Perfluoroalkyl sulfonates |
| MeFOSA | N-methylperfluorooctanesulfonamide |
| N-MeFOSE alcohol | N-methylperfluorooctane sulfonamidoetanol |
| PFHxA | Perfluorohexanoic acid |
| PFHpA | Perfluoroheptanoic acid |
| PFOA | Perfluorooctanoic acid |
| PFNA | Perfluorononanoic acid |
| PFDA | Perfluorodecanoic acid |
| PFUnA | Perfluoroundecanoic acid |
| PFDoA | Perfluorododecanoic acid |
| PFTDA | Perfluorotetradecanoic acid |
| PFBS | Perfluorobutanesulfonate anion |
| PFHS | Perfluorohexane sulfonate anion |
| PFOS | Perfluorooctane sulfonate anion |
| PFOSA | Perfluorooctane sulfonamide |
| PFDS | Perfluorodecane sulfonate anion |
| POSF | Perfluorooctanesulfonyl fluoride |
| Sulfuramide | N-ethylperfluorooctanesulfonamide |
| THPFOS | 1H,1H,2H,2H-perfluorooctane sulfonate |
| TBA | Tetrabutylammonium |

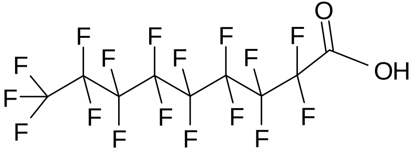
## Perfluoroalkylated substances: chemical names and structures

Name / Abbrevation /Chemical formula Structure

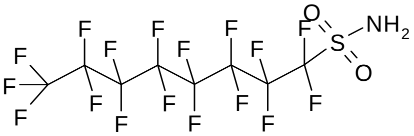
Perfluorooctane sulfonate anion / PFOS/
$C_8F_{17}SO_3^-$



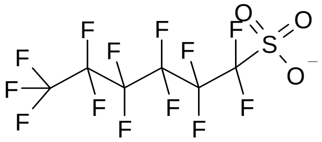
Perfluoroctanoic acid / PFOA/
$C_7F_{15}CO_2H$



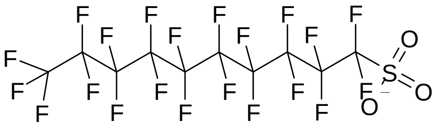
Perfluorooctane sulfonamide / (P)FOSA/
$C_8F_{17}SO_2NH_2$



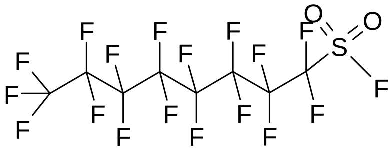
Perfluorohexane sulfonate anion / PFHxA/
$C_6F_{13}SO_3^-$



Perfluorodecane sulfonate anion / PFDS/
$C_{10}F_{21}SO_3^-$



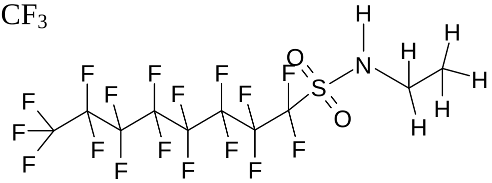
Perfluorooctanesulfonyl fluoride / PFOSF/
$C_8F_{17}SO_2F$



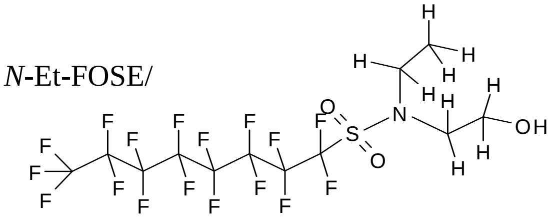
Polytetrafluoroethylene/ PTFE / $(CF_2{=}CF_2)_n$

Perfluoropolyether / PFO/ $F(CF(CF_3)CF_2O)n\text{-}CF_2CF_3$

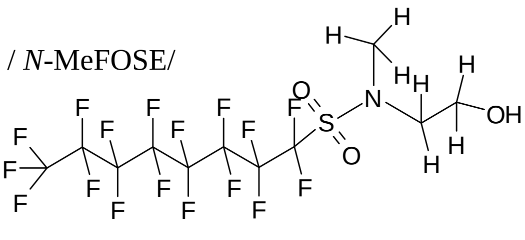
*N*-Ethyl-perfluorooctansulfonamid / *N*-Et-FOSA/
$C_8F_{17}SO_2NHC_2H_5$



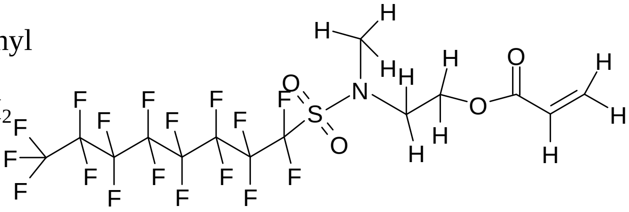
*N*-Ethyl-perfluorooctansulfonamidoethanol / *N*-Et-FOSE/
$C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OH$



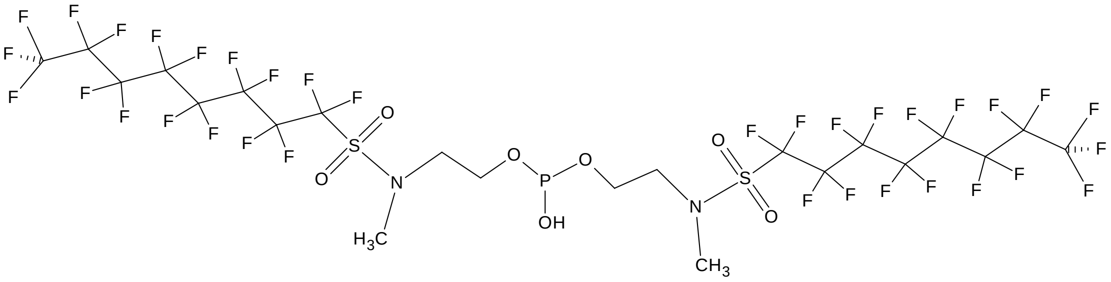
*N*-Methyl-perfluorooctansulfonamidoethanol / *N*-MeFOSE/
$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$



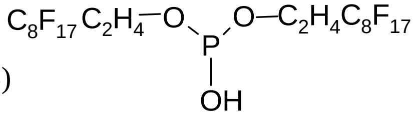
*N*-metylperfluorooctane sulfonamidoethyl
Acrylate/ N-MeFOSEA
$C_8F_{17}SO_2N(CH_3)CH_2CH_2OCOCH{=}CH_2$



MeFOSE alcohol phosphate ester

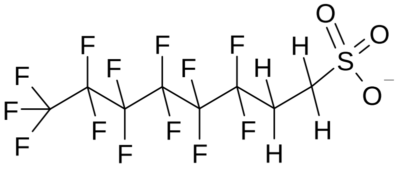


EtFOSE alcohol phosphate ester/
8:2 Telomer alcohol phosphate ester
("telomer"  refers to synthesis method, see section 1:3)

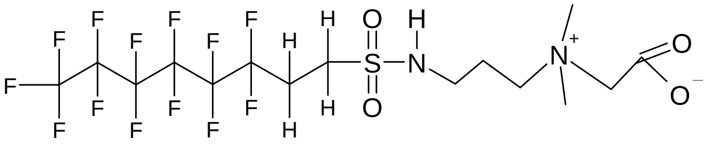


$$C_8F_{17}C_2H_4{-}O{-}\underset{\displaystyle OH}{\underset{|}{P}}{-}O{-}C_2H_4C_8F_{17}$$

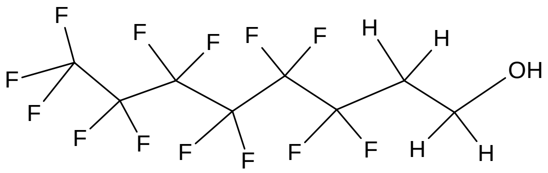
1H,1H,2H,2H-tetrahydroperfluorooctanesulfonate/
6:2 telomer sulfonate, $C_8H_4F_{13}SO_3^-$



1H,1H,2H,2H-tetrahydroperfluorooctylbetaine
(amphoteric)



6:2 telomer alcohol/ 6:2 FTOH



# Contents

## 1. Introduction to highly fluorinated organic compounds

Fluorinated organic compounds are chemicals where one or more hydrogen atoms bound to the carbon atoms have been exchanged with fluorine atoms. The carbon-fluorine bond is one of the strongest known chemical bonds. It gives fluorinated organic compounds, and particularly fully fluorinated compounds, superior thermal, chemical and biological stability. The small size of the fluorine atom is generally considered to contribute to a “shielding effect“, protecting the carbon atom from being attacked.

The stability of the fluoroorganic compounds is of great importance to many industrial and domestic applications but unfortunately also implies that several fluoroorganic compounds have a high potential for persistence in the environment. Their excellent properties in turn imply that the number of synthesized fluoroorganic compounds reported by far exceeds the number of chlorinated analogs.

The simplest fully fluorinated or *perfluorinated* organic compound, tetrafluoromethane, was described in 1886. The industrial expansion of fluorocarbon chemistry took place in the 1940:ies (Emeléus, 1969). The total number of described synthetic fluoroorganic compounds can be estimated from the literature and exceeds 10000. These substances cover a wide variety of applications including bulk chemicals used as intermediates as well as pharmaceutical, industrial and consumer products containing fluororganic monomeric compounds and polymers.

The actual number of fluororganic compounds in production can be estimated from the chemical suppliers lists to be less than one thousand, many of which are fine chemicals, whence very likely produced at low production volumes.

Table 1 exemplifies some highly fluorinated chemicals (mainly perfluoroalkylated) and their application fields, from the simplest representative, tetrafluoromethane, to the fluoropolymers. A common opinion encountered in discussions with production representatives is that fluorinated chemicals are relatively expensive, a fact that has possibly contributed to keeping production volumes down.

The production facilities of fluoroorganic compounds are globally distributed, and apart from the USA, Japan and possibly also Russia, Brazil, India and China, production facilities are also found in Europe in Germany, Poland, Great Britain, Italy, France, the Netherlands and Belgium (possibly Slovakia). At present, no known production exists in Sweden with the possible exception of pilot scale plants.

Small scale fluoroorganic synthesis can be performed either by gas phase fluorination or through the use of metal fluorides ($CoF_3$). Industrial fluorination is mainly accomplished through three routes; electrochemical fluorination (patented by 3M), telomerization (patented by Du Pont De Nemour, $CF_3I$ or $C_2F_5I$ and tetrafluoroethylene, produces odd and even number of carbon respectively) or oligomerization of tetrafluorethylene (patented by ICI, produces highly branched oligomers).

In Table 2 all producers and suppliers of fluorinated chemicals and fluorocarbon polymers that were encountered through literature and web searches are presented together with their respective trade names (Banks, 1979; OECD, 2002; Canada Gazette, 2000; web sites). Some producers of low fluorinated chemicals, e.g.

trifluoromethylated pharmaceuticals, have been omitted. Some of the listed companies may be formulating or supplying products originally manufactured by another company.

**Table 1.** Examples of perfluorinated chemicals listed in manufacturers and suppliers catalogs

| *Chemical* | *CAS-number* | *Usage* | *Acronym/Trade name* |
|---|---|---|---|
| Tetrafluoromethane | | refrigerant | R14 |
| Perfluoropentane | | Cleaning agent electronics, refrigerant | |
| Perfluorohexane | 355-42-0 | | Flutec PP1,Perflutel |
| Perfluoroheptane | 355-57-9 | | |
| Perfluorooctane | 307-34-6 | Medical; ophthalmologi, solvent fluoropolymer production | |
| Tetrafluoroethylen | | Monomer fluoropolymer production | TFE |
| Perfluoro-n-butylene | | | |
| Hexafluoropropylene | | Monomer fluoropolymer production | HFP, |
| Perfluoro-iso-butylene | | Intermediate fluoropolymer production, toxic! | PFIB |
| Perfluorocyclobutane | | Propellant | PC-318 |
| Perfluorohexadiene | | Monomer fluoropolymer production | |
| Hexafluorobenzene | | Solvent fluoropolymer production, process chemical | |
| Perfluoro-n-butyl-tetrahydrofurane | | Solvent fluoropolymer production | FC-75 |
| Perfluormethylcyclohexane | | Solvent l fluoropolymer production | Flutec PP2 |
| Perfluorodecaline | | Solvent fluoropolymer production, blood extenders (substitutes), cosmetics | FlutecPC6 |
| Perfluoromethyldecaline | | | FlutecPP9 |
| Perfluoroallylvinyl ether | | Solvent fluoropolymer production | |
| Perfluorometylvinyl ether | | Solvent fluoropolymer production | Kalrez |
| Perfluoropropylvinyl ether | | Solvent fluoropolymer production | PPVE |
| Perfluorobutylvinyl ether | | Solvent fluoropolymer production | |
| Perfluoroalkyl iodide, C1-C3 | | Process chemical,fluorination telomerisation | |
| Perfluorohexyl iodide | 355-43-1 | Process chemical,fluorination, photo etching electronics | |
| trifluoroethanol | | Solvent, fluorination | |
| nonafluoorhexanol | 2043-47-2 | Polyurethane production | |

| *Chemical* | *CAS-number* | *Usage* | *Acronym/Trade name* |
|---|---|---|---|
| tridecafluorooctanol | 647-42-7 | Polyurethane production | |
| Perfluoroalkyl sulfonamide-diol | | Polyurethane production | |
| C8f17so2n(ch2ch2oh)2 | | Polyurethane production, medical implants | |
| 2-Perfluoroalkyl ethanol (C6-C12) | | Surfactant production | |
| 2-(perfluoro-n-butyl) ethanol | | | |
| 2-(perfluoro-n-hexyl) ethanol | | | |
| Hexafluoroacetone | | Polyurethane production, fouling-release coating for small boats | HFA |
| Tri-perfluoroalkyl citrate | | | |
| 2-perfluoroalkylethyl stearate | | | |
| Ethyl-perfluoroglutarate | 424-40-8 | | |
| Ethyl-perfluorooctanoate | 3108-24-5 | | |
| bis[2-(perfluoroalkyl)ethyl] fosfat, NH4-salt | | | |
| 3-[2-(perfluoroalkyl)etylthio]propionate litium-salt | 65530-69-0 | | |
| 2-(perfluoroalkyl)ethyl methacrylate | 65530-66-7 | Surface treatment, textile, paper, leather, monomer fluoroacrylate polymerisation | |
| Pentafluoropyridine | | Process chemical | |
| Perfluoro(alkyl amine) | | Solvent  fluoropolymer production | FC-40 |
| Perfluoroalkylpolyamine | 135374-25-3 | | |
| Perfluorotriethylamine | 359-70-6 | | |
| Perfluorotributylamine | | Foam blowing agent, Calibrant Mass Spectrometry | PFTBA, FC-43 |
| Perfluoroalkylpolyamide | 147923-39-5 | | |
| Perfluorohexamethylen-bis-(dimetylsilane) | 40347-22-6 | | |
| Perfluorohexamethylen-bis-(trimetylsilane) | 23717-17-1 | | |
| methyltrifluoropropylsiloxane | | Monomer fluorosilicone polymer production | |

| *Chemical* | *CAS-number* | *Usage* | *Acronym/Trade name* |
|---|---|---|---|
| Polyfluoroalkylbetaine | 6525-646-4 | Surfactant | |
| Acids and salts: | | | |
| Trifluoro acetic acid | | Process chemical, fluorination | TFA |
| Perfluorocarboxylic acids C7-C13 | 68333-92-6 | | |
| Perfluorobutanoic acid | 3375-22-4 75-22-4 | | PFBA |
| Perfluoropentanoic acid | | | PFPA |
| Perfluorohexanoic acid | 307-24-4 | | PFHxA |
| Perfluoroheptanoic acid | 375-85-9 | | PFHpA |
| Perfluoroctanoic acid | 335-67-1 | Surfactant, emulsifying agent in production of fluoropolymer (TFE-HFP co-polymer) | PFOA, RM 258; FC26 |
| Perfluorononanoic acid | 375-95-1 | | PFNA |
| Perfluorodecanoic acid | 335-76-1 | | PFDA |
| Perfluoroundecanoic acid | 2058-94-8 | | PFUnA |
| Perfluorododecanoic acid | 307-55-1 | | PFDoA |
| Perfluorotetradecanoic acid | 376-06-7 | | PFTDA |
| Perfluorooctadecanoic acid | | | |
| Perfluorodecanoic-diacid | 307-78-8 | | |
| Perfluorooctanoic-diacid | 678-45-5 | | |
| Perfluoroalkylsulfonates, C6-C12, K-salt | 68391-09-3 | | |
| Trifluoromethane sulfonate, triflic acid | | Process chemical, catalyst | |
| Perfluorobutane sulfonate, K-salt | 29420-49-3 | | PFBS, RM 65 |
| Perfluoropentane sulfonate, K-salt | 3872-25-1 | | PFPS |
| Perfluorohexane sulfonate, K-salt | 3871-99-6 | | PFHxS |
| Perfluorocyclohexane sulfonate, K-salt | 3107-18-4 | Hydraulic fluid | |
| Perfluoro-4-ethylcyclohexane sulfonate K | 335-24-0 | | RM 98 |
| Perfluoroheptane sulfonate,K-salt | 60270-55-5 | | PFHpS |
| Perfluorooctane sulfonate, K-salt | 2795-39-3 | | PFOS, RM 95; FC-95 |
| Perfluorononane sulfonate, K-salt | 17202-41-4 | | PFNS |
| Perfluorodecane sulfonate ,NH4-salt | 67906-42-7 | Surfactant | PFDS |

| *Chemical* | *CAS-number* | *Usage* | *Acronym/Trade name* |
|---|---|---|---|
| Perfluorobutansulfonylfluoride | 375-72-4 | Process chemical, intermediate | RM 60 |
| Perfluorohexane sulfonylfluoride | 423-50-73 | Process chemical, intermediate | RM 70 |
| Perfluorooctane sulfonyl fluoride | 307-35-7 | Process chemical, intermediate | PFOSF, RM 90 |
| N-methyl-perfluorooctane sulfonamide | 31506-32-8 | | N-methylFOSA |
| N-ethyl-perfluorooctane sulfonamidoethanol | | | N-ethyl FOSE, FC10 |
| N-ethyl-perfluorooctane sulfonamide, sulfluramid | 4151-50-2 | Insecticide | RM 505, GX-071 |
| Tefluthrin | | Insecticide | |
| Fluorinated paraffins | 338-39 | | F65 A137 |
| Perfluorinated paraffins | 355-49-7 | | RM 270/RM 280/RM 290 |
| Perfluorokerosene | | Calibrant, Mass Spectrometry | PFK |
| Perfluoropolyether, PFPE | | Lubricant, oil, fat, cosmetics | Fomblin, Denum, Krytox |
| Polymeric substances: | | | |
| Polyfluoroacrylates | | Textile&leather finishes, protective coatings (electronics), hard contact lenses, cosmetics | |
| polyfluorourethanes | | Finishes for textile, leather, carpets, medical products | |
| Polytetrafluorethylene | | | PTFE; Teflon |
| Polytetrafluoroethylene-hexapropylene | | | FEP |
| Polytetrafluoroethylene-perfluorovinylether | | | PFA |
| Polyvinylidenfluoride | | | PVDF |

