PERFLUOROOCTANE SULFONATE (PFOS)

Dossier prepared in support for a nomination of PFOS to the UN-ECE LRTAP Protocol and the Stockholm Convention

The dossier is prepared by the Swedish Chemicals Inspectorate (KemI)
and the Swedish EPA, Sweden

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Contents

EXECUTIVE SUMMARY

Introduction

Perfluorooctane sulfonate (PFOS) is fully fluorinated anion, which is used as such in some applications or incorporated into larger polymers. Due to its surface-active properties it is used in a wide variety of applications. PFOS can be formed by degradation from a large group of related substances, referred to as PFOS-related substances. PFOS and 96 PFOS-related substances are part of the nomination. All these substances are members of a large family of perfluoroalkylated substances (PFAS), in which the substitutes to PFOS also can be found.

POP characteristics of PFOS

The conclusions of the POP characteristics of PFOS according to the UN-ECE criteria are presented in the table below.

Table 1. POP characteristics of according to the UN-ECE POP criteria.

Criterion	Meets the criterion (Yes/No)	Remark
Potential for Long-Range Atmospheric Transport	Yes	Vapour pressure = 3,31 x 10^{-4} Pa Atmospheric half life > 2 days (estimated value based on photolytic half life > 3,7 years)
Toxicity	Yes	Sub-chronic exposure: Mortality in monkeys at 4,5 mg/kg bw/day. Reproductive toxicity: mortality in pups at 1,6 mg/kg bw/day. Acute toxicity to fish: LC_{50} = 4,7 mg/L
Persistence	Yes	Extremely persistent. No degradation recorded in chemical or biological tests
Bioaccumulation	Yes	Found in highly elevated concentrations in top predators. Calculated hypothetical BMF = 22 - 160. BCF in fish = 2796 - 3100.

PFOS meets the criteria for POPs characteristics as outlined in executive body decision 1998/2.

According to available data, PFOS meets the criteria for the potential for long-range atmospheric transport. This is evident through monitoring data showing highly elevated levels of PFOS in various parts of the northern hemisphere. It is especially evident in the Arctic biota, far from anthropogenic sources. PFOS also fulfils the specific criteria for vapour pressure and atmospheric half-life.

PFOS fulfils the criteria for toxicity. It has demonstrated toxicity towards mammals in sub-chronic repeated dose studies at low concentrations as well as reproductive toxicity with mortality of pups occurring shortly after birth, probably caused by inhibition of lung maturation. PFOS is toxic to aquatic organisms with mysid shrimp being the most sensitive organism.

PFOS is extremely persistent. It has not showed any degradation in tests of hydrolysation, photolysation or biodegradation in any environmental condition tested. The only known condition whereby PFOS is degraded is through high temperature incineration.

With regard to bioaccumulation potential, PFOS meets the criterion through highly elevated concentrations that has been found in top predators such as the polar bear, seal, bald eagle and mink. Based on the concentrations found in their prey, high BMFs have been estimated. BCF values in fish, although (rather) high do not in themselves meet the specific criteria.

PFOS in the environment

PFOS and PFOS-related substances are released to the environment at their manufacture, during their use in industrial and consumer applications and from disposal after their use. Elevated concentrations of PFOS have been found in sewage effluents and leakage water from landfills. These findings display pathways of PFOS and its related substances to the environment. PFOS have been detected in a large variety of biota in locations all around the globe, as well as in water in the open oceans. Most notable and alarming is the high concentrations of PFOS that have been found in Arctic animals, far from anthropogenic sources.

Due to their intrinsic properties, PFOS and its related substances are used in a wide variety of applications, often at concentrations lower than is required for product information. Also, the rate and the extent of the formation of PFOS from its related chemicals are largely unknown, and it is therefore very difficult to estimate the releases of PFOS to the environment.

