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Overview of Existing Information on PFOS Production, Use, Emissions and Pathways to the Environment and Cost/Benefits with alternatives/substitutes.

Production and Use

Since the voluntarily phase out of PFOS production, in 2003, by the major global producer, 3M, the global production and use has been reduced dramatically. Quantitative data on production are only available for this company, but it is considered that the combined capacity of the other producers was very much less than that of 3M[1].

The dominating uses of PFOS (including the 96 PFOS-containing substances) in the past was to provide soil, oil and water resistance to textiles, apparels, home furnishings and upholstery, carpets and leather products. PFOS is not longer used for these applications. The remaining uses are in fire fighting foams, photographic industry, photolithography and semiconductors, hydraulic fluids and in metal plating industry[2].

In a recently published report from Norway[3] an inventory was made for the remaining quantities and historic emissions of fire fighting foams containing PFOS in Norway. The quantities of PFOS in the remaining foam were estimated to approximately 22 tons and the dominating uses were in offshore installations.

The estimated quantity for Fire fighting foams, held in current stock for the European Union, was 122 tonnes in 2004 [4].

The current demand (2004) in the European Union was estimated for the ongoing industrial/professional usage of PFOS and PFOS-containing substances (Table 1) [4]

Table 1: Estimated Current Demand for PFOS-Containing Substances in the Euoropean Union

Industry Sector	**Quantity (kg/year)**
Photographic industry	1,000
Semiconductor industry	470
Hydraulic fluids	730
Metal plating	10,000

In January 2005, OECD published a report with results from a survey on the production and use of PFOS and related substances in the OECD area[5]. The responses to the survey were limited and only 10 OECD countries responded to the questionnaire. Eight of these countries were signature to the LRTAP POPs protocol and one conclusion from the survey is that PFOS is still manufactured by Germany (20 – 60 tonnes in 2003) and Italy (< 22 tonnes in 2003). The total production volume today in the LRTAP-region or globally is not known.

Emissions and Pathways to the Environment

Releases of PFOS and its related substances are likely to occur during their whole life cycle. They can be released at their production, at their assembly into a commercial product, during the distribution and industrial or consumer use as well as from landfills after the use of the products[6].

One theory is that the dominating sources for PFOS emissions are the diffuse emissions from articles during use and disposal.

PFOS is found in surface water and sediment, downstream of productions sites, waste water treatment plant effluents, sewage sludge, landfill leachate, and in wildlife species all over the world, including very remote areas in the Arctic. At present, it is unclear which exposure pathways are responsible for the PFOS levels (and several other perfluorinated compounds) now found in the serum of the general population around the world[2].

In a study in Lake Ontario (Great Lakes) the wastewater treatment plants were suggested to be the primary source to the PFOS levels in the lake. The cleaning and care of surface-treated products (from clothing to carpets) by consumers and use in industrial processes are believed to release these compounds to municipal wastewater treatment system. Additionally treatment of landfill leachate municipal water treatment works may also introduce significant amounts of these compounds to the environment[7].

The durability of the protective PFAS layer on carpets has been studied by 3M. It is expected that 50% of the FC (fluorochemical) treatment will be removed over the nine-year life of the carpet due to walking and vacuuming, while an additional 45% of the FC treatment will be removed in steam cleaning throughout the carpet life[8].

In contrast to well documented persisted organic pollutants like polychlorinated biphenyls (PCB) chlorinated-p-dibenzodioxins and furans (PCDD/F) governments and scientists are today concerned that the most pervasive of the perfluorinated substances (e.g. PFOS) will never degrade in the environment due to the extraordinarily persistent properties[9].