**Table 2.** Primary and secondary producers of fluorochemicals and fluoropolymers**.**

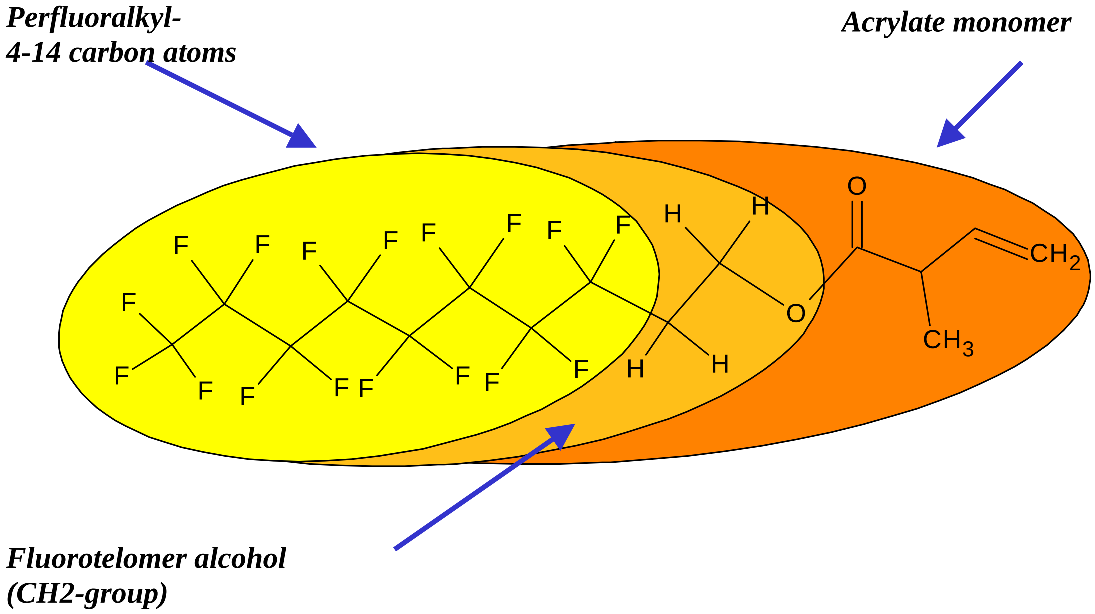
| *Producer/Location* | *Product categories* | *Trade names* |
|---|---|---|
| Minnesota Mining and Manufacturing company, 3M, USA, Belgium, Japan | Fluorochemicals, polymers | Scotchguard, Scotchban Fluorinert FC-series, Zero-mist |
| DuPont De Nemours, USA | Fluoropolymers, Fluorochemicals | Teflon, Viton, Tedlar, Krytox, K-lube, Tefzel, Freon, Zepel, Zonyl |
| DuPont Dow Elastomers, Schweiz | Fluoropolymers | Kalrez |
| Dow Corning, USA | Fluorinated grease, polymers | |
| Exfluor, USA | Fluoropolymers | |
| Air Products | Fluorochemicals | Surfynol, DF- |
| Union Carbide | Fluorochemicals | Silwet- |
| Bayer | Fluorochemicals | Baygard |
| BASF | Fluorochemicals | Pluronic F-series |
| Dyneon, Germany | Fluorochemicals, -polymers, | Kel-F, Fluorel, Aflas, THV |
| Hoechst | Fluoropolymers | Hostaflon, Hostinert, Nuva |
| Ciba-Geigy | Fluorochemicals | Tinotop, Lodyn |
| Solvay & Sie, France | Fluoropolymers | Solef |
| Elf Atochem; France, USA | Fluorochemicals, polymers | Kynar, Foraflon, Voltaflef |
| Daikin, Japan & Europe | Fluorochemicals<br>Fluoropolymers | Dai-El, Daiflon, Demnum, Neoflon, Polyflon, Unidyne |
| Asahi Glass Corp, Japan | Fluorochemicals<br>Fluoropolymers | Aflon, Cytop, Lumiflon, Asahigard |
| Pennwalt | Fluorochemicals | Pentel |
| BNFL Ltd UK | Fluorochemicals | |
| ICI, UK | Fluorochemicals, polymers | Fluon, Arcton |
| F2 (ISC) Chemicals, UK | Fluorochemicals | Flutec, Isceon |
| Imperial Smelting Corp. Ltd | Fluorochemicals | |
| Dainippon, Japan | Fluoropolymers | Fluonate |
| Toa Gosei, Japan | Fluoropolymers | Zaflon |
| Miteni (Rimar) | Fluorochemicals | Perflutel RM |
| Ausimont (Montecatini), Italy | Fluorinated grease, Fluoropolymers | Algoflon, Technoflon, Fomblin, Halar, Hylar, Fluorobase |

| | | |
|---|---|---|
| EniChem Synthesis SpA Italy | Fluorochemicals | |
| Ugine | Fluorochemicals | Foraperle |
| P&M Ltd, Russia | Fluorochemicals | |
| Interchim, Russia | Fluorochemicals | |
| ORGSTEKLO, Russia | Fluoropolymers | |
| Milenia Agro Ciensas SA Brazil | Fluorochemicals | |
| Changjiang Chemical Plant, China | Fluorochemicals | |
| Indofine Chemical Company. Inc. India | Fluorochemicals | |

## 2. Perfluoroalkylated substances (PFAS)

The perfluoroalkylated substances have gained increased attention among scientists and regulators during the last few years. In particular, perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and similar perfluorinated alkylated acids are regarded as the most stable end products of various perfluoroalkylated substances and have been shown to be extremely stable, bioconcentrate and biomagnify and have several toxicological effects. The industrial chemistry of perfluoroalkylated substances is extremely diverse and includes almost all chemical functionalities from simple pure alkanes to complex co-polymers (Table 1). Figure 1 illustrates a perfluoroalkyl-based building block for polymers used in textile surface treatment.

**Figure 1.** Building elements of perfluoroalkylated substances



## 3. Industrial synthesis of perfluoroalkylated substances

### *3.1. Electrochemical fluorination:*

The bulk chemical used for fluorination of organic compounds is anhydrous hydrofluoric acid which is produced from the mineral calcium fluorite **:**

$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$

The process results in the following impurities: fluorosulfonic acid, and silicon tetrafluoride ($SiF_4$).

Electrochemical fluorination (ECF) has been used for over fifty years by 3M. The fluorination reaction takes place during the electrochemical hydrolysis of anhydrous hydrofluoric acid at a cell potential of 4.5-7V. The reaction schemes below are examples of the ECF processes.

$C_nH_{2n+1}COOH + (2n+2)HF \rightarrow CnF_{2n+1}COOF$ + by-products (cyclic perfloroethers) (process now obsolete due to low yield).

$C_nH_{2n+1}COCl + (2n+2)HF \rightarrow C_nF_{2n+1}COF + HCl$ + by-products

$C_nH_{2n+1}SO_2Cl + (2n+2)HF \rightarrow C_nF_{2n+1}SO_2F + HCl$ + by-products (shorter chain sulfonyl fluorides)

Hydrolysis gives the carboxylic acid or sulfonic acid, respectively:

$C_nF_{2n+1}COF + NaOH \rightarrow C_nF_{2n+1}COONa$ ;

$C_nF_{2n+1}SO_2F + 2NaOH \rightarrow C_nF_{2n+1}SO_3Na + NaF + H_2O$

A chemical intermediate used for several derivatives is the perfluoroalkyl sulfonamide which is synthesized by reacting the sulfonyl fluoride with an alkyl amine:

$C_nF_{2n+1}SO_2F + NH_2(CH_2)_3NH_2 \rightarrow C_nF_{2n+1}SO_2\ NH_2(CH_2)_3NH_2\ )$

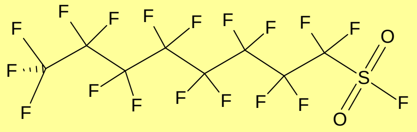
Example: Fluortensid FT 248 is made by reacting perfluorooctanesulfonyl fluoride with triethylamine and ethoxysilane in an anhydrous polar solvent.

The ECF process results in a mixture of linear and branched products and both odd and even numbered carbon chain products. The average product composition in the raw product usually amounts to:

$C_8F_{17}SO_2F$ (35-40%)
$C_6F_{13}SO_2F$, $C_7F_{15}SO_2F$, $C_9F_{19}SO_2F$ (7%)
Branched chain perfluoroalkylsulfonates (18-20%)
Other perfluoroalkylcompounds (20-25%)

An overview of the ECF-pathway PFOS product categories is depicted in Figure 2.

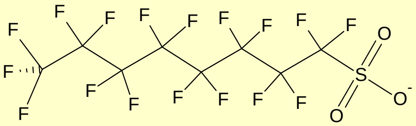
More details on industrial synthesis of fluorochemicals can be found in “Fluorine chemistry“, H.G. Bryce, Vol. V p.370-440, J.H. Simons, ed. Academic Press, N.Y., 1950; and ECF chemistry in 3M, 2000.



Perfluoroctanesulfonyl fluoride

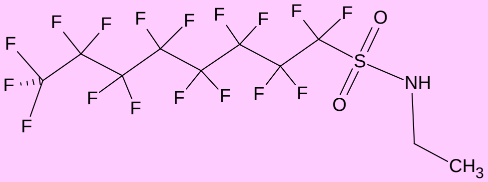
***Process intermediate***

-----------------***Low molecular weight derivatives***------------------------***High molecular weight derivatives***--



Perfluoroctanesulfonate

**$K^+$, $Li^+$, $DEA^+$, $NH4^+$ - salts**
Surfactant in firefighting foam
Surfactant in alkaline cleaners
Emulsifier in floor polish
Mist suppressant for metal plating baths
Surfactant for etching acids for circuit boards
Pestcide active ingredient for ant bait traps
**Amines**
Mist suppressant for metal plating baths
**Quaternary ammoinium salts**
Mist suppressant for metal plating baths
**Amphoterics**
Water/solvent repellant for paper/leather

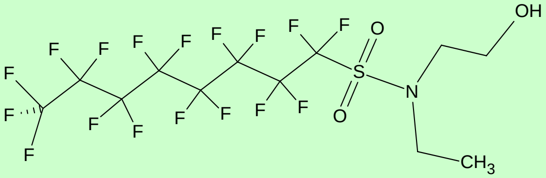


*N*-ethyl-Perfluoroctanesulfonamide

**Carboxylates**
Antistating agent in photographic paper

**Amides**
Pesticide active ingredient

**Oxazolidinones**
Waterproofing casts/wound dressings



*N*-ethyl-Perfluoroctanesulfonamidoethanol

**Alcohols**
**Silanes**
**Alkoxylates**
**Fatty acid esters**
**Adipates**
**Urethanes**
**Polyesters**
**Acrylates**
**Copolymers**
**Phosphate esters**

Soil/oil/water repellancy
Carpet
Fabric/upholstery
Apparel
Leather
Metal/glass

Oil/water repellancy
Plates
Food containers
Bags
Wraps
Folding cartoons
Containers
Carbonless forms
Masking paper

**Figure 2.** 3M PFOS-chemistry product line (adopted after OECD 2002)

### *3.2. Telomerization of tetrafluoroethylene and a perfluoroalkyliodide*

The second major industrial process is the chain elongation process referred to as the telomerization process. Depending on the starting material the process can result in odd carbon number compounds (trifluoromethyl iodide) - or even numbered carbon compounds (pentafluoroethyl iodide), although the latter category which produces even carbon numbered species seems to dominate.
The starting materials are named **telogen** (alkyliodide) and **taxogen** (ethylene) and the resulting product **telomer**
The first synthesis step yields a perfluoroalkyl telomer iodide according to:

$C_2F_5I + nCF_2{=}CF_2 \rightarrow C_2F_5(C_2F_4)_n I$ (Du Pont patent) (Telomer A)

Modifications of the process have been patented by Ciba, Daikin, Asahi, Kali-Chemie and Hoechst.
The perfluoroalkyl telomer iodide cannot be directly converted to a derivative such as a surfactant through reaction with a nucleophil. The perfluoroalkyl telomer iodide is first terminated by reaction with ethylene:

$C_2F_5(C_2F_4)_n I + C_2H_2 \rightarrow C_2F_5(C_2F_4)_nC_2H_2I$ (Telomer B)

The latter reaction yields a perfluoroalkylethyl telomer iodide which is readily converted to alcohols, thiols and sulfonyl chlorides used as intermediates for further reaction to surfactants and polymers. The perfluoroalkyl iodide may also be oxidized according to a patented procedure to form the corresponding carboxylate.
Due to the termination of the chain elongation using ethylene, this process usually results in products that contain a non-fluorinated part of the carbon chain, a property that distinguishes these products from the electrochemically produced fluorocarbons.

Another major industrial production route is based on the telomer B olefin:

$F_3C\text{-}(CF_2)n\text{-}CH{=}CH_2$ (ozon) $\rightarrow\rightarrow F_3C\text{-}(CF_2)n\text{-}CH_2\text{-}COOH$

This route gives products with odd numbered carbon chains and is sometimes referred to as the C9-chemistry. Several products having a terminal hydrogen atom (opposite to the acid end) are also produced by this route.

An overview of the perfluorochemical product categories involving the telomer process is depicted in figure 3.

The relative isomer ratios of the products provides a source signature which may be used for tracing the origin of a given signature (isomer ratio) found in environmental samples.
Trace analysis of PFAS is developing towards more and more detailed isomer specific analysis and therefore it is becoming possible to trace the source signatures in the environment.

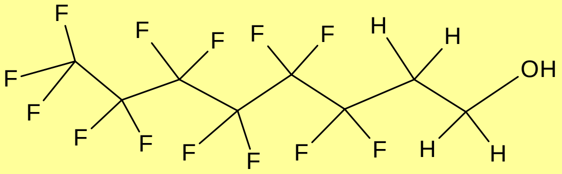
***Process intermediates:***

$CF_2=CF_2$ **TFE**

$F(CF_2\text{-}CF_2)_n\mathbf{I}$ **Telomer A iodide**

$F(CF_2\text{-}CF_2)_nCH_2CH_2\mathbf{I}$ **Telomer B iodide**

$F(CF_2\text{-}CF_2)_nCH_2CH_2OH$ **Telomer B alcohol**



$F(CF_2\text{-}CF_2)_nCH_2CH_2SH$ **Telomer B thiol**

$F(CF_2\text{-}CF_2)_nCH=CH_2$ **Telomer B olefin**

***Product categories:***

**Low molecular weight derivatives:**
*Surfactants:*
Anionic: phosphates, carboxylates, sulfonates
Nonionic: ethoxylates
Amphoteric: alkylbetaine
*Phosphate esters*

**High molecular weight derivatives:**

**Polymers:**
*Acrylic*: esters, amides
*Urethane*: alcohol- or thiolbased co-polymers

**FIGURE 3.** Product scheme of telomer A/B-chemistry showing starting materials and intermediates (left) and major product categories (right)

### *3.3. Oligomerization of tetrafluoroethylene*

The third industrial process is a polymerization reaction controlled to yield short chain compounds.

$4C_2F_4 + YF \rightarrow C_8F_{16}$ (were Y could be Cs, K or alkylammonium, ICI patent)

The process results in branched products: tetramer - $C_8F_{16}$; pentamer - $C_{10}F_{20}$; hexamer - $C_{12}F_{24}$.
These intermediates can be converted to a sulfonic acid or carboxylic acid etc.

### *3.4. Direct fluorination*

Small scale (custom) fluorination of specialty chemicals can be performed on an industrial scale by direct fluorination of the parent compound using $IF_5$. This technique is used for the production of partially fluorinated specialty chemicals.

## 4. Global industrial production of PFAS based products

As to date, no comprehensive compilation is available on production volumes of perfluoroalkylated compounds on a global cumulative basis. Some data available in open sources are given below.

### *4.1. ECF-chemistry:*

The ECF process for C-6 and C-8 compounds was operated by the Minnesota Mining and Manufacturing company (3M) between 1947 and 2002, when the C-4 chemistry replaced some of the former products. By the end of the period the 3M PFOS–production, expressed on a PFOSF equivalents basis amounted to 80-90% of the global market (OECD 2002; Brooke, 2004) and the following production volumes of PFOSF were noted:
3500 T/y – 1999
3665 T/y – 2000
The specific usage was divided into the following categories
Surface treatment textile&leather: 48% (polymeric)
Surface treatment paper: 33% (non-polymeric)
Performance chemicals: 15% (surfactants and other monomeric derivatives)
Firefighting foam 3% (surfactants)
The ECF process was also utilized for the production of ammonium perfluorooctanoate APFO which is used as a process aid in the polymerization of several fluoropolymers.

As pointed out in the description of the ECF process, the final product contains a mixture of odd and even numbered carbon chain compounds.

### *4.2. Fluorotelomer chemistry:*

Between 2000 and 2002 a total of 6500T/year of telomer A iodide ($F(CF_2CF_2)_nI$ ) was produced , a majority (80%) of which was reacted into polymeric products containing roughly 10% (w/w) perfluoroalkylated compounds (Du Pont 2004). The polymerically bound perfluoroalkylated compounds are not expected to be readily released to the environment.

As described in section 1.3 of the telomer processes, the telomer B chemistry yields even numbered C-chains while the fluorotelomer-olefin based (C9-) chemistry yields odd numbered C-chains.

The polymeric products contain small amounts of nonreacted residuals which may be released during the lifetime of the products. These residuals are typically present in the following concentrations (w/w):

| | |
|---|---|
| 4:2, 6:2, 8:2, 10:2 fluorotelomer alcohols (FTOHs): | 20 ppm |
| Fluorotelomer olefins: | 20 ppm |
| PFCA: | 20 ppm |
| Fluorotelomer acrylate monomers: | 100-200 ppm |
| *Estimated total monomeric residuals in telomer products:* | 500 ppm |

Given a total yearly production rate of 40 000 tons of polymeric product the release of perfluorocarboxylates through these residuals could potentially amount to 21 metric tonnes/year.

An extensive review of sources and fate of perfluorocarboxylate compounds was recently published (Prevedouros 2006) and some figures for C-8 and C-9 production volumes were reported. These production figures relate only to the surfactant products ammonium perfluorooctanoate and –nonanoate (APFO and APFN) and do not include the polymeric derivatives. The estimated total annual production rates for APFO and APFN were 200-300 t/y and 15-75 t/y respectively during the years 1995-2002

## 5. Perfluoroalkylated surfactants

### *5.1. Overview of fluorosurfactants*

A large use of fluoroorganic chemicals is related to surfactant use. The following chapter provides a brief overview of the fluorosurfactant chemistry with a focus on anionic fluorosurfactants. For a more detailed description the reader is referred to E. Kissa ; *Fluorinated surfactants, synthesis, properties, applications*., 2001

Usually the hydrofobic moiety is fluorinated but some surfactants have counterions which contain fluorine. Both perfluorinated and partially fluorinated surfactants exist. Fluorosurfactants can be classified as belonging to one of four major groups:
*Anionic, cationic, amphoteric, nonionic*

In water anionic fluorosurfactants can form insoluble ion pairs with cationic species.

### 5.1.1. Anionic fluorosurfactants:

Anionic fluorosurfactants can be divided into four major categories; *carboxylates, sulfonates, sulfates and phosphates*.

*Carboxylates* – perfluoroalkanoic-, perfluoroalkoxyalkanoic-, perfluoroalkoxybenzoic- perfluoroacylaminoalkanoic acid, perfluoroalkanesulfonamido-, perfluoropolyether carboxylic acid. Fluorad FC-118 is an example of a surfactant containing ammonium perfluorooctanoate and Surflon S-111, a mixture of ammonium perfluoroalkanoates between C7-C13.

*Sulfonates*- perfluoroalkanesulfonic-, perfluoroalkylethanesulfonates, perfluoroalkylbenzenesulfonates, perfluoroalkoxybenzenesulfonic, perfluoroacylbenzenesulfonates, perfluoroalkanesulfonamide, perfluoroacylcarbamide, perfluoroalkyl ether amides, perfluoroalkylethersulfonate. Zonyl® TBS is an example of a telomer-based perfluoralkylsulfonate.