Uses

In year 2000, 3M decided to voluntarily phase out the production of PFOS, which has resulted in a significant reduction in the use of PFOS related substances. The current sectors where PFOS and its related substances are used are:

- In existing fire fighting foam stock
- Photographic industry
- Photolithography and semiconductors,
- Hydraulic fluids and metal plating

Historically, PFOS and its related substances have been used in applications such as fire fighting foams, carpets, leather/apparel, textiles/upholstery, paper and packaging, coatings and coating additives, industrial and household cleaning products and pesticides and insecticides.

INTRODUCTION

Perfluorooctane sulphonate (hereafter referred to as PFOS) is a fully fluorinated anion that belongs to a large group of perfluorinated substances (PFAS). Also included amongst PFAS are PFOS-related substances, which can be degraded to PFOS.

PFOS has been on the global agenda since year 2000 when 3M (the major global producer of PFOS) announced that the company would voluntarily phase out its production. Since then, a number of activities in different forums have been undertaken.

The environmental protection agency (EPA) in USA have introduced Significant New Use Rules (SNUR), requiring companies to inform EPA before manufacturing or importing listed PFOS related substances. There are two SNURs, listing 88 substances.

A hazard assessment of PFOS, done by OECD in 2002, concluded that the presence and the persistence of PFOS in the environment, as well as its toxicity and bioaccumulation potential, indicate a cause of concern for the environment and human health.

At present, an environmental risk assessment is prepared by the UK-Environment Agency, and discussed by the EU member states under the umbrella of the existing substances regulation (ESR DIR 793/93). A PFOS risk reduction strategy is currently being prepared by the Department for Environment, Food and Rural Affairs (Defra, UK), which may also form a basis for EU risk reduction measures.

This dossier on PFOS mainly builds on information that has been gathered by the United Kingdom, i.e., in the hazard assessment report prepared by the UK and the USA for the OECD, and in the UK risk reduction strategy. Some recent information from the open scientific literature is also included.

PART I. RISK PROFILE

A. Chemical identity

Chemical name: Perfluorooctane Sulfonate (PFOS)
Molecular formula: $C_8F_{17}SO_3$
Structural formula:

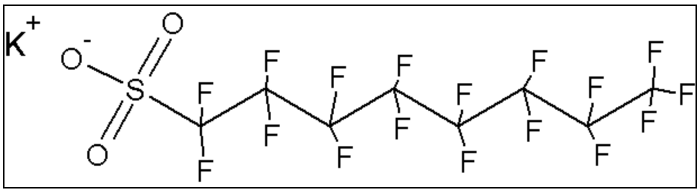
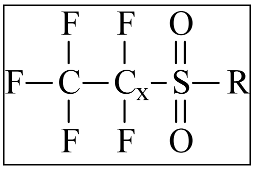


Figure 1. Structural formula of PFOS shown as its potassium salt

Synonyms:
1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro;
1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid;
1-Octanesulfonic acid, heptadecafluoro-;
1-Perfluorooctanesulfonic acid;
Heptadecafluoro-1-octanesulfonic acid;
Perfluoro-n-octanesulfonic acid;
Perfluoroctanesulfonic acid;
Perfluoroctylsulfonic acid

PFOS is a fully fluorinated anion, which is commonly used as a salt or incorporated into larger polymers. PFOS and its closely related compounds, which contain PFOS impurities or can give rise to PFOS, are members of the large family of perfluoroalkyl sulphonate substances (PFAS). The schematic structure of PFAS is given in Figure 2.



$$F-\underset{\displaystyle F}{\overset{\displaystyle F}{\underset{|}{\overset{|}{C}}}}-\underset{\displaystyle F}{\overset{\displaystyle F}{\underset{|}{\overset{|}{C_x}}}}-\underset{\displaystyle O}{\overset{\displaystyle O}{\underset{\|}{\overset{\|}{S}}}}-R$$

Figure 2. Schematic structure of PFAS.
R is equal to any given functional group such as OH, NH_2, etc.
For PFOS-related substances, x = 7.