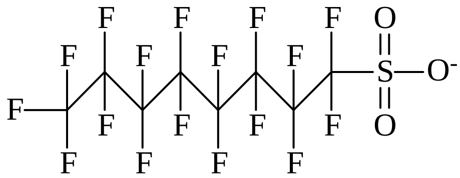
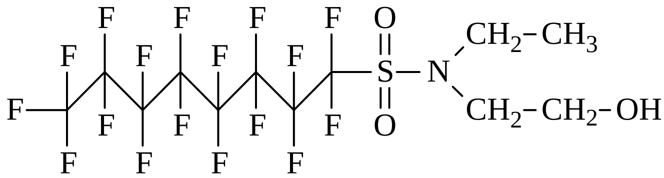
This circumstance indicates that there is need for a different approach to calculate the emission scenarios for PFOS today and in the future. The total accumulated production of PFOS since the beginning in the middle of the 1900 century is thus important to take into account as well as the different uses in the past. However, it’s not reasonable or even possible to make these emission scenarios in detail for all the 96 different PFOS potential precursors as well as for other possible PFOS precursors since that information is not available.

It is unlikely that PFOS is transported to remote regions in the vapour phase due to the low vapour pressure. Several authors have suggested that the presence of PFOS in Arctic wildlife may be due to long-range transport of volatile precursor compounds that degrade to give PFOS[10] One of the most likely precursors of PFOS are the electrochemically produced perfluorinated sulphonamidoethanols used to incorporate PFOS into polymeric materials[11] and perfluorinated sulphonamides, which has been used in a variety of consumer products and industrial materials[12]

A recent study performed with rainbow trout (*Onchorhynchus mykiss)* liver microsomes has demonstrated that *N*-ethyl perfluorooctanesulphonamide (N-EtPFOSA, see table 2) is a precursor of PFOS in fish[13]. These findings combined with the recent measurements of concentrations up to 92.8 ± 41.9 ng/g wet weight of *N*-EtPFOSA in aquatic organisms from Arctic regions[14] strengthen the hypothesis that perfluorinated sulphonamides are one of the volatile precursors of PFOS transported over long distances to the Arctic.
However, the hypothesis that these volatile precursors reach the Arctic latitudes by atmospheric transport has not yet been confirmed by atmospheric measurements[15].

In the production process N-EtFOSE and N-metFOSE are chemical intermediate in production of adipates, phosphate esters, fatty acid esters, urethanes copolymers and acrylates as commercialised products. The majority of the PFOS-related products made by 3M were from this group of products. [1] All these products above are PFOS precursors.

Table 2:

Abbreviation	Full name	CAS-number	Structure
PFOS	Perfluorooctyl sulphonate	1763-23-1	
n-EtFOSE n-EtPFOSA	n-Ethylperfluoro-octanesulphonamidoethanol	1691-99-2	

A recent screening of PFOS in fish, birds, and marine mammals from the eastern and western coasts of Greenland[16] has shown a geographical difference with higher concentration of PFOS in biota from the eastern coast. The same trend has been observed for persistent chlorinated compounds such as PCBs, whose concentrations in biota are significantly higher in East Greenland than in West Greenland. This spatial trend indicates a greater influence of long-range atmospheric and oceanic transport from European sources in East Greenland[17, 18].These data also confirm that the environmental concentrations of PFOS are still increasing and this trend is opposite those observed for polychlorinated biphenyls (PCBs) and chlorinated pesticides.

Alternatives / Substitutes - Cost and Benefits

<u>Historic Uses</u>

For the dominating uses in the past, e.g. PFOS used in textiles, apparels, home furnishings and upholstery, carpets and leather products, companies have already developed alternatives. According to the Swedish risk reduction strategy on PFOS-related compounds[19] the alternatives used today as in impregnating agents for textiles and leather are based on other highly fluorinated compounds like e.g. polytetrafluoroethylene (PTFE)

For water repellence a mixture of silicones and stearamidomethyl-pyridine-chloride can be used alone as an alternative to PFOS-related compounds or together with a combination of carbamid (urea) and melamine resin[19].