*Sulfates*- perfluoroalkylated methyl sulfate
*Phosphates*- perfluoroalkyl phosphates, perfluoroalkylethyl phosphates.
Fluowet®PL80 is an example of a perfluoroalkyl phosphate
The hydrophobic moiety can consist of a fluoroalkyl or fluoroaryl chain. Fluorinated carboxylic acids are insoluble in water containing di- or trivalent metal ions (Ca+). The sulfate group is a stronger hydrophile than the sulfonate group, but fluorinated surfactants have a lower hydrolytic stability.

Cationic and anionic surfactants are usually incompatible with each other. Cationic fluorinated surfactants adsorb on negatively charged surfaces; clay and sludge, and are efficiently separated in wastewater cleaning systems.

### 5.1.2. Cationic fluorosurfactants:

Surfactants containing (perfluoroalkyl)alkylamino-, perfluoroalkanamido-, perfluorooctanesulfonamido- or *N*-(perfluorooctanesulfonyl)piperazine groups belong to this category.
Fluowet®L3658 is an example of a (perfluoroalkyl)triethylamine-based cationic surfactant.

### 5.1.3. Amphoteric fluorosurfactants:

Derivatives of carboxybetaine, sulfobetaine, sulfatobetaine, amino acid, dialkylated heterocyclic nitrogen; n-dialkylpiperazine, n-dialkyl-1,4-oxazine compounds belong to this category.

### 5.1.4. Nonionics

Nonionic fluorosurfactants usually contain polyoxyethylene or polyoxyethylene-polyoxypropylene segments; oxyethylated alcohols, amines or thiols.

Ex.: oxyethylated perfluoroheptanol, perfluoroalkyl-2-ethanethiol derivatives. Zonyl® FSN/O-series are examples of oxyethylated fluorotelomer alcohol derivatives. Fluowet®OTN is a nonionic surfactant mixture containing perfluoroalkanolpolyglycolether Fluorinated surfactants without a hydrophile are usually copolymers of a perfluoroalkyl and a hydrocarbon group. Example: $(HFPO)_n$-Ar $(\text{hexafluoropropyleneoxide})_n$-aryl

.

## *5.2. Physico-chemical properties (selected)*

### 5.2.1. Chemical properties

The C-F bond is stable to acids, alkali, oxidation and reduction, even at relatively high temperature. The small fluorine atoms shield the carbon atom without steric stress.

### 5.2.2. Thermal stability

Perfluoroalkanecarboxylic acids and perfluoroalkanesulfonic acids are the most thermally stable fluorinated surfactants. The pure perfluoroalkanecarboxylic acids can be heated to 400° C in borosilicate glass without significant decomposition, but carboxylate salts decompose by decarboxylation , c.f. sintering step in PTFE production:

$\text{PFOA-NH}_4 \rightarrow C_5F_{11}CF{=}CF_2 + CO_2 + NH_3 + HF$ (at 167º C)

Anhydrous perfluoroalkanesulfonic acids are stable at 400° C in the absence of air ($O_2$) but decompose to form HF when moisture is present

### 5.2.3. Hydrolysis

$\text{PFOS}^-K^+$ was stable at 300° for 8 h in a water solution. A slight decomposition was observed in 10% KOH. PFOS decomposed slightly in water at 400° for 3 h. PFOS heated for 12 h in concentated nitric acid at 160° did not show any decomposition. Anionic perfluorinated surfactants were stable in 60% $HNO_3$ and 98% $H_2SO_4$/10 g/L chromic acid over a 28 day period (Gloeckner, 1989).

### 5.2.4. Acidity

Fluorinated organic acids are considerably more acidic than their nonfluorinated analogues. Dissociation constants have been determined in 50% aqueous ethanol. $pK_a$ for $C_8F_{15}OOH$ was 2.80 (ref 159) as compared to 6.13 for $C_8H_{15}OOH$. For PFOS the pKa has been estimated to be –5.

### 5.2.5. Boiling points

The boiling points of fluorinated surfactants are generally considerably lower than for the corresponding non-fluorinated surfactant. ($C_8F_{15}OOH$: approx. 170° C, PFOS 258-260° C). Salts are expected to vaporize more easily.
(Kauck and Diesslin, 1951; Gramstad and Haszeldine, 1957)

### 5.2.6. Surface tension

Fluorinated surfactants are much more surface active than their hydrocarbon counterparts. Surface tension figures for perfluorosurfactants range from between 15.2

mN/m for $C_8F_{17}OOH$ to 29.8 mN/m for PFOS-Li. With some fluorosurfactants as little as 100-200 ppm is sufficient to lower the surface tension to below 20 mN/m.

### 5.2.7. Solubility

The rigidity of the C-F bond causes stiffening of the perfluoralkane chain and limits interactions with other molecules. As a consequence, perfluoralkanes are insoluble in common organic solvents (except alcohols) and they are more hydrophobic than the corresponding hydrocarbons. Perfluorohexanoic acid and shorter chain perfluoroalkanoic acids are miscible with water in all proportions but perfluorooctanoic acid and perfluordecanoic acid are only slightly soluble in water (Kauck and Diesslin,1951). The perfluoroalkanesulfonic acids, $C_7$ and $C_8$ , are moderately soluble in water. The solubility of perfluorocarboxylic acids probably can be approximated by their critical micelle concentration, CMC (Fig 4).

### 5.2.8. Critical micelle concentration, cmc

The cmc generally decreases with increasing chain length of the fluorosurfactant and is lower for the carboxylate than for the sulfonate. A rapid drop in CMC is observed between $C_4$ and $C_{10}$. The lowest cmc observed for $C_7F_{15}COOH$ was 8.7 mmol/L ($C_7F_{15}COONH_4$: 33mmol/L; $C_8F_{17}SO_3NH_4$: 5.5 mmol/L). Micelle formation of surfactants can influence the apparent water solubility of fluorosurfactants but also influence the solubility of other substances.

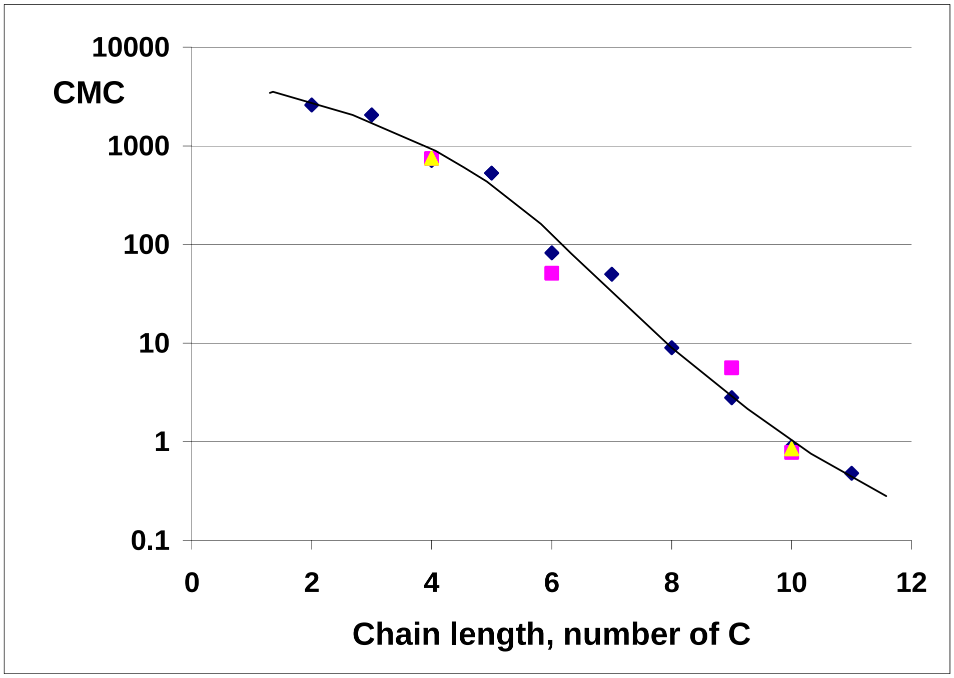


**Figure 4** Critical micelle concentration for perfluorocarboxylic acids (Kissa 2001)

## *5.3. Applications (36 listed)*

The listed applications are examples of published patent areas and applications and do not necessarily represent actual uses. The list gives an insight into the broad range of applications where fluorinated surfactants may be found.

*Adhesives:* Zonyl FSN-100, FSO-100 FSA
*Antifogging:* PFOS-K in PVC, Zonyl FSN in PVC
*Antistatic agents:* $C_4$-$C_{16}$-perfluorocarbon chain $SO_3$-Li (anionic), perfluorocarbon chain and poly(oxyethylene) chains (nonionic) both in PVC, Monflor 51,52 internal antistats for LDPE, carboxymethyl-3nonadecafluorodecaneamidopropylammonium hydroxide in propanol for magnetic tapes and records
*Cement additives:* improve weather resistance of pigment in cement tiles and primers for cement mortar (Fluorad FC-340)
*Cleaners for hard surfaces (textiles, cars, air planes, nickel plating):* $C_8F_{17}SO_2N$(ethyl)$CH_2COO$-K in cyclic alcohol for removal of cured epoxy resins on integrated circuits, PFOS in trichlortrifluoroethane for cleaning metal parts in nickel plating
*Coatings:* Perfluoroalkylphosphate in high temperature paints
*Cosmetics:* PFOA, $C_8F_{17}SO_2N$-(H,alkyl)-phosphate or carboxyl (referenced papers from: Unilever, Procter & Gamble, LOreal, Gilette)
*Crystal growth regulators:* PFOS-K
*Dispersions:*
*Electroless metallisation:*
*Electronics:* Fluorad FC-432 (fluorinated alkyl ester), Saflon S-111 (perfluoralkanoic acid salt) in PE for cable insulation, Zonyl FSN in ZnO electrolyte, perfluoroalkylcarboxylate in $MnO_2$ electrolyte
*Electroplating:* Chromium, copper, nickel, tin, fluoropolymer plating
*Electropolishing*
*Emulsions*: water-oil emulsion breakers in oil wells
*Etching:* Glass polishing and etching PFOS-TEA, PFOS-K, PFOA-Ca, IC-manufacturing Al- and steel ecthing
*Fire-fighting foams and powders:* High-, medium- and low expansion foams. Fluoroprotein foams, indoor or closed use; AFFF, low expansion foams, contain fluorinated surfactants.
*Floatation of minerals:* perfluoroalkanoates for $Al_2O_3$, Zonyl FSP for uranium
*Graphic imaging*: Zonyl FSP: gravure printing, water-resistant water based inks, ink for ball-point pens, ink-jet ink correction fluids
*Greases and lubricants:* dispersant for PTFE-grease
*Herbicides and insecticides:* dispersant and adjuvant, Fluorad FC-128
*Leather:* hydrating, bating, pickling, degreasing, tanning and dying process
*Liquid crystals*
*Medical and dental use:* FC-161 (perfluoro-*n*-octyl-*N*-ethylsulfonamidoethyl phosphate),
Fluorosurfactant in toothpaste enhances fluorapatite formation and inhibits caries, Lodyne S-110(fluoroalkylaminocarboxylic acid + fluoroalkydamide) in toothpaste increases enamel-fluoride interactions, Fluorad FC-128 dispersion of cell aggregates from tissues.

*Metal finishing:* anionic, cationic and nonionic fluorinated surfactants are used in various metal treatment processes; phosphating process for Al, bright dips for Cu and brass; pickling and escaling baths; corrosion inhibitors (Atsurf F-21); antiblocking agents on Al-foil (Monflor 91); penetration oil (Monflor 31)
*Molding and mold release:* mold release agents for thermoplastics, epoxy resins, polyurethane elastomer foam
*Oil containment:* $C_8F_{17}SO_2N$(propyl)$CH_2COO$-K prevents spreading of oil and gasoline on water (remediation at spills)
*Oil wells*
*Paper:* fluoroalkyl phosphates impregnation of liner board, food containers and papers (snack foods, cake mixes, fast food, margarine, candy wrap, bakery products, pet food) duplicator and reproduction paper, fluorinated surfactants: heat sensitive recording paper, ink-jet printing paper
*Photography*
*Plastics, resins and films:* antiblocking agent for synthetic rubber, coplating PTFE on metal,
*Polishes and waxes:* self-polishing liquid floor finishes (50 ppm fluorinated surfactant)
*Polymerisation*: PTFE is commercially produced by free radical polymerization of tetrafluoroethyelene in water containing a fluorinated surfactant, usually $NH_4$-PFOA or Li-perfluoroalkanoates. Polymerization of vinylidene fluoride: $NH_4$-PFOA, Na-PFOA, $NH_4$-PFisoOA, perfluorinated surfactants emulsifiers in polymers of vinyl fluoride, ethylene, styrene.
*Repellancy:* perfluoroalkyl-$CH_2O$-acrylates, polymeric fluorochemical repellants
*Surface treatment of glass:*optical glasses: cationic or anionic ($C_6F_{13}SO_3$-) fluorinated surfactant, windshield wiper fluids
*Textiles:* $C_{6-8}$-perfluoroalkyl carboxylic acid, PVAC and acrylic polycarboxylate facilitates weavability
*Vapour barrior, evaporation retarders*
*Wetting agent*
*Surface treatment products*
Monomers or oligomers of perfluoralkylsulfonate-acrylates or metacrylates for imparting water-, oil and soil repellency in textile, leather and paper (Scotchguard, Zepel).

Products containing fluorosurfactans are listed in Table 4. The chemical identity of the fluorosurfactants are only known in a few cases, i.e. several of the 3M FC-series fluorosurfactants and some of the Zonyl fluorosurfactants. The total world production in 1979 was estimated to be 200 metric tonnes including all fluorosurfactants. The production has increased dramatically during the last 20 years.

**Table 4.** Producers and retailers of fluorosurfactants and their respective trade names (derived mainly from Banks 1979 and manufacturers and retailers web-sites)

| *Company* | *Trade name* |
|---|---|
| 3M: Minnesota Mining and Manufg. Co | Fluorad FC# series<br>Fluorad FC-143 and –118 (ammonium perfluorooctanoate) |
| Du Pont | Zonyl series, Forafac |
| ICI | Monflor, Atsurf F# series |
| Clariant | Licowet, Fluowet |
| Ugine | |
| Asahi Glass Co | Surflon, S-111 (ammonium perfluorononanoate) |
| Bayer | |
| Atochem | |
| Sandoz | |
| Hitachi Cable Co. | Saflon S-111 |
| Ciba-Geigy | Lodyne |
| Mobay Chemical Corporation | FT-248 (Tetraethylammonium perfluoroalkylsulfonate) |
| Atotech | Zylite |

One major use of fluorosurfactants is in firefighting (*A*queous Fire*F*ighting *F*oam, AFFF) foams where the concentration in the foam concentrate often is only a few percent. Foam producers and their trade names are listed in Table 5. The chemical identity of the fluorosurfactant is known only for a few products. Some brand names may have been transferred to another company or the production has been discontinued.

**Table 5.** Producers & retailers of fire fighting foams and their respective trade names.

| *Company* | *Trade name* | *Surfactant* |
|---|---|---|
| 3M | Light Water, FC-203, 206, 602, 600 | PFOS, PFOA |
| National Foam Inc. | Aero Water | Fluorinated surfactant |
| Angus Fire Armour | Tridol, Petroseal, Alcoseal, Niagara,<br>FP70 | Fluorinated surfactant telomer product)<br>Fluorinated protein |
| Chubb-Pyrene | Fluoro-Film | Fluorinated surfactant |
| Total Walther | Towalex | |
| Sthamer | Sthamex, Moussol APS, Foamusse | Fluorinated surfactant<br>fluorinated protein |
| Wormald Fire Systems | Komet Extrakt | Fluorinated surfactant |
| Integrated Fire Protection Pvt. Ltd India | Unilight AR | polyfluoralkylbetaine, perfluoralkylpolyamide, -amine |
| Ansul | Ansul, Ansulite | Fluorinated surfactant/ protein |
| Atofina | | |
| Buckeye | Buckeye | Fluorinated surfactant |
| Chemguard | Chemguard, Ultraguard | Fluorinated surfactant |
| Du Pont | | |
| Dynax Corporation | Dynax | Perfluoroalkyl substituted surfactant |
| Kidde | Aer-O-Lite, Universal, Centurion | Fluoroalkyl surfactant |

## 6. Fluorosilicones

In this group polysiloxanes containing perfluoroalkylamide groups are found.

## 7. Polymeric fluorochemicals

Polymeric fluorochemicals can be divided into two categories on the basis of their chemistry; those that are based on short-chain fluorochemical intermediates (fluoropolymers) such as tetrafluoroethylene based PTFE and those that are based on longer chain perfluoroalkylsubstances (fluorinated organic polymers) where the length of the tail is essential for the performance of the product such as textile finish products. Although the former group doesn’t contain the substructural units of primary focus for this report, several investigations have shown that thermal processes may result in vaporization of perfluoroalkyl containing substances e.g. PFOA (Ellis, 2001). Furthermore, during the manufacture of certain fluoropolymers, perfluorocarboxylic acids (mainly ammonium perfluorooctanoate APFO) and ammonium perfluorononanoate (APFN) are utilized as emulsifiers in the aqueous polymerization process. The following fluoropolymers are examples where APFO or APFN may be used as an emulsifier.

### *7.1. PTFE, Polytetrafluoroethylene*

PTFE itself is a perfluoroalkylpolymer built from tetrafluoroethylene. The Du Pont procedure involves a step for efficient removal of residual PFOA while other manufacturers may produce PTFE with trace amounts of PFOA in the final product. Experiments with heated Teflon® (Du Pont PTFE) frying pans indicate release of perfluorocarboxylic acids (TFA, PFOA) at temperatures of 360 degrees C. The temperature of a PTFE-coated pan can reach 400 degrees centigrade. Experiments with water in the frying pans at temperatures not exceeding 100 degrees centigrade showed no traces of PFOA.

### *7.2. ETFE, Polytetrafluoroethylene-ethylene*

ETFE is a copolymer of tetrafluoroethylene and ethylene.

### *7.3. PVDF, Polyvinylidenefluoride*

PVDF is a polymer of vinylidene fluoride, either as a homopolymer or as a copolymer with hexafluoropropylene.

### *7.4. PFA, Polytetrafluoroethylene-perfluorovinylether*

PFA is a polymer of tetrafluoroethylene and perfluorinated vinylether.

### *7.5. FEP, Polytetrafluoroethylene-hexapropylene*

FEP is a polymer of tetrafluoroethylene and hexafluoropropylene.

### *7.6. THV, Polytetrafluoroethylene-hexafluoropropylene- vinylidene fluoride*

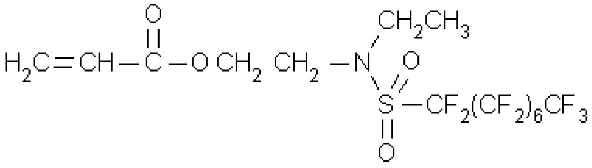
THV is a polymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride.

### *7.7. Fluoroelastomers (FFKM)*

Viton® is an examples of a fluoroelastomer (rubber-type) commonly used as sealant in various applications.