PFOS is not listed as a substance on EINECS and has no classification. The acid form of PFOS is not classified on Annex I of Directive 67/548/EEC, and neither are any of the usual salts (potassium, ammonium, and lithium).

Perfluorinated substances with long carbon chains, including PFOS, are both lipid-repellent and water-repellent. Therefore, the PFOS-related substances are used as surface-active agents in different applications. The extreme persistence of these substances make them suitable for high temperature applications and for applications in contact with strong acids or bases. It is the very strong carbon-fluorine bindings that cause the persistence of perfluorinated substances.

The physical and chemical properties of the potassium salt of PFOS are listed in Table 2.

Table 2. Physical and chemical properties of PFOS potassium salt. (Data from OECD, 2002, unless otherwise noted).

Property	Value
Appearance at normal temperature and pressure	White powder
Molecular weight	538 g/mol
Vapour Pressure	3,31 x 10^{-4} Pa
Water solubility in pure water	519 mg/L (20 ± 0,5ºC) 680 mg/L (24 - 25ºC)
Melting point	> 400 ºC
Boiling point	Not measurable
Log K_{OW}	Not measurable
Air-water partition coefficient	< $2x10^{-6}$ (3M, 2003)
Henry's Law Constant	3,05 x 10^{-9} atm m^3/mol pure water

PFOS can be formed (by environmental microbial degradation or by metabolism inside larger living organisms) from PFOS-related substances, i.e., molecules containing the PFOS-moiety depicted in Figure 2. The majority of PFOS related substances are polymers of high molecular weights in which PFOS is only a fraction of the polymer and final product (OECD, 2002). PFOS-related substances have been defined somewhat differently in different contexts and there are currently a number of lists of PFOS-related substances (Table 3). The lists contain varying numbers of PFOS-related substances that are thought to have the potential to break down to PFOS. The lists overlap to varying extent and it is therefore not clearly evident which substances that are believed to be precursors to PFOS.

Table 3. Number of PFOS-related substances as proposed by UK – DEFRA, US – EPA, OECD and OSPAR

Source	Number of PFOS-related substances
UK – DEFRA (2004)	96
US - EPA (2002)	88
OECD (2002)	172 (22 classes of PFAS)
OSPAR (2002)	48

Since a large number of substances may give rise to PFOS and thus contribute to the contamination problem, the most recent grouping of 96 PFOS-related substances, by DEFRA, UK, is proposed in this nomination. These substances are listed in *annex 1*.

B POP Characteristics

1. Potential for long-range transboundary atmospheric transport

The potassium salt of PFOS has a measured vapour pressure of 3,31 x 10^{-4} Pa (OECD, 2002). Due to this vapour pressure and a low air-water partition coefficient (< $2x10^{-6}$), PFOS itself is not expected to volatilise significantly. It is therefore assumed to be transported in the atmosphere predominantly bound to particles, because of its surface-active properties, rather than in a gaseous state.

Note that some of the PFOS-related substances have a considerably higher vapour pressure than PFOS itself, and are as a result more likely to be volatile. This may allow a wider transport of PFOS-related substances through air than is possible for PFOS itself. Examples of these are EtFOSE alcohol, MeFOSE alcohol, MeFOSA, EtFOSA, and FOSA. These precursors to PFOS could evaporate into the atmosphere. Once in the atmosphere they can remain in gas phase, condense on particles present in the atmosphere and be carried or settle out with them, or be washed out with rain (3M, 2000).

The atmospheric half-life of PFOS is expected to be greater than two days. This has not been specifically tested but the statement is based on the fact that PFOS has exhibited extreme resistance to degradation in all tests performed. The indirect photolytic half-life of PFOS at 25°C has been estimated to be more than 3.7 years (OECD, 2002).