In June 2003, the 3M Company replaced the PFOS-compound in their Scotchgard products by PFBS (perfluorobutane sulphonate). 3M´s Scotchgard products are cleaners and stain protectors for carpets, leather, furniture, automotives, hard surfaces and other apparels. After the phase-out of PFOS in the Scotchgard product, the 3M Company first presented a product in an aerosol-can based on non-perfluoro chemistry. However, the product worked on water but not on grease. Therefore, 3M now uses the perfluoro-compound with a shorter chain length – C_4[20]

An overview of the identified possible alternatives for impregnation of textiles, leather and carpets is available in a Danish study:[21]

- Highly fluorinated compounds
- A mixture of silicones and stearamidomethyl-pyridine-chloride
- A mixture of silicones and stearamidomethyl-pyridine chloride together with carbamide (urea) and melamine resin
- Perfluorobutane sulphonate based substances (PFBS)
- Telomer-based polymers
- Silicone-based products
- PTFE (polytetrafluoroethylene)

Remaining Uses

Fire fighting foams

As already described in the dossier a number of alternatives to the use of PFOS based fluorosurfactants in fire fighting foams are now available[22]. These alternatives include:

- Non-PFOS based fluorosurfactants
- Silicone based surfactants
- Hydrocarbon based surfactants
- Fluorine-free fire fighting foams (different technologies)

An extensive review of these foams is available in the Danish study[21].
The overall picture is that there has been a shift from PFOS based fire fighting foams in most of the countries but the existing stock of fire fighting foams is still in use.

Photographic Industry

Accorded to the UK reduction strategy for PFOS-related substances, the work on substituting PFOS-related compounds within the photographic industry has been ongoing since the year 2000. This work has resulted in a reduction of 83% of the use of PFOS-related compounds within this industry. This reduction is primarily due to digital techniques, where a dry process technique is used [4] .
The possible alternatives identified for the photographic industry are:

- Digital techniques
- Telomer-based products
- C3 and C4 perfluorinated compounds
- Hydrocarbon surfactants
- Silicone products

Manufacturing of semiconductors

According to the European Semiconductor Industry Association new techniques are being developed where PFOS-related substances are not being used. However, these techniques are not yet ready for commercial use and will not be for the next 2 to 5 years. The most critical manufacturing processes are photoresist (PAG) and anti-reflex treatment [19, 4]

Hydraulic oils within the airplane industry
A change in the formulation of the hydraulic oils seems to be the only alternative solution. This will, however, demand a comprehensive testing together with an approval from the airplane manufacturers, which may take as long as 10 years, as the safety measures within this industry are very high [19].

According to the UK risk reduction strategy on PFOS, manufacturers of hydraulic fluids used in the airplane industry are looking for manufactures that would be willing to produce the needed PFOS substances, when the existing stocks are exhausted. The 3M Company formerly produced the potassium salt of perfluoroethylcyclohexyl sulphonate used in hydraulic fuels, but they also withdrew the production of this substance from the market [4] .

Metal surface treatment
At the moment, EU funded research is trying to identify alternatives, as use of chromium(VI) is a serious health risk (carcinogenic) in the chromium-plating and chromating processes. If alternatives to chromium(VI) can be found the use of PFOS-related chemicals is most likely eliminated within the area of metal surface treatment [19, 4]

An alternative process already exists for decorative chromium plating. In this process chromium(III) is used instead and no PFOS-chemicals are necessary. However, the problem is that the process with chromium (III) does not function as well for hard plating. Instead larger closed tanks or increased ventilation are suggested as (expensive) alternative solutions for the applications where a use of chromium (III) is not possible yet [19, 4].

Legislative Controls
Both UK and Sweden have made notifications to the European Comission concerning proposed restrictions on marketing and use of PFOS and their 96 known derivatives[23].

The proposed UK regulation prohibits the import into the United Kingdom of fire fighting foams containing perfluorooctane sulphonate. The regulation also prohibits the supply, storage and use of perfluorooctane sulphonate for any uses and time limited derogations for certain uses.

The proposed Swedish regulation prohibits products which wholly or partly contain PFOS or PFOS related substances. These products must not be offered for sale or handed over to consumers for individual use or offered for sale and handed over or used commercially.
This prohibition shall not apply to hydraulic fluids intended for use in aircraft.

The EU commission has also proposed a ban on marketing and use on PFOS metal salt, halide, amide, and other derivatives including polymers for certain uses.
The proposed Directive would cover the great part of the exposure risks by preventing the use of PFOS in carpets, textiles, upholstery, leather, apparel, paper, packaging and other applications. These uses seem already to be phased out and the proposal would prevent their reintroduction [24].

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