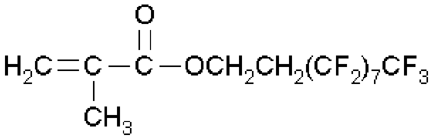
**Figure 5.** Perfluoroalkylated polymers used in textile applications

**a) acrylates**



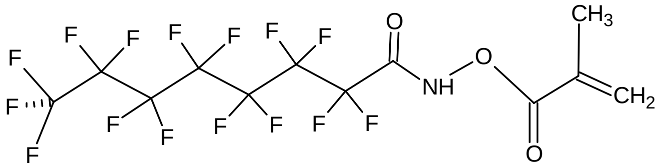
$H_2C{=}CH{-}C({=}O){-}OCH_2CH_2{-}N(CH_2CH_3){-}S({=}O)_2{-}CF_2(CF_2)_6CF_3$

Acrylate based on *N*-ethyl-perfluoroctylsulfonamidoethanol (PFOSA-based)



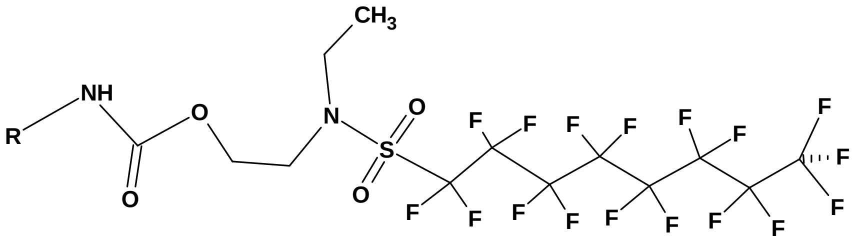
$H_2C{=}C(CH_3){-}C({=}O){-}OCH_2CH_2(CF_2)_7CF_3$

Acrylate based on perfluordecyl-telomeralcohol

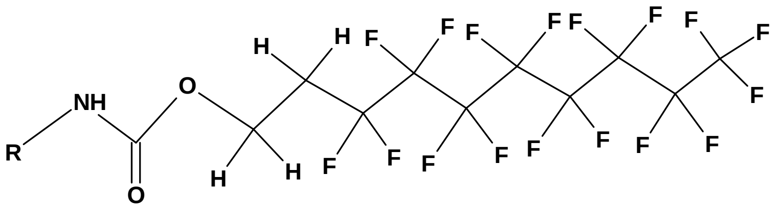


Acrylate based on perfluoroheptanoic amide (CIBA Geigy patent)

**b) urethanes**



Urethane based on *N*-etyl-perfluoroctyl sulfonamidoethanol (PFOSA-based)



Urethane based on perfluorodecyl-telomeralcohol (Slade,1998;  Shimizu, 1997)

## *7.8. Perfluoroalkylated polymers used in textile applications*

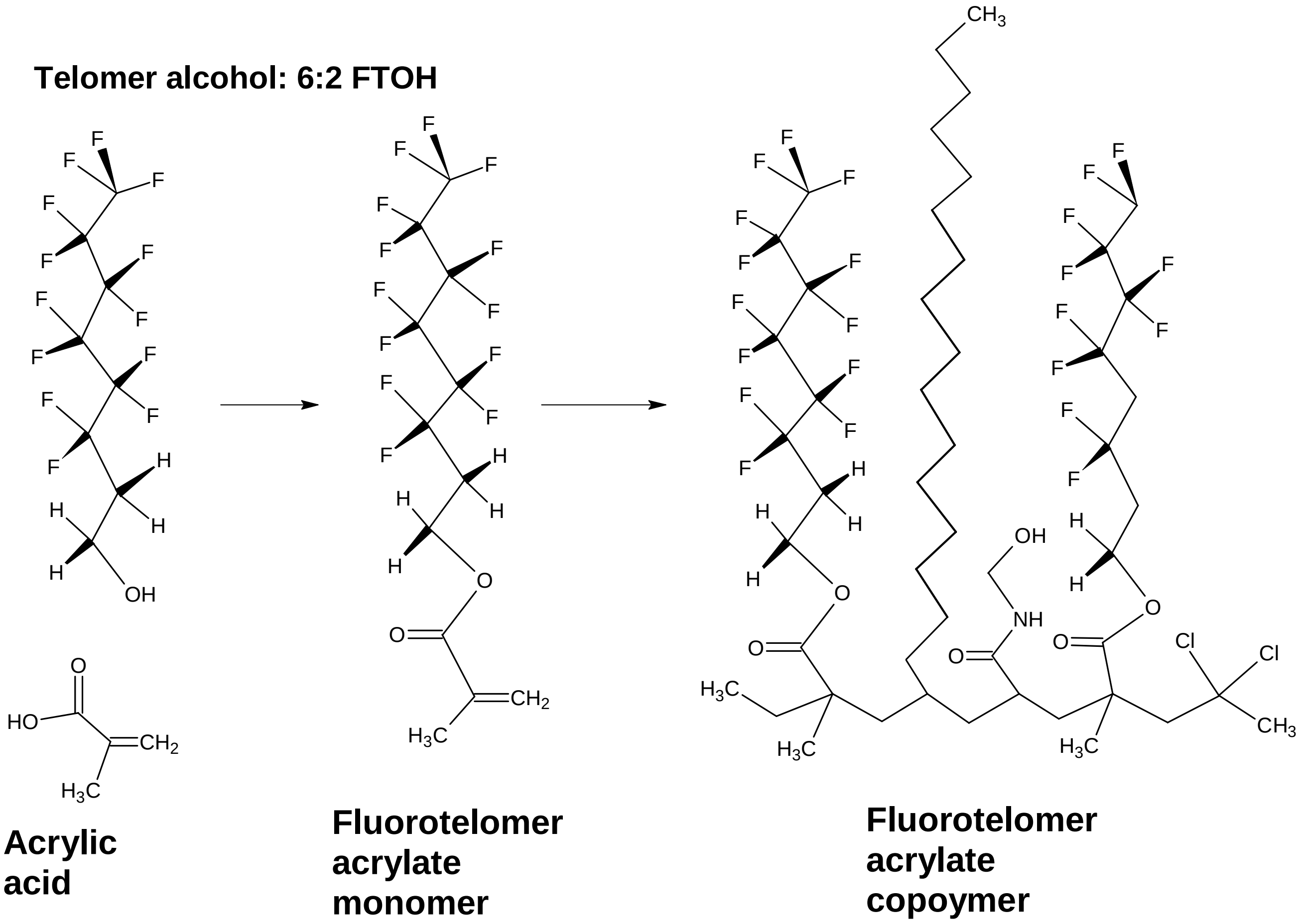
Fluorochemical impregnants are used both industrially in textile finishing and laundry and in household use. Most of these products contain a perfluoroalkyl chain with 6 fully fluorinated carbon atoms or more and are based on either electrochemically fluorinated alcohols, carboxylic acids or sulfonamide containing or telomer based alcohols. They are contained in both spray-can and water-emulsion based products for garments, leather products, furniture, carpets, covers for leisure boats etc. Numerous patents on perfluoroalkyl based chemicals for imparting water, grease and soil repellency on textile surfaces have been reported in the literature. The major products are of the acrylate or urethane type (Fig 2 a-b), but adipates, ethers and esters are also produced. The polymer is usually a co-polymer, containing both a perfluoroalkyl group, a nonfluorinated alkyl chain which provides film forming properties, and a vinyl chloride unit and cross-linking unit for durability (Figure 6). Table 6 lists some of the manufacturers of textile impregnating formulations with their respective trade names.

**Table 6.** Textile impregnating formulations / trade names

| *Company* | *Trade name* | *Composition* |
|---|---|---|
| 3M | Scotchguard FC 251/FX1801 | PFOSA-urethane |
| Atofina | Foraperle | |
| Bayer | Bayguard, Bayguard-K | |
| Du Pont | Teflon/Zonyl-series | Telomer acrylate/urethane |
| Daikin | Unidyne TG series | Telomer acrylate |
| CIBA | Lodyne, Oleophobol-series | Telomer acrylate/urethane |
| Clariant | Nuva-series, Pekophob | |
| Henkel | Repellan | |
| Asahi Glass Company | Asahiguard | |
| Unilever | Clara Proof | |
| Rudolf Chemie | Rucoguard | Telomer acrylate |

Other fluoropolymers used for textile finishes include perfluoropolyethers and perfluoropolyesters.

**Fig 6.** Example of chemical composition of a telomer-based acrylate for textile impregnation (Rudolph GmbH, 2000)



## *7.9. Perfluoroalkylated polymers used in paper and board treatment*

Fluorochemicals, which improve grease, oil and water repellency for food packaging. They include fluorinated acrylic copolymers, phosphate esters. They may be added at the wet end, size press, calender stack, or off-machine.

**Table 7.** Paper impregnating formulations trade names

| *Company* | *Trade name* | *Composition* |
|---|---|---|
| 3M | Scotchban, FC807 | diphosphate ester of N-EtFOSE |
| Bayer | Baysize-S / Baysynthol | |
| Du Pont | Zonyl | |
| Ciba | Lodyne P201/208E | |
| Clariant | Cartafluor | |
| Atofina | Foraperle | |
| Hopton Technologies | | |
| Omnova solutions | Sequapel | |

## *7.10. Perfluoroalkylated polymers used for brick, tile and cement*

Several companies offer products for providing brick, tile, stone and cement with water and stain repellency. One product is dedicated for use as anti-graffiti treatment of stone and concrete. The base unit of these types of products is likely the 8:2 FTOH- acrylate

## *7.11. Perfluoroalkylated polymers in cosmetic applications*

The use of perfluoroalkyl acrylates as an ingredients in cosmetic creams has been patented. One cosmetic product for topic application based on the 8:2 FTOH based acrylate was encountered at Internet search.

# 8. Distribution of perfluoroalkylated substances into and within the environment

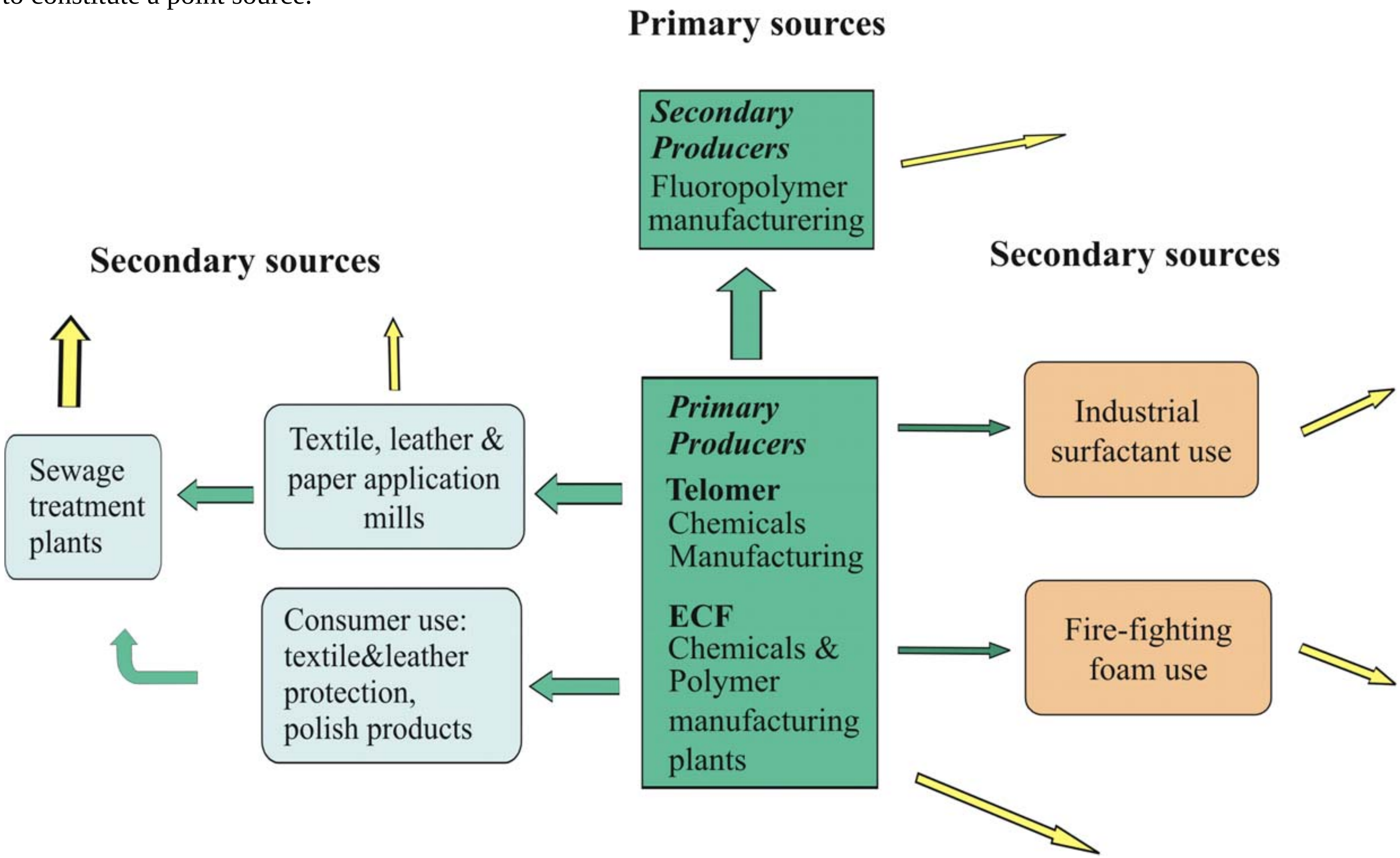
## *8.1. Emissions*

Due to the complexity of the chemistry and the versatility of perfluoroalkylated substances, the routes into the environment are numerous. In the following text, sources are divided into two major categories; *point sources*, including primary sources (primary and secondary manufacturing sites) and secondary source usage sites such as fire-fighting foam usage sites, industrial users such as electroplating industries and municipal sewage treatment plants (STPs) and; *dispersive sources*, including single household sewage water effluent and landfill sites. The primary source category can be depicted as in Figure 7. As illustrated, direct emission to the environment can occur at manufacturing sites, both where perfluoroalkylated raw materials are being produced (primary sources) and while processing, reformulating or applying products on an industrial scale (secondary sources).

The emissions result from release to the air and water phase of the intentionally produced perfluoroalkylated monomeric chemicals but also from unintentionally produced residuals in e.g. polymeric products. These residuals, which may be acids, alcohols, olefins or monomers constitute typically less than 500 ppm of the product. No primary point sources are presently located in Sweden, but several sources are found in the neighboring countries Germany, Poland, the Netherlands and Belgium. Secondary point sources found in Sweden are e.g. textile, leather and paper treatment plants, electroplating industries and fire-fighting training sites (municipal, airport and military fire brigades). Use of firefighting foam at accidents in Sweden has not been recorded for this report.

Various consumer products containing perfluoroalkylated substances are sold in Sweden, e.g. impregnated textile and leather articles; spray can products for the impregnation of garments, tents, car & boat covers; polish products and products for tile, brick and cement protection and firefighting foam containers. The use of carpet protectors can be expected to be a less important source in Sweden than in e.g. the US, the UK and France where wall-to-wall carpets are more common. Impregnated paper is produced in Sweden but it has not been investigated to what extent the products are sold in or imported to Sweden. During the life cycle of the PFAS containing products, PFAS in the form of acids or precursors can be released to the air in gaseous or particulate form during application and by abrasion, or released into aqueous media during laundering of impregnated goods. Diffusive release of PFAS can also result from cleaning and weathering of impregnated tents or car & boat covers. Dispersive release to the aqueous phase could also result from disposal of PFAS-containing waste at landfill sites.

**Figure 7** Point sources of PFAS. Diagram illustrates the flow of PFAS chemicals (green arrows) and sources to the environment (yellow arrows). Consumer use may also be regarded as a dispersive source, but is commonly redirected through the municipal waste stream to constitute a point source.



## 8.2. Distribution in the aqueous environment

Perfluorinated alkylated carboxylic and sulfonic acids are present in the environment predominantly as anionic species (carboxylates and sulfonates) at the natural pH generally occurring in the aqueous environment. As pointed out earlier in section 1.3, the aqueous solibility of perfluorocarboxylates is influenced by the presence of $Ca^{2+}$ and $Mg^{2+}$, which implies that solubility is decreased in seawater and calciferous water. The soil/sediment-to-water distribution is not well investigated. Partition experiments with PFOS in soil columns indicated almost no sorption to particulates, although no details were given on the organic carbon content (3M assessment, also referenced in OECD 2002). A more recent study on soil-water partitioning of perfluoroalkyl carboxylates states a linearly increasing sorption to particulates with increasing organic carbon content as well as with increasing carbon chain length of the PFCA (Sullivan 2001, referenced by Prevedourous 2006). A considerably higher sorption of PFCAs to sewage sludge than to natural sediment could thus be expected due to the much higher organic content of sewage sludge.

## 8.3. Uptake and distribution in biota

Perfluroalkylated acids are efficiently transferred into fish both via water-mediated exposure and through ingested food. Table 8 gives bioaccumulation factors (BAF) and bioconcentration factors (BCF) for experiments with rainbow trout, illustrating a pronounced increase of BCF with each additional carbon up to a chain length of 12 carbon atoms. Perfluoroalkylated acids are olephobic and thus do no partition into lipids in a similar manner as conventional halogenated pollutants like PCBs. Their partioning cannot be described by the octanol-water coefficient (log $K_{ow}$) as they tend to form a three-phase system in distribution experiments. Their partitioning may be more accurately described by the CMC as indicated by the values for PFOA, PFDA and PFUnA. The uptake rate of sulfonates however, is higher than their corresponding carboxylate chain length analogue. Once taken up by the organism the acids tend to distribute into the tissues of liver, blood, and kidney and to some extent also into the brain. The mechanims for tissue enrichment is unknown but covalent binding to proteins in the plasma, liver and testes of rat has been noted for perfluorooctanoic acid (PFOA) (Vanden Heuvel et al 1992, Jones et al 2003).

**Table 8.** Uptake of PFAS in fish via ingested food (BAF) and through water (BCF) (Martin 2003, Kissa 2001)

| *Compound* | *BAF* | *BCF* | *CMC* |
|---|---|---|---|
| PFOA | 0.038 | 4 | 9 |
| PFDA | 0.23 | 450 | 0.89 |
| PFUnA | 0.28 | 2700 | 0.48 |
| PFDoA | 0.43 | 18000 | |
| PFTDA | 1.0 | 23000 | |
| PFHxS | 0.14 | 9.6 | |
| PFOS | 0.32 | 1100 | 8 |

## 9. Transformation of perfluoroalkylated substances

Fully halogenated fluorinated organics have very long lifetimes and breakage of the C-F bond is a highly energetic process that requires extremely high temperature or that the substances migrate to the stratosphere where fluorine can be released by photolysis (Molina & Rowland, 1974; Key 1997)
Reductive defluorination requires reducing conditions which could occur under methanogenic conditions. Hydrolytic defluorination of fluoroalkyl compounds with two or more fluorine substituents is likely to be too slow to be of environmental significance (Key 1997). PFOS is suspected to be the stable degradation product from several other perfluorinated compounds, and it has been shown that N-ethyl-perfluorooctanesulfonamide (N-EtPFOSA) can be biotransformed to PFOS via perfluorooctanesulfonamide (PFOSA) (Tomy, 2003). It has also been stated that N-EtFOSE (2-N-ethylperfluorooctane sulfonamido ethyl alchol) used as paper- and packaging protection and the corresponding N-MeFOSE (used as surface treatment) can form PFOSA and therefore also PFOS through oxidation and metabolism (Olsen, 2003a&b and 2004). Sulfluramide (insecticide; cockroaches and ant control) is deethylated to perfluoroctanesulfonamide in rats, dogs and rabbit renal mitochondria (Arrendale 1989; Grossman 1992; Key 1997) and probably converted to PFOS. PFOS is resistant to further biological attack and is probably mainly eliminated through the urine(Key, 1997). Telomer 8:2 alcohol has been shown to be metabolized to PFOA in rats (Hagen 1981) and to transform to PFOA in smog chamber experiments (Ellis 2004). Figure 8 illustrates the proposed transformation of some potential precursors to PFOA. The transformation of sulfonamide precursors to PFCAs as indicated in the figure from *N*-ethyl FOSE to PFOA has been suggested but not experimentally proven.