PFOS has through monitoring data been found in a wide range of biota in the Northern Hemisphere such as the Canadian Arctic, Sweden, the US and the Netherlands. In a study by Martin et al (2004), the levels of PFOS was measured in liver samples from biota in the Canadian Arctic and was found in the vast majority of the species examined (all except the black guillemot). The presence of PFOS in Arctic biota, far from anthropogenic sources, demonstrates the properties of PFOS for long-range transport. The mechanisms of this transport are not known, but it cannot be excluded that it is due to volatile PFOS-related substances that have been degraded to PFOS.

Conclusion

PFOS meets the criteria for the potential for long-range atmospheric transport. This is evident through monitoring data showing highly elevated levels of PFOS in various parts of the northern hemisphere. It is especially evident in the Arctic biota, far from anthropogenic sources. PFOS also fulfils the specific criteria for vapour pressure and atmospheric half-life.

2. Toxicity and Ecotoxicity

Toxicity

Evidence of the toxicity of PFOS is available from acute, sub-chronic and chronic exposures to rats, sub-chronic exposures to monkeys, and a two-generation study on rats. Results are available from reproductive and teratogenicity studies on rats and rabbits. Details of these studies are not included here, they can be found in the assessment made by OECD (2002). The most relevant for this notification are:

- A 90-day study on rhesus monkeys exposed to PFOS potassium salt via gavage at the doses 0; 0,5; 1,5 and 4,5 mg/kg bw/day. At 4,5 mg/kg bw/day all monkeys (4) died or were sacrificed in moribound condition. No deaths were observed at 0,5 or 1.5 mg/kg bw/day, but there were signs of gastrointestinal toxicity. NOAEL could not be established since the lowest dose was a LOAEL. The results of this test show that PFOS fulfils the EU criteria for classification as Toxic, with the risk phrase R48.

- A 90-day oral repeated dose toxicity study in rats that were fed diets containing 0, 30, 100, 300, 1000 and 3000 ppm of PFOS potassium salt. All rats died when fed diets containing 300 ppm PFOS and above (equivalent to 18 mg/kg bw/day and above). At 100 ppm (6 mg/kg bw/day), 50% (5/10) of the animals died. All rats receiving diets containing 30 ppm PFOS (2.0 mg/kg/day) survived until the end of the study, but small changes in body and organ weights were reported. Since the lowest dose tested was a LOAEL, a NOAEL could not be established. Also in rats, classification for chronic toxicity (R 48 according to EU criteria) is warranted.

- A two-generation reproductive toxicity study on rats that were fed PFOS potassium salt via gavage at the doses 0,1; 0,4; 1,6; and 3,2 mg/kg bw/day. At the doses 1,6 and 3,2 mg/kg bw/day a significant reduction in the viability of the F1 generation was observed. In the 1,6 mg/kg bw/day group, 34% (86/254) of the F1 pups died within four days after birth. In the 3,2 mg/kg bw/day group, 45% (71/156), of the F1 pups died within one day after delivery. None of these pups survived beyond day 4.

  Maternal toxicity at 1,6 and 3,2 mg/kg bw/day was manifested as reduced food consumption, body weight gain, and terminal bodyweight. Localised alopecia was also observed at 3,2 mg/kg bw/day. LOAEL in this study was 0,4 mg/kg bw/day based on significant reductions in pup weight gain in the F1 generation animals. The NOAEL was 0,1 mg/kg bw/day.

  A study by Grasty et al. (2003) concluded that exposure to PFOS late in gestation is sufficient to induce 100% pup mortality and that the causative factor may be inhibition of lung maturation.

Ecotoxicity

Environmental toxicity data for PFOS is predominantly found for aquatic organisms such as fish, invertebrates and algae.