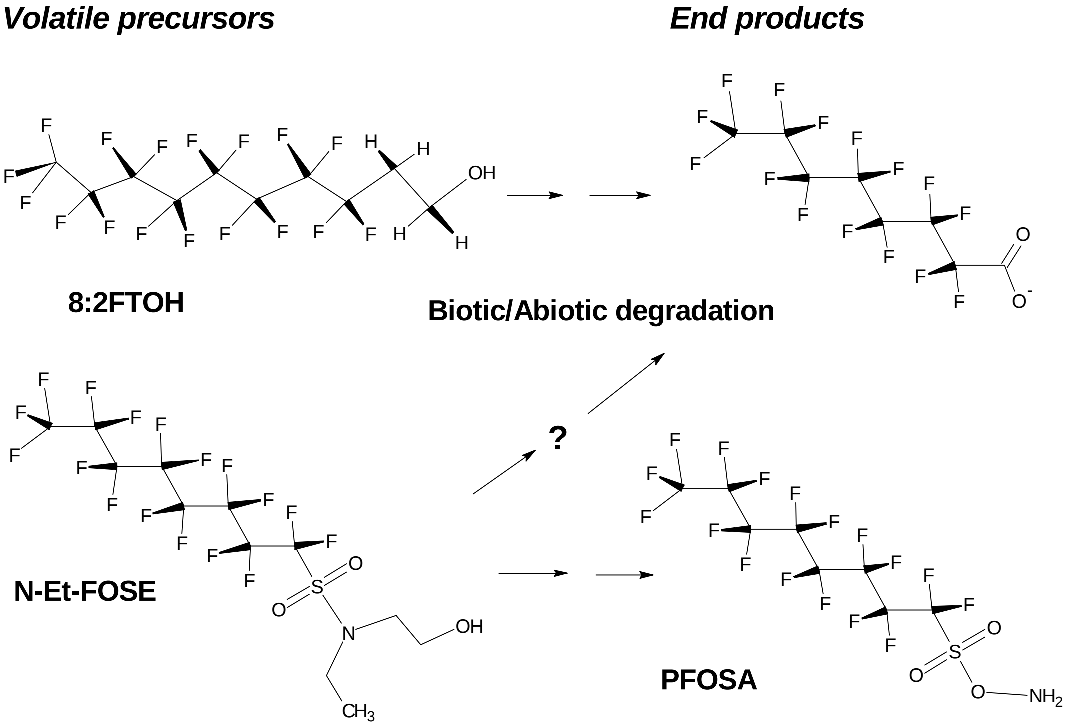


**Figure 8** Transformation of PFAS precursors.

The extent to which a release of monomeric PFAS can result from degradation of perfluoroalkyl-based polymers is debated. Generally, acrylates and adipates are considered to be the least chemically stable polymers with a lifetime of one year, while urethanes are much more stable. Investigations on degradation of polymers are currently being undertaken by the telomer research program (TRP; Du Pont, Asahi, Daikin) and an Italian research group and results are due the coming year.

## 10. Environmental investigations

This section summarizes all results available from several investigations performed within Sweden during the years 2001-2005. All data are listed in Table X in Annex 2.

### *10.1. Spatial trends*

In a survey of Swedish urban aquatic environments, fish muscle from perch, eelpout and dab caught close to the major cities were analyzed for PFOS and PFOA. No PFOA was detected in any of the samples. High PFOS concentrations (30-60 ng/g fresh weight) were found in L. Mälaren (Stockholm) and L. Hammarsjön (Kristianstad). Elevated PFOS concentrations (5-10 ng/g) were clearly associated with urban areas, while low concentrations (<1-4 ng/g fresh weight) were found in samples from lakes with no direct input from STP:s, industries or fire-fighting foam activities and in samples from remote marine sites.

A detailed urban gradient for PFOS in perch muscle was described for the waterways of L. Mälaren and the Stockholm archipelago where concentrations dropped by a factor of ten between stations in the interior waterways of Stockholm and stations farthest out in the archipelago (Fig.10).

Since all these data were based on muscle samples and most of the previously published data on fish were reported in liver tissue, a comparison was made between paired muscle and liver samples from almost all investigated sites. Close comparison showed that the liver-to-muscle PFOS concentration ratio varied slightly between individuals and between sites, but averaged 10 for ten individuals and the total set of samples. PFOS liver concentrations in the lower range (34-120 ng/g fresh weight) were found in samples from urban areas while the highest value was found in perch liver from L.Hammarsjön (670 ng/g). No liver samples from the remote sites were available. In comparison, low concentrations (0,5-3 ng/g) of PFNA were found in almost all samples, while one pooled liver sample from the L Hammarsjön showed slightly elevated levels compared to the other samples (6,3 ng/g). PFOA was found close to the detection limit only in the samples from the west coast of Sweden (0,5-0,9 ng/g).

The high values found in perch from L. Hammarsjön, Kristianstad were followed-up by a repeated sampling campaign of perch upstream and downstream and samples from the STP of Kristianstad. The results illustrate that in areas where a high discharge of sewage water occurs into a recipient of limited volume (shallow) and with a low water flow relative to flow of sewage effluent water, considerable concentrations accumulate in biota. Two municipalities discharge sewage water into the small river Helgeån. PFOS concentrations in fish liver samples taken downstream of the first city were elevated more than five times compared to fish from remote areas. Downstream of the second city levels were 4 times further elevated compared to background concentrations. The STP in Kristianstad, the second city, has been investigated in detail and did not show particularly high concentrations of PFAS. These STPs probably are representative of many Swedish STP without any industrial sources of PFAS.

Within the Nordic screening program conducted in 2003-2004 (Kallenborn 2004), cod and grey seal livers from the Baltic Sea were analysed. Cod liver from the coastal area of Skåne (Hanöbukten) showed almost 10 times higher PFNA concentrations (9 and 18ng/g, n=2) compared to cod liver from St Karlsö (0.5-0.9 ng/g), while PFOS concentrations were only slightly higher (23/62 and 6-20). The higher value from one Hanöbukten cod liver was from one male individual while the lower figure was found for a pooled sample of four females.

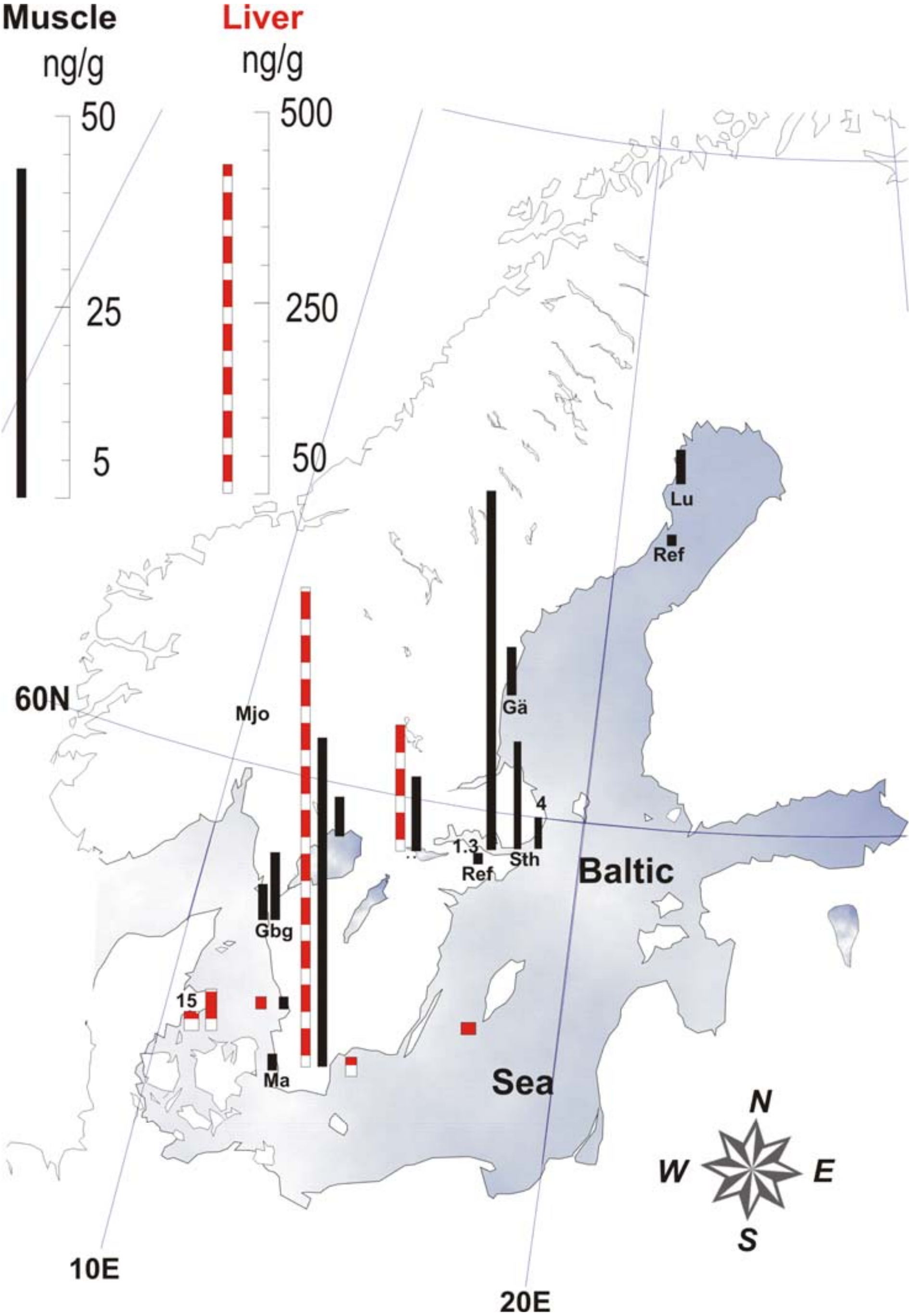


**Figure 9** Spatial trends of PFOS in fish muscle (black) and liver (striped red, 10 times scale of muscle concentrations)

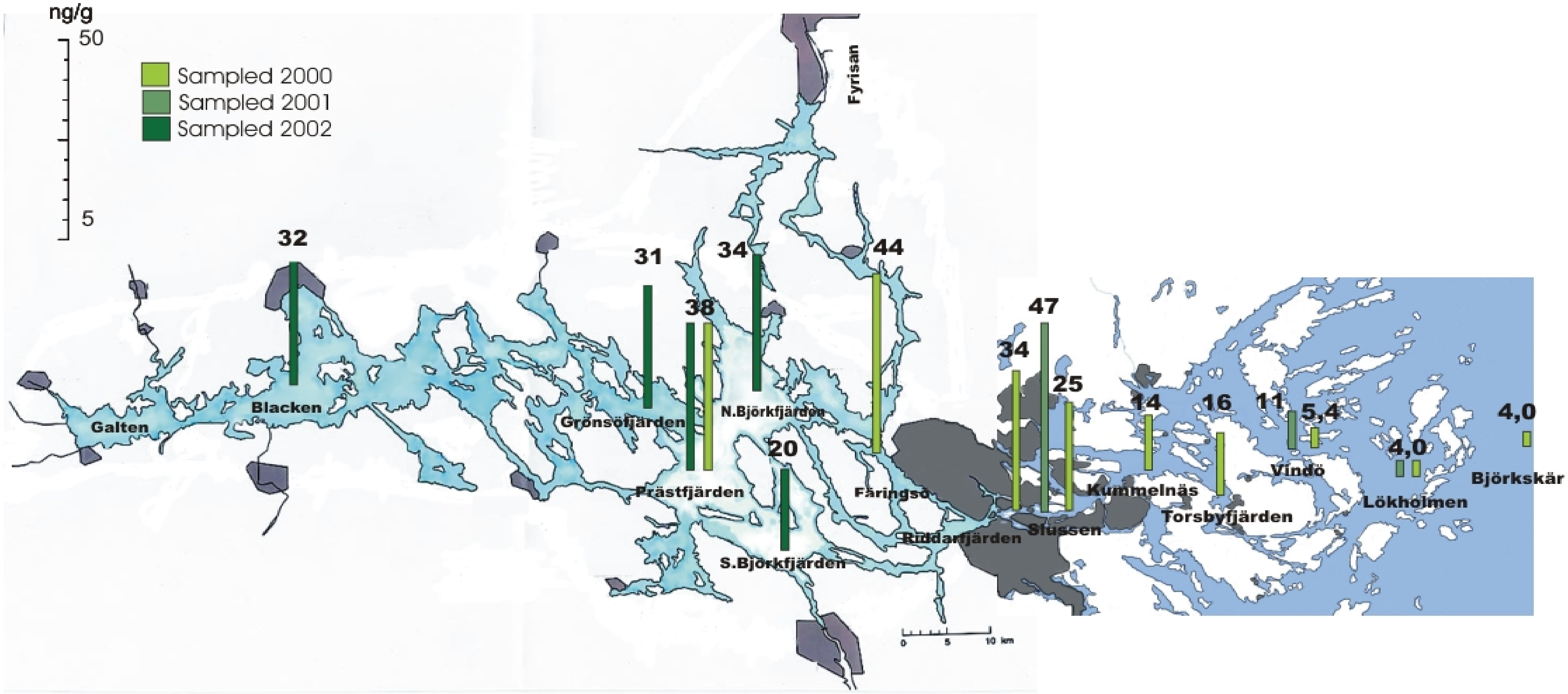


**Figure 10** Urban gradient of PFOS concentration in perch (*Perca fluviatilis*) muscle showing a tenfold decrease from highest values in L. Mälaren to remote stations in the outermost part of Stockholm archipelago.

PFOS data on grey seal liver indicated that concentrations are slightly higher in the southern part of the Baltic Sea as well as in the Skagerack (537 and 609-1054 ng/g respectively) as compared to the more northerly stations along the coasts of Gästrikland  and Uppland (331 and 422 ng/g). Although care was taken to prepare pooled samples of similar number, age of individuals and the same sex (males), the individual variation is unknown and may have influenced the results. However, previously published data on grey seal liver from the Bothnian Bay (120-360 ng/g, Kannan 2001) seem to support this trend.  PFNA concentrations in greyseal liver were tenfold lower than PFOS concentrations in the Baltic samples (29-36 ng/g) and even lower in the Skagerack samples (2.5-9 ng/g).

The highest concentrations of perfluoroalkylated acids measured so far in Swedish wildlife were recently encountered in freshwater otter (*Lotra lotra*). Total concentrations of all measured PFAS acids in otter liver ranged between 0.6 μg/g and 21 μg/g, of which PFOS alone accounted for 40 to 90 % and perfluorodecanoic and perfluoroundecanoic acid were frequently found at concentrations exceeding 100 ng/g. The concentrations found in the higher end of the range are approximately ten times higher than highest values found in liver of grey seal from the Swedish Baltic coastal area.

Sediment and settling particulate matter (SPM) from the inner parts of Stockholm and sediment from two reference lakes were analysed for PFOS and PFOA. No PFOA could be detected. PFOS concentration in sediment from the inner parts of Stockholm showed ten times higher PFOS values on a wet weight basis (0.3-0.6 ng/g **wet weight,** 1.2-2.7 ng/g **dry weight**) compared to the reference lakes (0.03-0.06 ng/g **wet weight**, 0.2-0.8 ng/g **dry weight**). The SPM samples showed only slightly higher concentrations (1.7-4.7 ng/g **dry weight**) compared to the corresponding sediment samples.

## *10.2. Urban sources*

### 10.2.1. Sewage treatment plants

Composite samples from two seven-day sampling periods of both influent and effluent sewage water as well as monthly composite samples of digested sludge from two sewage treatment plants (STPs) in Stockholm were investigated in 2001. PFOS was found in all samples (8-33ng/g dry weight, 7-57 ng/l). A more detailed survey was conducted in the year 2003 when influent and effluent water and sludge from four STPs were analyzed for 14 PFAS. The latter survey included plants receiving wastewater from industrial laundries and textile after-treatment mills. The results confirmed that although some PFOS was found in the sludge (4-42 ng/g dry weight, total PFAS concentration 15.5-267 ng/g dry weight), the major release pathway is through the effluent water (9-100 ng/l, total PFAS 76-850 ng/l), when translated into total emissions. The distribution between the aqueous and sludge phases is highly dependent on the chain length of the alkyl chain as illustrated in Table 9.

The concentration interval of PFOS in sludge samples are in excellent agreement with values reported by a German lab for sludge samples from 20 STPs in the southwestern part of Sweden in 2002 (<20-160ng/g dry weight). The investigation was performed by the regional authorities of Västra Götaland (Svensson, 2002) and two of the STPs were re-sampled and analysed 2003 in the detailed survey reported above.

**Table 9**. Ratio of amount released through effluent water to amount released through sludge for different PFAS in four municipal STPs

| | *PFHxA* | *PFHpA* | *PFOA* | *PFNA* | *PFDA* | *PFUnA* | *PFHxS* | *PFOS* |
|---|---|---|---|---|---|---|---|---|
| STP1 | 25 | 561 | 367 | 45 | 31 | 29 | 192 | 30.5 |
| STP2 | 3.6 | 65 | 4.7 | 51 | 20 | 1.1 | 258 | 46.8 |
| STP3 | 52 | 154 | 7.4 | 1.4 | 8.8 | 0.5 | 16 | 2.2 |
| STP4 | no data | 48 | 195 | 50 | 13 | 2.2 | 56 | 17.9 |

Assuming a total sewage water flow of 240000m$^3$/day through one of the major STPs to the Stockholm waterways, a yearly load of 2 kg PFOS can be estimated based on these values.

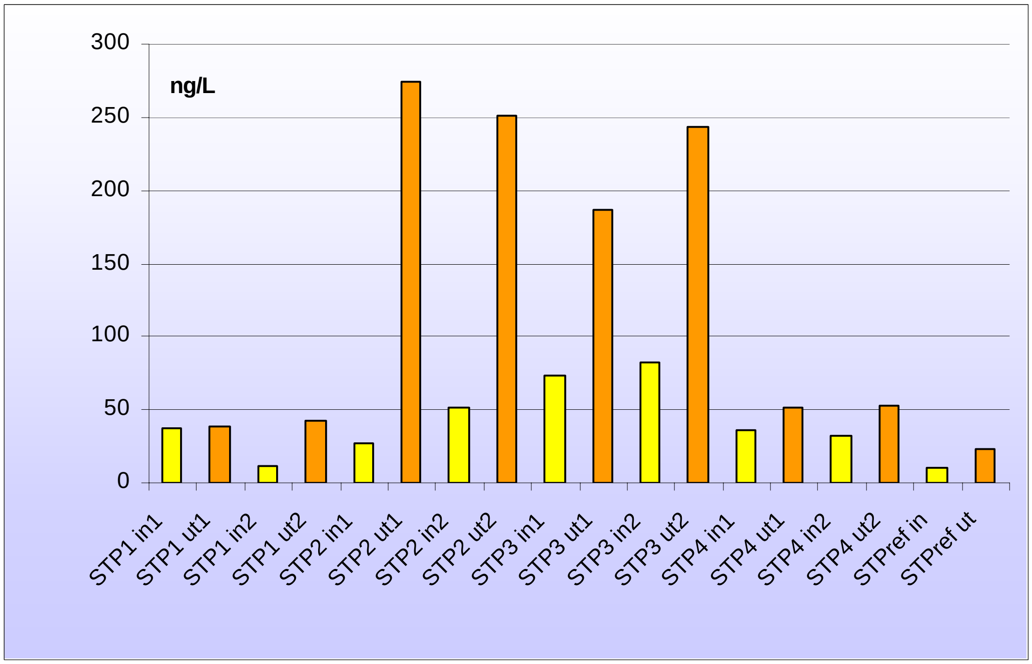


**Figure 11.** PFCA (Sum of $C_6$-$C_{10}$) concentrations in untreated influent (yellow bar) vs treated effluent (orange bar) water from five municipal STPs. Plants 1 through 4 were sampled on two separate occasions (index 1/2).

### 10.2.2. Textile treatment and industrial laundries

A distinctive feature was revealed for the perfluorocarboxylate concentrations in influent and effluent sewage water of all investigated plants. This finding was however particularly pronounced for the plants receiving process water from textile after-treatment mills (STP2&3). Higher values were found in the effluent water compared to the untreated influent water for the same sample period (see Figure 10). This feature has been confirmed by other research groups and may be attributed to the transformation of precursors to the acids during the sewage water treatment.

The perfluorocarboxylate profile in the process water of one of the mills could be clearly associated with the perfluorocarboxylate profile in the influent water of the receiving STP (see Figure 12). This typical isomer distribution is related to the use of textile impregnating formulations used in the process and present on the fabric and depends on the production process of the original monomeric PFAS chemical as described in the section on chemistry. In this case the profile was dominated by even-numbered isomers (Figure 13).

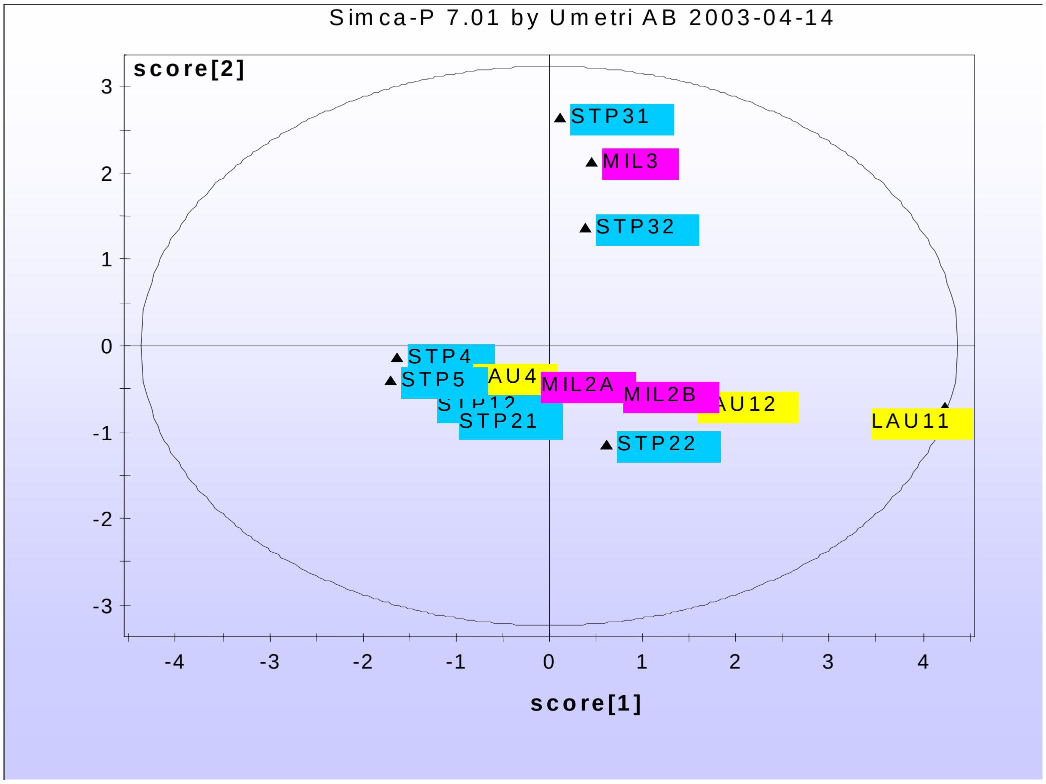


**Figure 12**. PCA-plot of perfluorcarboxylates ($C_6$-$C_{10}$) in water samples, illustrating a close association between effluent process water from the textile mill (MIL3) and untreated raw sewage water in plant 3 (STP31 &32). The textile mill is labeled pink, the industrial laundry yellow, and the STP blue. The circle describes a 95% confidence interval.

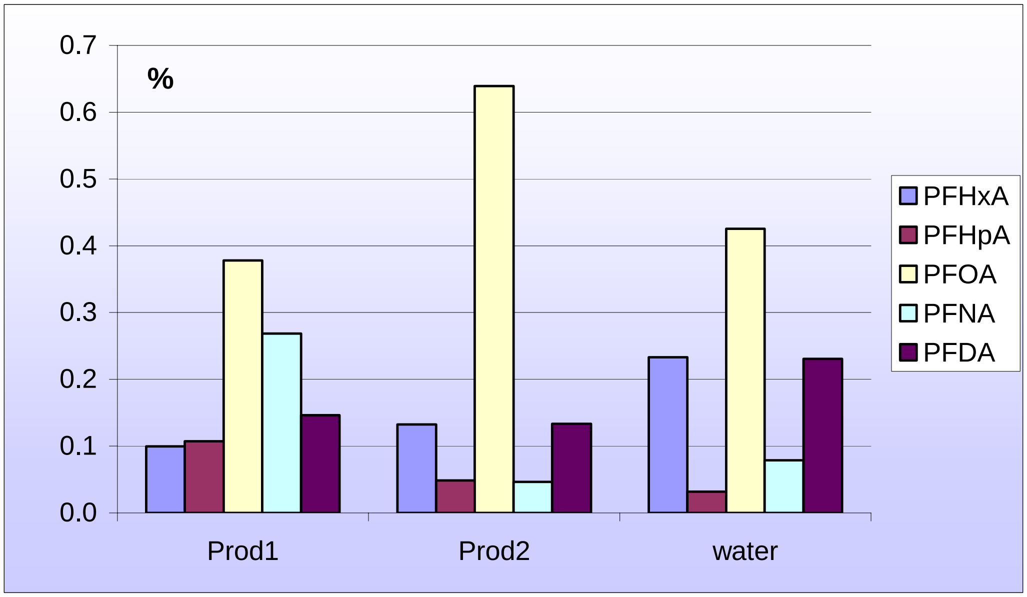


**Figure 13**. Perfluorocarboxylate isomer profile of an untreated influent water sample illustrating the close resemblance with the profile of one of the two impregnating formulations.

### 10.2.3. Landfill sites

Percolate water from two landfill sites currently in use were sampled in 2001. PFOS was found in high concentrations in all water samples (38-152 ng/l) compared to urban reference lake water (<0.5ng/l), while PFOA was not detected above the detection limit (6 ng/l). The highest concentrations were found in the aerated ponds.

## *10.3. Temporal trends*

Guillemot eggs were collected annually in early to mid May and transported to the Swedish Environmental Specimen Bank. The guillemot eggs used in this study were collected on Stora Karlsö (56 53' N 18 38' E). Eggs from approximately every third year between the years 1968 and 2003 were analyzed for PFOS and PFOA.
A clear increase in PFOS concentration was seen during the time period studied, from 25 ng/g in 1968 to 614 ng/g (wet weight) in 2003. During 1997-2000 a peak in PFOS concentrations was observed (1260 ng/g), after which concentrations fell to levels that in 2003 were comparable with levels in 1996 (see Figure 14). For further information see Holmström et al. (2005).

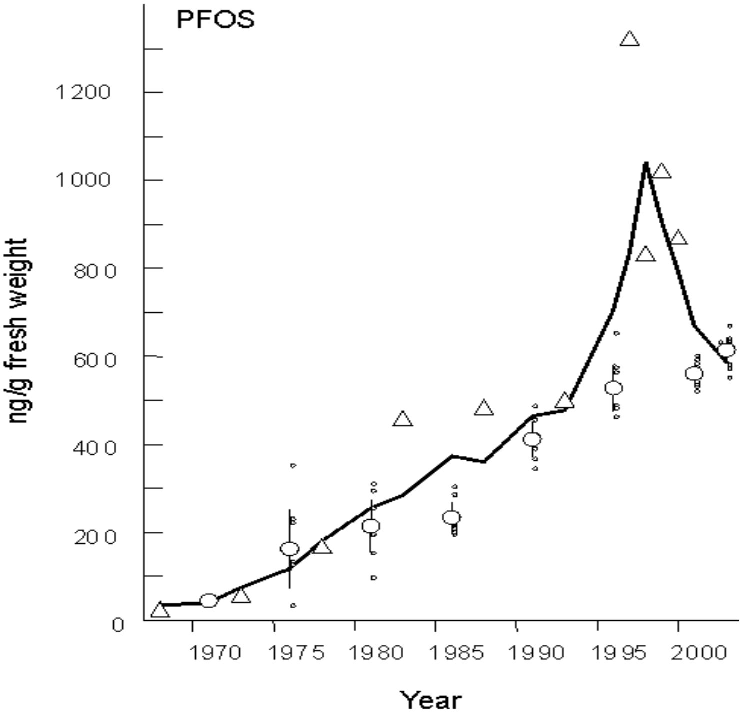


**Figure 14:** Temporal trend of PFOS in Baltic Guillemot eggs indicating an average 7-11% yearly increase during the period 1971-2003 (Holmström, 2005). Yellow circles represent individual values and white represent values obtained from pooled samples of 8 individuals.

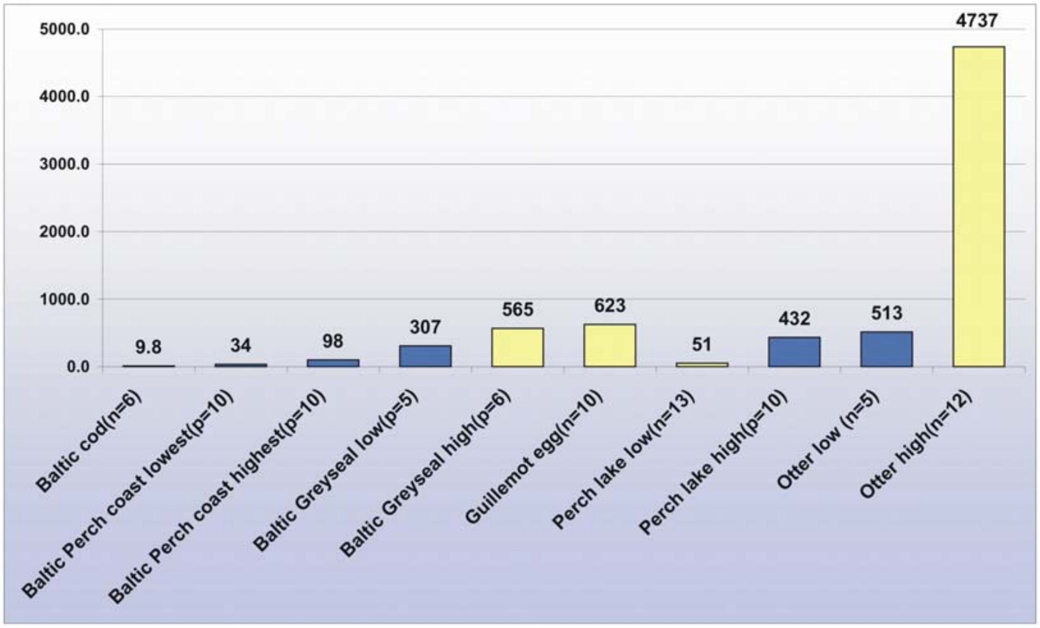


**Figure 15**. Comparison of PFOS concentrations in liver of fish predators and fish (except Guillemot) illustrating trophic level transfer. Pooled samples designated by p= and averaged data by n= respectively.

## *10.4. Biomagnification*

Persistent organic pollutants typically are reported on a fat weight basis and estimates of transfer efficiency between trophic levels in food chains are based on lipid normalized or organic carbon content. Perfluorochemicals do not distribute in a similar manner to lipid rich tissues but are instead found at the highest concentration in blood rich tissues i.e. liver, kidney and brain. So far no convention exists on the normalization of perfluorochemical concentrations and trophic transfer efficiencies (biomagnification factor, BMF) can thus not be calculated. Although liver concentrations cannot strictly be compared between species, comparison of concentrations in fish and predators usually suggest a strong magnification. This can be illustrated by a comparison of concentration ranges in Swedish fish vs. guillemot, greyseal and otter (Figure 15). As illustrated, the highest values are encountered in freshwater species. As pointed out previously, the highest concentrations found in otter are roughly ten times those of greyseal, while the highest values found in freshwater perch are approximately ten times higher than those of coastal perch.

## *10.5. Point source distribution*

### 10.5.1. Fire fighting foam use

A firefighting training site was studied. The investigation area is depicted in Figure 16. The site was chosen for several reasons. Various fire brigades have been using the training field for many years. Furthermore, it was initially expected that several different brands of fire-fighting foams would have been used at the field, and thus that the probability of finding fluorochemicals would be high. The Swedish Rescue Services Agency (SRSA) also keeps a record on the use of chemicals and water flow through the field, and willingly enabled complimentary information to be accessed. They had previously carried out studies on environmental impact of fire fighting surfactants.

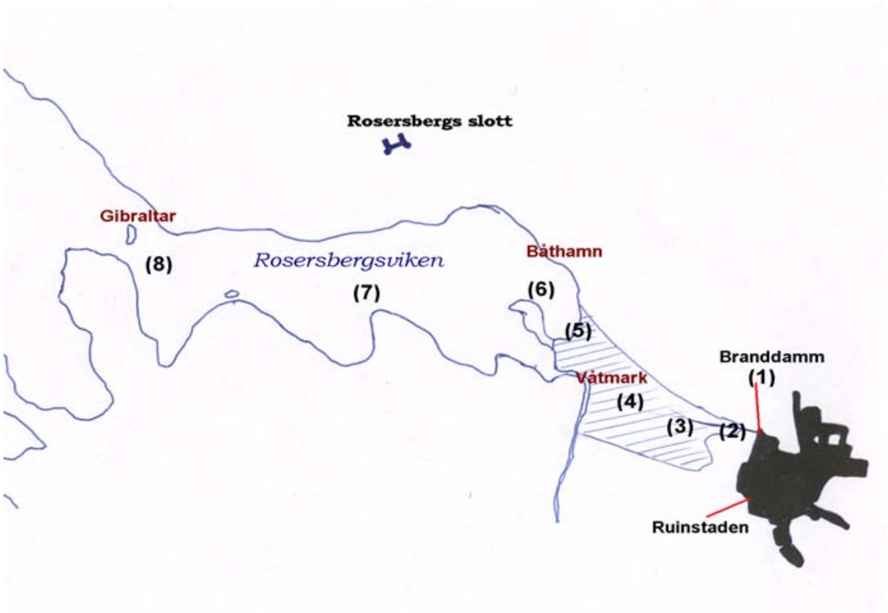


**Figure 16.** Sketch of the fire fighting trainings site close to the Rosersberg cove

Runoff water from the training field is collected in a pond. The water overflows into a ditch and infiltrates into a wetland, from where it leaches into Rosersberg Cove. The sampling points are shown in Figure 16. Samples were collected on two occasions: during the autumn of 2001, and during the spring of 2002 (see Table 10). In addition, weekly-integrated water samples from the pond (1) were taken at five occasions by the SRSA during 2002. At points (3) and (4), samples were collected at transects across the wetland and prepared as pooled samples of five equal volumes of surficial water. At point 7 water was sampled at the surface approximately 0-2 cm to include a possible surface film and at 20 cm depth were the surface film was carefully avoided. Surface sediment was collected at three points (5,6,7) using a core sampler and carefully selecting the top layer (0-2cm). The water depth varied between 2.5 m and 3 m.

**Table 10.** Sampling scheme

| *Location description* | *Location number* | *Sample type* | *Time* |
|---|---|---|---|
| Pond | (1) | water | autumn 2001/2002 |
| Ditch 10 m downstream | (2) | water | autumn 2001 |
| 100m into wetland | (3) | water | autumn 2001 |
| 200m into wetland | (4) | water | autumn 2001 |
| Shore | (5) | water | autumn 2001 |
| Leisure boat harbour | (6) | water/sed | spring 2002 |
| Centre of cove | (7) | water/sed | spring 2002 |
| Gibraltar, outer point | (8) | sed | spring 2002 |

### 10.5.2. Results

The results are summarized in Table 11. Compared to one reference lake (L. Insjön, S-E of Stockholm, PFOS<0.5 ng/l) the PFOS concentrations were elevated in all water samples. The highest concentrations in surface water at the first sampling event were found in the center of the wetland (4; 1 ug/L), which may indicate that the pollution source is historical. PFOS is still leaching from the training site and the values found in the effluent collected at five occasions during one year indicate that the concentration is dependant on dilution by runoff from the training site during use, since the highest value was obtained during training intermission at a low water flow. The sediment concentration rapidly decreased from 6.5 ng/g at the point close to the outlet from the wetland (6) to below the detection limit of 0.05 ng/g at the outermost point at the outlet of the cove (8)

PFOA was present at low concentrations in several of the water samples but not in the sediment samples. The small fraction of PFOA compared to PFOS found in water samples probably reflects the trace content of PFOA present in AFFF products which are based on PFOS. This indicates that no PFOA-based foams were used.

**Table 11.** PFOS and PFOA concentrations in water and sediment samples from the fire fighting training site.

| | PFOS µg/l | PFOA µg/l |
|---|---|---|
| Surface water | | |
| Pond (1) | | |
| (2001-10-30, during training) | 0.2 | 0.04 |
| (2002-01-14, during intermission) | 2.1 | 0.04 |
| (2002, first quarter) | 0.84 | 0.005 |
| (2002, second quarter) | 1.7 | 0.04 |
| (2002, third quarter ) | 0.65 | 0.09 |
| (2002, fourth quarter) | 1.0 | 0.05 |
| Ditch (2001-10-30) (2) | 0.3 | 0.04 |
| 100m into wetland (2001-10-30) (3) | 0.4 | 0.03 |
| 200m into wetland (2001-10-30) (4) | 1.0 | 0.03 |
| Shore (2001-10-30) (5) | 0.05 | <5ng/l |
| Leisure boat harbour (spring 2002) (6) | 0.05 | <2ng/l |
| Centre of cove; 0-2 cm (spring 2002) (7) | 0.06 | 2.5ng/l |
| Centre of cove sub-surface 20 cm (spring 2002) (7) | 0.03 | <1ng/l |
| Sediment | PFOS ng/g | PFOA ng/g |
| Leisure boat harbour (spring 02) (6) | 6.5 | <0.05 |
| Centre of cove (spring 02) (7) | 1.1 | <0.05 |
| Gibraltar, outer point (spring 02 (8) | <0.05 | <0.05 |

## 11. Human exposure

The routes of human exposure to PFAS are still poorly understood. Occupational exposure in production plants clearly gives rise to blood concentrations that are elevated by several orders of magnitude (ppm vs ppb). The principles governing human tissue distribution are largely unknown, except that PFOS and PFOA do not distribute into lipid tissue like classical POPs but rather associate with liver and blood proteins. Hence, blood and in particular serum has been the matrix commonly analyzed for PFOS/PFOA in humans. Liver to serum concentration ratios for humans have been reported for a limited number of individuals and indicate a ratio of 1.3 (Olsen 2003) For other PFAS like the less polar PFOSA and *N*.ethylPFOSA, whole blood measurements might be more suitable.