PFOS has shown moderate acute toxicity to fish. The lowest observed LC_{50} (96h) was estimated to 4,7 mg/l in a study where Fathead minnow (*Pimephales promelas*) were exposed to the lithium salt of PFOS. The lowest NOEC, 0,3 mg/l, has been observed in *Pimephales promelas* at prolonged exposure (42d) and was based on mortality (OECD, 2002). By this toxicity to fish PFOS fulfils the EU criteria for the classifications R 51 with the risk phrase ”toxic to aquatic organisms” and R 53 ” May cause long-term adverse effects in the aquatic environment.

The lowest LC_{50} (96h) for aquatic invertebrates has been observed in the Mysid shrimp (*Mysidopsis bahia)* and was estimated to 3,6 mg/l. The lowest NOEC-value has been observed in *Mysidopsis bahia* at 0,25 mg/l (OECD, 2002).

The most sensitive algae appear to be the green algae *Pseudokirchnerilla subcapitata* with a IC_{50} (96h, cell density) of 48,2 mg/L. The lowest NOEC-value for algae was determined in the same study for *Pseudokirchnerilla subcapitata*, 5,3 mg/L (Boudreau et al., 2003).

Conclusions

PFOS fulfils the criteria for toxicity. It has demonstrated toxicity towards mammals in sub-chronic repeated dose studies at low concentrations (a few mg/kg bw/day) and displayed reproductive toxicity with mortality of pups occurring shortly after birth, probably caused by inhibition of lung maturation.

PFOS is toxic to aquatic organisms with the lowest NOEC (0.25 mg/L) observed in mysid shrimp.

3. Persistence

PFOS is extremely persistent. It does not hydrolyse, photolyse or biodegrade in any environmental condition tested (OECD 2002).

A study on the hydrolysis of PFOS in water has been performed following US-EPA OPPTS protocol 835.2210. The study was conducted at pH varying from 1.5 – 11.0 and at a temperature of 50°C, to facilitate hydrolysis, but did not indicate any degradation of PFOS. The half-life of PFOS was set to be greater than 41 years.

A study on the photolysis of PFOS in water following US-EPA OPPTS protocol 835.5270 has been conducted. No evidence of direct or indirect photolysis was observed under any of the conditions tested. The indirect photolytic half-life of PFOS at 25°C was calculated to more than 3.7 years.

Biodegradation of PFOS has been evaluated in a variety of tests. Aerobic biodegradation of PFOS has been tested in activated sewage sludge, sediment cultures and soil cultures in several studies. Anaerobic biodegradation has been tested in sewage sludge. Neither of the studies demonstrated any signs of biodegradation.

The only known condition whereby PFOS is degraded is through high temperature incineration (3M, 2003).

Conclusion
PFOS has not showed any signs biodegradation in any tests, and therefore fulfils the criteria for persistence.

4. Bioaccumulation

Tests on the bioconcentration of PFOS in fish have been performed, but the bioaccumulation in mammals has not been studied.

It should be noted that PFOS does not accumulate in fat tissue, which is typical of many persistent organic pollutants. This is a consequence of the fact that PFOS is both hydrophobic and lipophobic. Instead, PFOS binds to proteins in the blood and the liver (3M, 2003).

In a study following OECD protocol 305, the bioaccumulation of PFOS in bluegill sunfish (*Lepomis macrochirus*) have been tested. The kinetic bioconcentration factor (BCFK) for whole-fish was there determined to 2796 (OECD, 2002).

In another study on Rainbow trout (*Oncorhynchus mykiss*), a bioconcentration factor (BCF) in liver and plasma was estimated to 2900 and 3100 respectively (Martin, *et al*., 2003).

When strictly looking at the BCF-values, it is clear that these values are below the BCF-criteria, but in this particular case, the BCF may not adequately represent the bioaccumulation potential of the substance. Thus, monitoring data from top predators at various locations show highly elevated levels of PFOS and demonstrates substantial bioaccumulating and biomagnifying (BMF) properties of PFOS. It is notable that the concentrations of PFOS found in livers of arctic polar bears exceeds the concentrations of all other known individual organohalogens (Martin et al., 2004). Based on the concentration of PFOS in predators (e.g., the polar bear) in relation to the concentration in their principal food (e.g., seals) hypothetical BMF-values can be calculated. Such data are reported in Table 4. It should be noted that there are uncertainties in these comparisons. Even if either liver or blood concentrations are compared in two species, species-differences in specific protein binding in that particular compartment may affect the concentration in the organ without having affected the whole-body concentration of the substance.