### *11.1. Dietary exposure*

The exposure through food has not been investigated in detail except for a limited food basket study on PFOS performed by the 3M company in the U.S.A. This study did not show any detectable concentrations of PFOS in any of the food items (3M 2001). A more recent independent study showed a clear time trend of precursors to PFOS (perfluorooctane sulfonamides; *N*-ethyl-PFOSA and PFOSA) in archived fast food samples (Tittlemier 2003). The authors concluded that prior to the phase-out of PFOS chemicals in 2002, dietary intake of *N*-ethylPFOSA was a significant route of human exposure. Considering the pronounced biomagnification of PFOS as indicated from available aquatic food web studies, dietary exposure from fish, and in particular fresh water fish, should be considered.

## 11.2. Exposure to volatile precursors or dust

Although most PFAS are not considered volatile, particle mediated exposure and exposure to volatile precursors such as alcohol derivatives (e.g. perfluorooctane sulfonamide-alcohols and telomer alcohols) may be possible routes of human exposure. In particular, exposure to aerosols during application of PFAS impregnating products can be expected to be a route of exposure, but this has not been investigated. The presence of volatile precursors has been verified in indoor air and PFOS has been found on indoor dust particles (Moriwaki 2003, Kubwabo 2005).

## 11.3. Measurements in human blood

### 11.3.1. Fish consumer study

Whole blood samples from 108 Swedish women with a varying fish intake were analyzed for PFOS and PFOA (Berglund 2004). This group of high-consumers was defined as people who eat fish several times each week. Details on food intake were recorded by each subject. The average concentrations found were 17.7 for PFOS and 1.3 for PFOA. The ranges were 3-67 for PFOS and 0.4-4.8 for PFOA. No correlation was found between PFOS of PFOA concentration in whole blood and total fish intake. A significant positive correlation ($p<0.01$) was found between PFOS and intake of fresh water predatory fish species and seafood. The concentration of PFOA was significantly correlated with the PFOS concentration as illustrated in figure 17.

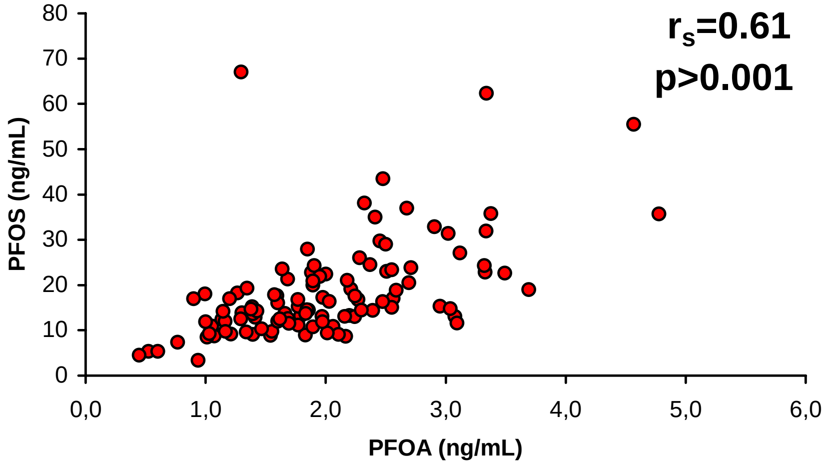


**Figure 17.** Concentration of PFOA vs concentration of PFOS in whole blood of humans showing a significant correlation between the two acids.

### 11.3.2. Average population

The levels of five perfluoroalkylated compounds (PFOS, PFOA, PFHxS, PFOSA and PFNA) were determined in whole blood and plasma from 47 males and 36 females (66 whole blood samples and 17 plasma samples) representing the average Swedish population (Kärrman 2004). The studied samples were control samples (sons and mothers) in a testicular cancer study (MPR 2336) drawn from the Swedish population registry (Stockholm, Sweden), and collected during 1997-2000. The average concentrations found in whole blood were 18.2 ng/ml (PFOS, 1.7-37.0) and 2.7 ng/ml (PFOA, 0.5-12.4). Regarding the plasma samples, the average PFOS concentration was highest (33.4 ng/ml) followed by PFOA (4.0 ng/ml). The frequency distributions of PFOS in whole blood as displayed in Figure 18 illustrates that PFOS and PFOA concentrations show an almost perfect normal distribution. Levels of PFOS in both men and women are consistent with a Gaussian distribution based on the Shapiro-Wilk normality test. For PFOA only levels in women meet such criteria. This is in contrast to concentrations of other persistent organic pollutants (POP:s) which generally show a skewed (log-normal) distribution.

The range in PFOS concentration in these studies was relatively small compared to previously published data, which indicates that no occupationally exposed person was included in these studies. One outlier was found for PFOA in the data set. Other PFAS were also detected in the ‘normal’ population and measurable amounts of PFHxS, PFNA, PFUnDA were found in almost all samples in addition to PFOSA. This sulfonamide seems to have a different distribution pattern in human blood as compared to the sulfonic acid and carboxylic acids (Kärrman 2006). No data are yet available for many of the other PFAS and reliable analytical methods for a large number of the compounds are not available.

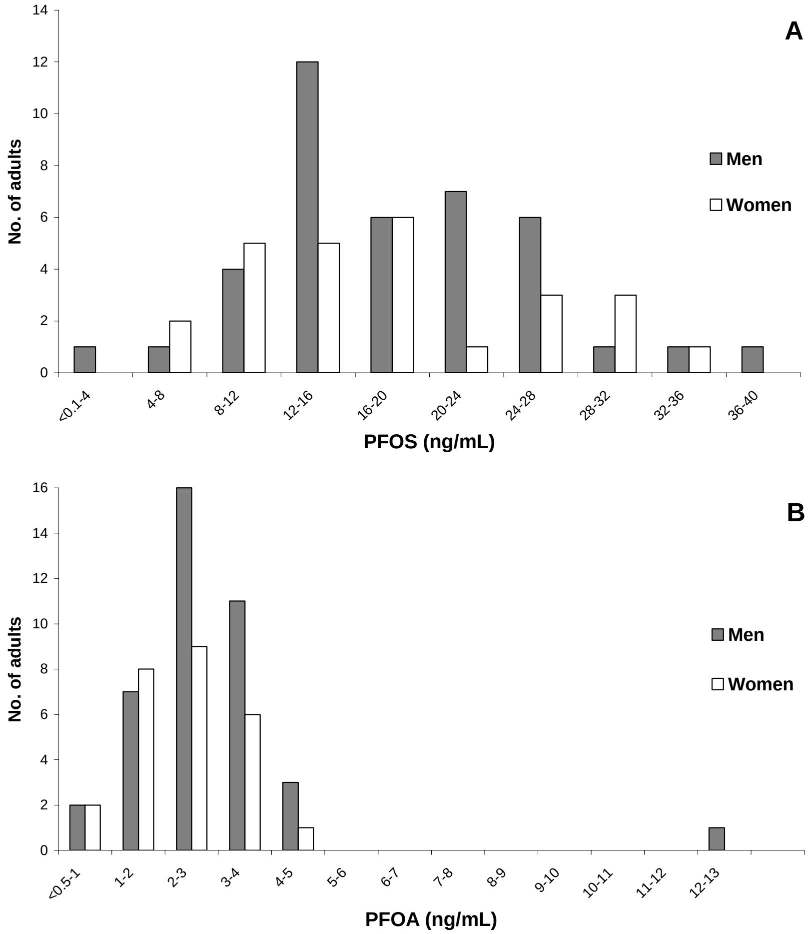


**Figure 18.** Frequency distribution of concentrations in whole blood samples from the Swedish population for PFOS (A) and PFOA (B).

## *11.4. Transfer of perfluorochemicals through lactation*

A recent study on matched human milk and serum samples from primipara women in Sweden showed relatively low concentrations of perfluoroalkylated substances in milk compared to serum (Kärrman 2006). The average total concentration of the measured PFC:s in milk was 0.34ng/ml compared to 32ng/ml for serum. Expresssed on a daily intake basis however, these results indicate a daily intake of 200ng of the measured substances, which suggests that childrens exposure to PFAS through breast feeding need to be further assessed.

## 12. Conclusions and recommendations for future studies

PFOS is present at relatively high levels in the Swedish wildlife considering the fact that no primary sources are located in Sweden. PFNA is generally found at much lower levels (1/10) while PFOA is even lower and mostly below detection limit.

The extremely high concentrations of PFOS found in some individuals of otter can be expected on the basis of the high efficiency of trophic level transfer indicated by the concentration ratios between Baltic fish to seal or Baltic fish to Guillemot egg and the elevated concentrations found in several freshwater fish samples. No data on PFAS in biota from contaminated sites or recipients receiving water from STPs with elevated PFAS concentrations are yet available for Sweden, but results from other European areas indicate extremely high concentrations in biota from contaminated areas. Future studies should include food web studies of recipients with a slow turnover and a high on-going load of perfluorocarboxylates from STPs. The highest concentrations of PFOS in top predators, in particular otter, in Sweden approach the interval where reproduction effects have been observed in rat exposure studies (Predicted No-Effect Concentration, PNEC: 10.7 ug/g wet weight of liver, 3M 2003). Subtle effects on critical early development stages may show out at considerably lower levels (Hoff 2005).

The present levels of PFAS in human blood, as indicated from the limited studies performed so far, are lower than those found in wildlife samples. However, since liver is a target organ in animals, a relation between liver and blood levels in human needs to be established in order to provide necessary background for risk assessment in humans. The general population shows levels of PFOA and PFOS that are somewhat lower than in the US, but are among the highest in Europe. Both PFOS and PFOA show a nearly perfect normal frequency distribution, in contrast to the traditional POPs, and in contrast to data from the US population (3M 2003). This may indicate that no occupationally exposed individuals have yet been studied. Occupational settings where exposure to precursor compounds can take place are present in Sweden and should be included in future studies.

Sources for PFAS in Sweden are effluent water from municipal sewage treatment plants, leakage from waste disposal sites and sites where firefighting foam has been used. Industrial use of textile and leather impregnating formulations result in elevated concentrations of perfluorocarboylates in effluent water from sewage treatment plants.

Exposure routes and distribution behavior are yet incompletely described for many PFAS and their precursors. Environmental levels, human levels and human exposure data are lacking for a wide variety of PFAS discussed in this report.

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## *13.2. Other sources of information:*

**Government sites, fluorochemical manufacturers, retailers and suppliers web sites:**

U.K. Department for Food and Rural Affairs, DEFRA: http://www.defra.gov.uk
U.S Environmental Protection Agency: www.epa.gov
Government of Canada: http://canadagazette.gc.ca/index-e.html
Australian Government, National Industrial Chemicals Notification and Assessment Scheme – NICNAS: nicnas.gov.au
Atofina: www.atofina.com
Ciba-Geigy: www.cibasc.com
Miteni Spa: www.miteni.it/
Fluorine: www.fluorine.ru
Daikin: www.daikin.com
Du Pont: www.dupont.com
3M Company:mmm.com
Clariant: www.clariant.com
Bayer: www.bayer.com
Dyneon: www.chemie.de
www.kidde-fire.com
www.angusfire.co.uk
Rudolph GmbH: www.rudolf.de

## *13.3. List of contributing organizations, companies and persons*

US-EPA (CD-ROM and e-dockets documentation on PFOS and PFOA)
Swedish Rescue Services Agency (Statens Räddningsverk)
Robert Buck, Du Pont USA
Dietrich Sinnaeve, 3M, Belgium, Specialty Materials Markets Europe & MENA
Sveriges Färgfabrikanters Förening SVEFF
Stora-Enso
Stockholms Brandförsvar
DAFO Brand AB (Werner)
Tempus Svenska AB
NOHA Försäljnings AB
Kemibolaget
Ragnsells

## Annex 1.Chemicals and methods used

*Chemicals*
Perfluorohexane sulfonate, potassium salt (98%, Interchim), perfluorooctane sulfonate, potassium salt (98%, Fluka), perfluorodecane sulfonate, 37% aqueous ammonium solution (97%, Aldrich), perfluorohexanoic acid (>97%, Fluka), perfluoroheptanoic acid (99%, Aldrich), perfluorooctanoic acid (96%, Aldrich) perfluorononanoic acid (97%, Aldrich), perfluorodecanoic acid (>97%, Fluka), perfluoroundecanoic acid (95%, Aldrich) and perfluorooctane sulfonamide (97%, ABCR) were used for quantification. Methyl-tertiary butyl ether (MTBE, 99.5%) was purchased from Fluka. Methanol used for extraction and as HPLC eluent was of HPLC grade (Hipersolv, BDH), and water was laboratory produced ultra-pure reagent water (MilliQ, Millipore corp.). Tetrabutyl ammonium sulfate (analytical grade) was obtained from Merck (WWR International). The technical product FC-203 containing technical PFOS was obtained as a kind gift from the 3M company (Ghent, Belgium) and was used as reference material for evaluation of the method.

*Methodology*
The methods for water, sediment, settling particulate matter and sewage sludge were developed to account for the fact that PFAS are relatively water soluble but also distribute to particulate matter. Thus, water samples were thoroughly shaken before subsamples were taken and analysed for total content, dissolved and particulate bound PFAS.

Sediment, settling particulate matter and sewage sludge samples were extracted, without prior removal of water, using methanol in an ultrasonic bath for 30 minutes. The methanol was evaporated under nitrogen and MilliQ-water was added to constitute approximately 50 ml. The aqueous extract was washed with n-hexane in two steps (pH 8 and 4 respectively) to remove matrix components after which the extract was treated as the water samples

Water samples, usually 200 ml, were concentrated on solid phase extraction cartridges (SPE) containing porous graphitic carbon (Hypersep, Thermoquest) and eluted with 11 ml methanol into a polypropylene tube. The methanol was gently evaporated using nitrogen until only water remained and the volume adjusted to approximately 1 ml. The aqueous extract was taken to ion-pair extraction.

Biological samples were homogenized in MilliQ-water with an Ultra-Turrax mixer. The sample is diluted six times (5+1) with MilliQ water in this step. From this homogenate, exactly 1 ml is taken to ion-pair extraction. Blood, serum and human milk samples were extracted either by ion-pair extraction as described below or by an SPE-method as described in detail elsewhere (Kärrman, 2004, 2006)

The aqueous extracts were extracted by ion-pair extraction as described by Hansen et al (2001) and Ylinen et al (1997). One ml extract was mixed with two ml of a 1M sodium carbonate buffer and one ml of a 2mM tetrabutylammonium solution adjusted to pH=10 by sodium hydroxide. The mixture was vortex mixed for 20 sec and then five ml methyl tertiary butyl ether (MTBE) was added and the tube gently turned for 20 minutes. The MTBE was quantitatively transferred to a secondary PP-tube and another five ml MTBE portion added to the first tube and the procedure repeated. The combined MTBE extract was then gently evaporated until dryness using dry nitrogen and exactly 500µl methanol added. All extracts were finally filtered through a 0.46µm PP-filter prior to LC/MS determination.

Samples were quantified on a LC/MS system (Micromass Quattro II) using either selected ion recording (SIR) of the ions 499 and 369 for PFOS and PFOA respectively or MRM (MS/MS) argon as a reaction gas and measuring the transitions 399-99, 499-99/80 599-99 for PFHxS, PFOS, PFDS and 313-269, 363-319, 413-369, 463-419, 513-469, 563-519 for PFHxA, PFHpA, PFOA, PFNA, PFDA and PFUnA respectively and 498-78 for perfluorooctane sulfonamide. The MS/MS instrumental conditions were as described by Giesy and Kannan (2001) and tuned for maximum sensitivity of each substance. Quantification was done by standard addition using spiked and extracted samples. The calibration curve was generally linear over the quantification range (r2>0.98).

Instrumental conditions for human serum and milk samples are described in detail in Kärman et al 2005& 2006. In  short, single quadrupole MS (HP/Agilent 1100 LC-MSD system) using the deprotonized (M-1; 313; 363; 413; 463; 513; 563) molecular ion for quantification was shown to be adequate for these sample types.

## Annex 2. Sample information and results (environmental samples).

**Concentrations of perfluoroalkyl sulfonates and –carboxylates in biological samples.** All results are given on a wet weight basis and based on pooled samples unless specifically stated. All values are corrected for recovery. Detection limit is approximately 0.5ng/g for fish samples. Range is given in brackets for samples from individuals.

| *Location* | *Year* | *species* | *pooled (#)* | *weight (g)* | *length (cm)* | *PFOS ng/g muscle* | *PFOS ng/g liver* | *PFNA ng/g liver* |
|---|---|---|---|---|---|---|---|---|
| Luleå | | | | | | | | |
| Svartösundet | 2001 | Perch | 4 | 216.5 | 282.9 | 4.5 | 82 | 0.9 |
| Svartösundet | 2001 | Pike | 3 | 219.8 | 322.7 | 2.9 | | |
| Krokabusk | 2001 | Perch | 5 | 92.9 | 199 | 6.4 | 109 | 1 |
| Umeå | | | | | | | | |
| Holmöarna | 2001 | Perch | 10 | 102.1 | 193 | 1.3 | | |
| Gävle | | | | | | | | |
| Inre fjärden | 2001 | Perch | 10 | 332.6 | 287.4 | 3.6 | 88 | 1.4 |
| Yttre fjärden | 2001 | Perch | 10 | 56.7 | 158.1 | 3.5 | 34 | <0.7 |
| Hallstavik | 2003 | Perch | 10 | | | | 81 | 3 |
| Karlstad | | | | | | | | |
| Alstergrund | 2001 | Perch | 10 | 137.8 | 222.6 | 5.5 | | |
| Jäverön | 2001 | Perch | 10 individuals | 140.5 | 229.3 | 5.0 (3.8-9.9) | 51 (44-68) | |
| Örebro | | | | | | | | |
| Hemfjärden inner | 2002 | Perch | 10 | 69,6 | 187.7 | 8.4 | 120 | <0.7 |
| Hemfjärden remote | 2002 | Perch | 10 | 77,9 | 179.6 | 10 | 173 | <0.7 |
| L. Mälaren | | | | | | | | |
| S.Björkfjärden | 2002 | Perch | 10 | 53.7 | 174.7 | 20 | | |
| N.Björkfjärden | 2002 | Perch | 10 | 52.2 | 169.9 | 34 | | |
| Prästfjärden | 2002 | Perch | 25 individuals | 57.3 | 174.2 | 37 (21-52) | | |