Table 4. Measured concentrations of PFOS in biota from various locations. Calculated BMF is shown where applicable.

Species and Location	Concentrations of PFOS	Reference
• Polar Bear, Canadian Arctic	- Concentrations of PFOS in liver (1700 – 4000 ng/g) exceeding all other individual organohalogens. - BMF > 160 based on concentrations in Arctic seals.	Martin et al., 2004.
• Arctic fox	- Very high concentrations of PFOS in liver (6.1 - 1400 ng/g)	Martin et al., 2004.
• Mink, US	- Very high concentrations of PFOS in liver (40 - 4870 ng/g). - BMF = 22 based on data from fish in the same area.	3M, 2003. Giesy and Kannan, 2001.
• Bald Eagle, US	- Very high concentrations of PFOS in plasma (1 – 2570 ng/g).	Kannan and Giesy, 2001.
• Dolphin, US	- Very high concentrations of PFOS in liver (10 – 1520 ng/g).	3M, 2003.
• Seal in the Bothnian Sea, Finland	- Very high concentrations of PFOS in liver (30 – 1100 ng/g). - BMF > 60 based on data from salmon in the same area.	Kannan et al., 2002.

Conclusions

PFOS fulfils the criteria for bioaccumulation based on the extremely high concentrations that have been measured in top predators at various locations such as the Arctic, the US and Sweden.

Part II. SUMMARY REPORT

A. Extent of release to the environment

1 Production

Three different production processes can be used to produce fluorinated substances:

1. *Direct fluorination, electro-chemical fluorination, ECF*

$C_8H_{17}SO_2Cl + 18\ HF \rightarrow C_8F_{17}SO_2F + HCl$ + by products

This method was used by 3 M and is called 'Simons Electro Chemical Fluorination'. (The major product categories and applications for perfluorooctylsulphonates is shown in *annex 2*)

2. *Telomerisation*

$C_2F_5I + 3\ C_2F_4 \rightarrow C_8F_{17}I \rightarrow C_8F_{17}$-tensides.

This method is used by Du Pont and it gives a more well-defined product containing fewer isomers.

3. Oligomerisation

This method gives branched carbon chains and fewer isomers.

On 16 May 2000, 3M (the major global producer of PFOS based in the United States) announced that the company would phase-out the use of PFOS voluntarily from 2001 onwards. The 3M global production was in year 2000 approximately 3,700 metric tonnes. In the beginning of 2003 the production ceased completely.

The US Environmental Protection Agency (US EPA) compiled a list of non-US companies, which are believed to supply PFOS related substances to the global market. Of these (and excluding the plant of 3M in Belgium), six plants are located in Europe, six are located in Asia (of which four are in Japan) and one in Latin America (OECD, 2002)

It has been suggested that, at the end of the last decade, there were a total of six companies manufacturing PFAS by the ECF process with a total global capacity of 4,650 metric tonnes per year. (UK Stage 4 Final Report)

2 Uses

3M´s voluntary phase out of PFOS production has led to a significant reduction in the use of PFOS related substances. This is due not only to the limited availability of these substances (3M had at the time the greatest production capacity of PFOS related substances in the world), but also to action within the relevant industry sectors to decrease companies´ dependence on these substances.