| *Location* |  | *Year* | *species* | *pooled (#)* | *weight (g)* | *length (cm)* | *PFOS ng/g muscle* | *PFOS ng/g liver* | *PFNA ng/g liver* |
|---|---|---|---|---|---|---|---|---|---|
| Grönsöfjärden |  | 2002 | Perch | 10 | 53 | 173 | 31 |  |  |
| Blacken |  | 2002 | Perch | 10 | 56 | 171 | 32 |  |  |
| Stockholm |  |  |  |  |  |  |  |  |  |
| Slussen |  | 2001 | Perch | 10 | 348.2 | 275.4 | 41 |  |  |
| Vindön |  | 2001 | Perch | 3 | 326.3 | 387.3 | 9.1 |  |  |
| Lökholmen |  | 2001 | Perch | 1 | 215.1 | 260 | 3.4 |  |  |
| Himmerfjärden |  | 2003 | Perch | 10 |  |  |  | 98 | 2.4 |
| Regional background lakes, Stockholm |  |  |  |  |  |  |  |  |  |
| L. Yngern |  | 2001 | Perch | 10 | 387 | 301.8 | 1.24 |  |  |
| L. Vällingen |  | 2001 | Perch | 10 | 345 | 279.8 | 1.7 |  |  |
| Göteborg |  |  |  |  |  |  |  |  |  |
| Göta Älv, inner |  | 2001 | Eelpout | 7 | 55 | 239 | 5.8 |  |  |
| Göta Älv, remote |  | 2001 | Eelpout | 6 | 39.9 | 219.7 | 2 |  |  |
| Halmstad |  |  |  |  |  |  |  |  |  |
| Laholmsbukten |  | 2002 | Flounder | 10 | 221.9 | 275.1 | 1.3 | 22 | 0.88 |
| Nissan |  | 2002 | Ide | 1 | 998.6 | 420 | 40 |  |  |
| Malmö |  |  |  |  |  |  |  |  |  |
| Klagshamn |  | 2001 | Eelpout | 10 | 93.3 | 283.3 | 1.3 | 22 | 1 |
| Öresund |  | 2001 | Eelpout | 10 | 85.2 | 269.7 | 3.3 | 34 | 2.2 |
| Kristianstad |  |  |  |  |  |  |  |  |  |
| L. Hammarsjön |  | 2001 | Perch | 10 | 161.2 | 66 | 672 | 0.7 |  |
| Gummastorpasjön |  | 2003 | Perch | 10 |  |  | 172 | 0.23 |  |
| Araslövssjön |  | 2003 | Perch | 10 |  |  |  | 172 | 0.63 |
| Hammarsjön Ö |  | 2003 | Perch | 10 |  |  | 427 | 1.5 |  |
| Hammarsjön N |  | 2003 | Perch | 10 |  |  | 169 | 6.3 |  |
| L. Bolmen |  | 2001 | Pike | 10 | 1255 | 57.5 |  | 24.9 |  |

| *Location* | | *Year* | *species* | *pooled (#)* | *weight (g)* | *length (cm)* | *PFOS ng/g muscle* | *PFOS ng/g liver* | *PFNA ng/g liver* |
|---|---|---|---|---|---|---|---|---|---|
| <u>Baltic Sea</u> | | | | | | | | | |
| Hoburgen | | 2003 | Cod | 6 individuals | | | | 9.8 (6.4-20) | 0.7 (0.5-0.9) |
| Hoburgen | | 2003 | Cod, female | 5 | | | | 23 | 9 |
| Hanöbukten | | 2003 | Cod, male | 1 | | | | 62 | 18 |
| | | | | | | | | | |
| <u>BEEP-samples Stockholm gradient</u> | | | | | | | | | |
| Adelsö | | 2000 | Perch | 20 | | | 38 | | |
| Färingsö | | 2000 | Perch | 20 | | | 44 | | |
| Riddarfjärden | | 2000 | Perch | 20 | | | 34 | | |
| Slussen | | 2000 | Perch | 20 | | | 25 | | |
| Kummelnäs | | 2000 | Perch | 20 | | | 14 | | |
| Torsbyfjärden | | 2000 | Perch | 20 | | | 16 | | |
| Vindön | | 2000 | Perch | 20 | | | 5.4 | | |
| Lökhomen | | 2000 | Perch | 20 | | | 4 | | |
| Björkskär | | 2000 | Perch | 20 | | | 4 | | |

Concentrations of perfluoroalkyl sulfonates and –carboxylates in Baltic guillemot egg. Values are given in ng/g fresh weight.

| *Collection date* | *egg length, mm* | *Total egg weight, g* | *PFOS* |
|---:|---:|---:|---:|
| 19680530 | | | 17 |
| 19710520 | 87.2 | 108.9 | 44 |
| 19710520 | 84.3 | 112.2 | 34 |
| 19710520 | 79.1 | 94.6 | 55 |
| 19710520 | 86.5 | 108.3 | 47 |
| 19710520 | 82.8 | 99.5 | 39 |
| 19710520 | 86.1 | 120.9 | 48 |
| 19710520 | 86.8 | 104.2 | 45 |
| 19710520 | 87.2 | 124.0 | 42 |
| 19730511 | | | 45 |
| 19760530 | 78.9 | 83.4 | 33 |
| 19760530 | 85.2 | 79.1 | 133 |
| 19760530 | 81.9 | 84.6 | 221 |
| 19760530 | 80.7 | 102.2 | 125 |
| 19760530 | 79.4 | 79.9 | 351 |
| 19760530 | 87.1 | 101.1 | 230 |
| 19760530 | 87.4 | 89.3 | 32 |
| 19760530 | 89.8 | 106.7 | 170 |
| 19780512 | | | 139 |
| 19810601 | | | 254 |
| 19810601 | | | 96 |
| 19810601 | 90.9 | 107.7 | 195 |
| 19810601 | 79.9 | 97.3 | 193 |
| 19810601 | 78.0 | 102.8 | 152 |
| 19810601 | 85.7 | 98.2 | 219 |
| 19810601 | 83.5 | 89.9 | 309 |
| 19810601 | 80.6 | 93.9 | 294 |
| 19830515 | | | 346 |
| 19860519 | 87.8 | 117.2 | 208 |
| 19860519 | 78.6 | 95.1 | 216 |
| 19860519 | 84.6 | 103.7 | 200 |
| 19860519 | 84.4 | 97.0 | 303 |
| 19860519 | 81.3 | 101.3 | 241 |
| 19860519 | 78.6 | 99.7 | 195 |
| 19860519 | 82.1 | 102.5 | 219 |
| 19860519 | 78.6 | 88.1 | 285 |
| 19880524 | | | 494 |
| 19910512 | 95.2 | 111.5 | 455 |
| 19910512 | 82.2 | 103.2 | 423 |
| 19910512 | 82.8 | 103.0 | 418 |
| 19910512 | 84.4 | 108.1 | 404 |
| 19910512 | 83.8 | 107.5 | 366 |

| *Collection date* | *egg length, mm* | *Total egg weight, g* | *PFOS* |
|---:|---:|---:|---:|
| 19910512 | 88.0 | 103.2 | 487 |
| 19910512 | 85.0 | 102.5 | 390 |
| 19910512 | 82.9 | 102.6 | 344 |
| 19930510 | | | 388 |
| 19960603 | 83.2 | 107.6 | 574 |
| 19960603 | 84.4 | 112.6 | 652 |
| 19960603 | 83.9 | 114.1 | 563 |
| 19960603 | 88.2 | 117.6 | 489 |
| 19960603 | 83.5 | 120.5 | 482 |
| 19960603 | 82.5 | 121.9 | 462 |
| 19960603 | 84.4 | 111.7 | 517 |
| 19960603 | 84.4 | 115.0 | 481 |
| 19970517 | | | 1324 |
| 19980527 | | | 1072 |
| 19990506 | | | 1023 |
| 20000515 | | | 871 |
| 20010513 | 83.3 | 112.5 | 536 |
| 20010513 | 85.1 | 117.3 | 592 |
| 20010513 | 85.7 | 116.2 | 601 |
| 20010513 | 84.8 | 94.2 | 542 |
| 20010513 | 84.1 | 112.1 | 583 |
| 20010513 | 81.8 | 107.1 | 566 |
| 20010513 | 78.9 | 110.3 | 520 |
| 20010513 | 87.7 | 121.3 | |
| 20010513 | 84.5 | 118.9 | 574 |
| 20010513 | 91.8 | 112.2 | 532 |
| 200305xx | 84.2 | 107.6 | 617 |
| 200305xx | 83.7 | 110.8 | 669 |
| 200305xx | 84.9 | 118.3 | 640 |
| 200305xx | 78.7 | 100.0 | 572 |
| 200305xx | 94.9 | 105.0 | 631 |
| 200305xx | 81.2 | 98.4 | 631 |
| 200305xx | 87.8 | 111.0 | 581 |
| 200305xx | 89.3 | 107.6 | 634 |
| 200305xx | 80.1 | 105.3 | 551 |

Concentrations of perfluoroalkyl sulfonates and –carboxylates in fresh-water otter (*Lutra lutra*).
Values are given in ng/g wet weight.

| *Location* | | *PFOA* | *PFNA* | *PFDA* | *PFUnA* | *PFDoA* | *PFTrDA* | *PFTDA* | *PFHxS* | *PFOS* | *PFDS* | *PFOSA* | *Sum PFCA* | *Sum PFSA* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flen | 5148 | 8 | 47 | 97 | 69 | 17 | 11 | <2 | 7 | 2926 | 15 | 200 | 270 | 2948 |
| Tranås | 5068a | 12 | 57 | 180 | 109 | 22 | 27 | <2 | 8 | 5727 | 8 | 93 | 422 | 5743 |
| Grisslehamn | 5226 | 17 | 159 | 157 | 191 | 52 | 85 | <2 | 6 | 1891 | 3 | 26 | 782 | 1899 |
| Råneå | 5228 | 8 | 207 | 208 | 195 | 44 | 51 | <2 | 3 | 1525 | 5 | 16 | 697 | 1533 |
| Bollnäs | 5244 | 6 | 70 | 70 | 114 | 37 | 57 | <2 | 2 | 807 | 7 | 58 | 382 | 816 |
| Hassela | 5245 | 7 | 67 | 56 | 92 | 33 | 56 | <2 | 2 | 432 | 4 | 25 | 327 | 438 |
| Avesta | 5258 | 7 | 50 | 93 | 142 | 54 | 64 | <2 | 5 | 5150 | 15 | 60 | 360 | 5170 |
| Ydre | 5263 | 23 | 35 | 38 | 85 | 38 | 46 | <2 | 2 | 425 | 3 | 12 | 311 | 430 |
| Ydre | 5264 | 17 | 30 | 35 | 76 | 24 | 41 | <2 | 2 | 387 | 2 | 8 | 202 | 391 |
| Katrineholm | 5266 | 15 | 38 | 71 | 41 | 13 | 15 | <2 | 24 | 5090 | 26 | 33 | 197 | 5140 |
| Hallsberg | 5274 | 58 | 131 | 360 | 303 | 112 | 40 | <2 | 68 | 11323 | 101 | 154 | 1035 | 11492 |
| Åkersberga | 5293 | 11 | 98 | 122 | 119 | 39 | 46 | <2 | 4 | 1642 | 15 | 29 | 432 | 1661 |
| Malå | 5298 | 14 | 220 | 134 | 204 | 47 | 68 | <2 | 1 | 513 | 0 | 48 | 699 | 514 |
| Ösmo | 5299 | 16 | 111 | 226 | 151 | 65 | 46 | <2 | 13 | 4466 | 30 | 44 | 624 | 4509 |

Concentrations of perfluoroalkyl sulfonates and –carboxylates in water samples. Values are given in ng/liter

| *Location* | *Year* | *Type* | *Comment* | *PFOS* | *PFOA* |
|---|---|---|---|---|---|
| Sewage treatment plants: | | | | | |
| Henriksdal | | | | | |
| raw 04 | 2001 | sewage water. 24h. | | 9 | <8 |
| raw S12 | 2001 | sewage water 7-day | | n.a. | n.a. |
| raw H12 | 2001 | sewage water 7-day | | n.a. | n.a. |
| effluent 04 | 2001 | sewage water 7-day | | 7 | <8 |
| effluent 12 | 2001 | sewage water 7-day | | 20 | <8 |
| Bromma | | | | | |
| raw S151 | 2001 | sewage water 7-day | | 25 | <8 |
| effluent S151 | 2001 | sewage water 7-day | pH=2 | 57 | <8 |
| Waste disposal sites: | | | | | |
| Söderhall. Löt (SÖRAB) | | | | | |
| pumping station | 2001 | percolate leachate water | | 38 | <6 |
| aeration reservoir | 2001 | percolate leachate water | ice covered | 54 | <6 |
| Högbytorp | | | | | |
| percolate water reservoir | 2002 | percolate leachate water | ice covered | 38 | <6 |
| aeration reservoir | 2002 | percolate leachate water | ice covered | 152 | <6 |
| flyash disposal site. | | | | | |
| mixing station | 2002 | percolate leachate water | | 38 | <6 |

Concentrations of perfluoroalkyl sulfonates and –carboxylates in sewage sludge samples. Values given in ng/g dry weight.

| *Location* | *Year* | *Type* | *PFOS* | *PFOA* |
|---|---|---|---|---|
| Stockholm | | | | |
| Henriksdal Apr. | 2001 | digested composite 1 month | 33 | <0.05 |
| Henriksdal Dec. | 2001 | digested composite 1 month | 8 | 0.5 |
| Bromma Apr. | 2001 | digested composite 1 month | 16 | <0.05 |
| Bromma Dec. | 2001 | digested composite 1 month | 12 | 0.5 |

Concentrations of perfluoroalkyl sulfonates and –carboxylates in sediment samples.

| *Location* | *Year* | *Depth* | *Comment* | *PFOS wet weight* | *PFOS dry weight* | *PFOA dry weight* |
|---|---|---|---|---|---|---|
| L.Yngern reference lake | 1996 | 7m | Gravity corer sampler 0-4cm | 0.04 | 0.2 | n.d. |
| L.Insjön reference lake | 2001 | 7m | Gravity corer sampler 0-4cm | 0.06 | 0.8 | n.d. |
| L.Mälaren Klubbensborg | 2001 |  | Gravity corer sampler 0-4cm | 0.3 |  | n.d. |
| L.Mälaren Riddarfjärden | 2001 |  | Gravity corer sampler 0-4cm | 0.5 |  | n.d. |
| Saltsjön. Kastellholmen | 2001 | 20m | oxidized | 0.6 |  | n.d. |
| Saltsjön. Blockhusudden | 2001 | 20m | black. oil. odour rich | 0.5 |  | n.d. |
| Rosersbergsviken Y.club | 2002 | 3m | Gravity corer sampler 0-4cm | 6.5 |  | <0.05 |
| Rosersbergsviken Middle | 2002 | 3m | Gravity corer sampler 0-4cm | 1.1 |  | <0.05 |
| Rosersbergsviken ”Gibr.” | 2002 | 3m | Gravity corer sampler 0-4cm | <0.05 |  | <0.05 |

Concentrations of perfluoroalkyl sulfonates and –carboxylates in settling particulate matter (seston). Values given in ng/g dry weight

| *Location* | *Year* | *Comment* | *PFOS* | *PFOA* |
|---|---|---|---|---|
| L.Insjön | 1998-2001 | three year sample | n.d. | n.d. |
| Saltsjön. Kastellholmen | 1998 | one year sample | 4.7 | n.d. |
| L.Mälaren. Klubben | 1999 | one year sample | 2.6 | n.d. |
| L.Mälaren. Riddarfjärden | 1999 | one year sample | 2.9 | <0.05 |
| Saltsjön. Kastellholmen | 1999 | one year sample | 1.7 | n.d. |

Concentrations of perfluoroalkyl sulfonates and –carboxylates in sewage sludge. Values are given in ng/g dry weight Samples were composites of two weeks each of digested sewage sludge. **PFDoA** was not analyzed.

| | *PFHxA* | *PFHpA* | *PFOA* | *PFNA* | *PFDA* | *PFUnA* | *PFTrDA* | *PFTDA* | *PFHxS* | *PFOS* | *PFOSA* | *PFDS* | *Sum PFSA 6.8.10* | *Sum PFCA 6-11* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| STP1 July | 0.6 | <0.1 | 0.2 | 0.3 | 2.4 | 0.8 | 0 | 0 | 0.4 | 11 | 9.5 | 4.3 | 15 | 4.4 |
| STP1 Sept | 0.5 | <0.1 | 0.2 | 0.2 | 1.9 | 0.5 | 0 | 0 | 0.3 | 8.5 | 6.7 | 3.2 | 12 | 3.3 |
| STP3 July | 0.5 | 0.4 | 41 | 27 | 52 | 98 | 0 | 0.7 | 3.0 | 42 | 10 | 3.5 | 49 | 218 |
| STP3 Sept | 0.9 | 0.6 | 37 | 39 | 43 | 76 | 7 | 0.5 | 1.7 | 16 | 8.4 | 2.8 | 20 | 197 |
| STP4 July | 0.1 | <0.1 | 0.7 | 0.3 | 2.4 | 5.9 | 13 | 0.9 | 0.1 | 4.1 | 3.4 | 6.3 | 10 | 9.3 |
| STP4 Sept | 0.4 | 0.1 | 0.6 | 0.2 | 2.6 | 8.9 | 0 | 0 | 0.1 | 7.0 | 6.3 | 7.7 | 15 | 12.9 |
| STP2 Aug | 0.8 | 0.5 | 7.4 | 6.6 | 27 | 123 | 0 | 0 | 0.3 | 17 | 6.3 | 17 | 34 | 166 |
| STP2 Sept | 1.3 | 0.6 | 5.6 | 5.7 | 23 | 87 | 11 | 1.4 | 0.2 | 7.7 | 3.9 | 8.9 | 36 | 122 |

Concentrations of perfluoroalkyl sulfonates and –carboxylates in sewage water. Values are given in ng/liter Samples were composites of two weeks. STP5 is a reference plant receiving only household sewage water.

| | *PFHxA* | *PFHpA* | *PFOA* | *PFNA* | *PFDA* | *PFHxS* | *PFOS* | *PFUnA* | *S PFAS* | *S-PFCA* |
|---|---|---|---|---|---|---|---|---|---|---|
| STP1 raw | 0 | 1 | 20 | 3.1 | 7 | 8 | 26 | 6 | 34 | 31 |
| STP1 effluent | 3.5 | 2.0 | 19 | 2.6 | 8.1 | 13.6 | 40 | 4 | 54 | 35 |
| STP1 raw | 2.7 | 0.47 | 7.8 | 0.76 | 0.0 | 7.9 | 27 | <2 | 35 | 12 |
| STP1 effluent | 2.9 | 1.50 | 19 | 2.1 | 14 | 13.2 | 63 | 4 | 76 | 39 |
| STP3 raw | 13.3 | 12.2 | 26 | 3.4 | 13 | 5.5 | 18 | 6 | 23 | 68 |
| STP3 effluent | 19.7 | 35 | 80 | 13.1 | 25 | 10.9 | 6.2 | 14 | 17 | 173 |
| STP3 raw | 4.7 | 10.8 | 33 | 4.6 | 21 | 5.8 | 22 | 7 | 28 | 74 |
| STP3 effluent | 12.3 | 26 | 76 | 15.0 | 103 | 6.7 | 9.4 | 11 | 16 | 233 |
| STP4 raw | <0.1 | 0.92 | 18 | 3.2 | 6.8 | 1.5 | 34 | 7 | 35 | 29 |
| STP4 effluent | <0.1 | 1.3 | 34 | 3.5 | 8.3 | 1.5 | 23 | 4 | 24 | 48 |
| STP4 raw | <0.1 | 0.73 | 20 | 1.9 | 4.0 | 2.8 | 24 | 6 | 26 | 26 |
| STP4 effluent | <0.1 | 1.4 | 33 | 3.2 | 9.1 | 2.0 | 34 | 5 | 36 | 47 |
| STP2 raw | <0.1 | <0.1 | 3.7 | 3.7 | 10.7 | 9.3 | 60 | 9 | 69 | 18 |
| STP2 effluent | 6.7 | 21 | 6.0 | 26 | 170 | 14.8 | 74 | 44 | 89 | 230 |
| STP2 raw | <0.1 | 1.1 | 2.9 | 17.3 | 23 | 5.1 | 91 | 7 | 96 | 44 |
| STP2 effluent | 1.3 | 11 | 7.2 | 81 | 123 | 16.0 | 100 | 27 | 116 | 224 |
| STP5 raw | <0.1 | 0.47 | 9.3 | 0.00 | 0.0 | 0.0 | 5.6 | <2 | 6 | 10 |
| STP5 effluent | <0.1 | <0.1 | 18 | 1.68 | 0.0 | 0.0 | 7.0 | 3.7 | 7 | 20 |