The historical use of PFOS related substances in the following applications has been confirmed either in the UK (the first six) or the EU (the remaining two)

- Fire fighting foams
- Carpets
- Leather/apparel
- Textiles/upholstery
- Paper and packaging
- Coatings and coating additives
- Industrial and household cleaning products
- Pesticides and insecticides

In the UK study, detailed information has been received from the following sectors that currently use PFOS related substances:

- Use of existing fire fighting foam stock
- Photographic industry
- Photolithography and semiconductors
- Hydraulic fluids
- Metal plating

The table below outlines the estimated current demand for PFOS related substances in these applications in the EU. (UK Stage 4 Final Report)

Estimated Current Demand for PFOS Related Substances in the EU	
Industry Sector	Quantity (kg/year)
Photographic industry	1,500
Photolithographic and semi-conductors	500
Hydraulic fluids	730
Metal plating	2,500

Uses for PFOS can be shown in more detail in the table in *annex 3*.

2.1 Textile, Carpet and Leather Protection

PFOS related substances have been used to provide soil, oil and water resistance to textiles, apparels, home furnishings and upholstery, carpets, and leather products. They were used because they were able to modify the surface properties of these materials to provide repellence and resistance.

When applied to a material's surface, the perfluorocarbon chain tends to be oriented away from the surface, lowering the surface energy of the material, thereby creating a protective barrier.

Since 3M´s withdrawal from the market, PFOS related substances are no longer used for these applications. (UK Stage 4 Final Report)

2.2 Metal Plating

The main uses of PFOS related substances in metal plating are for chromium plating, and anodising and acid pickling.

PFOS related substances lower the surface tension of the plating solution so that mist containing chromic acid from the plating activity is trapped in solution and is not released to air. Before the introduction of PFOS based applications to control the emissions of hexavalent chromium, mist was controlled through extraction. Hexavalent chromium is a known carcinogen. (UK Stage 4 Final Report)

2.3 Paper and Packaging Protection

PFOS related substances have been used in the packaging and paper industries in both food packaging and commercial applications to impart grease, oil and water resistance to paper, paperboard and packaging substrates. According to 3M, fluorochemicals were used for both food contact applications (plates, food containers, bags and wraps) and non-food applications (folding cartons, containers and carbonless forms and masking papers). Since 3M´s withdrawal from the market, PFOS related substances are no longer used for these applications. (UK Stage 4 Final Report)

2.4 Fire Fighting Foams

Water is vital and effective in extinguish a majority of fires. However, when fighting fires involving flammable liquids (Class B), water tends to sink below the burning fuel due to its specific gravity and, thus, has a little effect in extinguishes the fires (and in some cases could even result in the flammable liquid spilling out of its contained area). Fire fighting foams were therefore developed for use on flammable liquids fires and have proven to be one of the most important and effective tools for dealing with such fires. Fire fighting foams are produced by a combination of foam concentrate (the form in which it is stored) and water, which is then aspirated with air to form the finished foam. The resulting foam forms a low-density blanket that extinguishes fires from flammable liquids.

The fire fighting foams can be grouped in two main categories:

- Fluorine containing foam types (some of them consists of PFOS related substances)
- Fluorine-free foam types

Since the announcement of the voluntary cessation of production of PFOS related substances by 3M, the presence of PFOS in fire fighting foams has gradually decreased. (UK Stage 4 Final Report)

2.5 Industrial and Household Cleaning Products (Surfactants)

3M PFOS based products were sold in the past to a variety of formulators to improve the wetting of water based products marketed as alkaline cleaners, floor polishes (to improve wetting and levelling), denture cleansers and shampoos. Several of these products (alkaline cleaners, floor polishes, shampoos) were marketed to consumers; some products were also sold to janitorial and commercial services. A number of the alkaline cleaners were spray-applied.

With regard to the UK cleaning products industry, the responses received to-date does not indicate the use of PFOS related substances in Industrial and household cleaning products. Based on information provided in product registers, the Swedish National Chemicals Inspectorate (KemI) has indicated that PFOS related substances are still being used in Sweden for both industrial and household use. (UK Stage 4 Final Report)

2.6 Coatings and Coating Additives

3M indicates that prior to the voluntary phase out of PFOS production, the company would sell fluorochemical polymer coatings and coating additives which were used undiluted or diluted with water or butyl acetate to impart soil or water repellence to surfaces (including printing circuit boards and photographic film). These polymers contained fluorocarbon residuals at a concentration of 4% or less. Other application where aqueous coatings used to protect tile, marble and concrete. It is unclear which of these products were actually based on PFOS related substances.

A survey in UK among members to the British Coatings Federation (BCF) showed that the use of PFOS related substances for these purposes is very limited. (UK Stage 4 Final Report)

2.7 Photographic Industry

PFOS based chemicals are used for the following purposes in mixtures in coatings applied to photographic films, papers, and printing plates:

- Surfactants
- Electrostatic charge control agents;
- Friction control agents;
- Dirt repellent agents; and
- Adhesion control agents

According to the European Photographic Chemicals Industry Sector Group of CEFIC (EPCI), PFOS coating aids have a combination of surface-active properties that are unique and not found with any other type of coating aid. Only small quantities of PFOS materials are required to function as coating aids in imaging media. This property is important because the required addition of non-photoactive materials to coatings in significant quantities diminish the ability of the imaging material to form the sharpest images. In short, thinner coatings make clearer, sharper images. (UK Stage 4 Final Report)

2.8 Photolithography and Semiconductors

Photoresist

Semiconductor manufacturing comprises up to 500 steps, of which there are four fundamental physical processes:

- Implant
- Deposition
- Etch
- Photolithography

Photolithography is the most important step towards the successful implementation of each of the other steps and, indeed, the overall process. It shapes and isolates the junctions and transistors; it defines the metallic interconnects; it delineates the electrical paths that form the transistors; and joins them together. Photolithography reportedly represents 150 of the total of 500 steps mentioned above (UK Stage 4 Final Report).

Photolithography is also integral to the miniaturisation of semiconductors: Miniaturisation makes integrated circuits smaller, cheaper, faster and better, which is critical to continuing the electronic revolution (ESIA, 2003), and to EU manufacturers remaining competitive in the global market.

Miniaturisation refers to the ability to reduce objects, as well as the gap between objects. The ability to effect this separation is proportional to the wavelength of light that is used to pattern the separation. This relationship between separation, i.e. optical resolution, and wavelength is well established. To improve resolution, the semiconductor industry has shortened the wavelength that it uses in photolithography four times since 1980, from 436nm through 365nm and 248nm to 193nm. The latter wavelength is just entering use. A fifth wavelength, 157nm, is expected to be introduced in 2004-5. This shortening of wavelength, however, comes at a price; the composition of the photoresist must be adjusted to appropriately respond to whichever wavelength for the exposure. The role of the photoresist is to record the exposure pattern, known as the aerial image, produced by the photolithography equipment
(UK Stage 4 Final Report).

The introduction of imaging at 248 nm changed the way in which the acidity of an exposed, positive photoresist is altered. The shorter wavelength uses a mechanism called *chemical amplification* (to make the process more efficient).

Chemical amplification depends on a catalyst to chemically amplify the effect of the exposing light. The catalyst-precursor is called a photo-acid generator (PAG). A PAG is decomposed by light into and acid and the acid catalyses another reaction, which also produces and acid. This chain reaction continues to produce acid and to lead to the positive photoresist being chemically transformed in the areas that have been exposed.

The catalytic process is most effective when the photo acid produced from the PAG is a strong Bronsted acid. The first generations of 248 nm resist were formulated without PFOS in the PAG. PFOS PAG was included in formulations to improve performance.

Antireflective Coatings

A number of resist suppliers sell antireflective coatings (ARC), subdivided into Top (TARC) and Bottom (BARC) coatings and used in combination with deep ultra violet (DUV) photoresist. The process involves placing a thin, top coating on the resist to reduce reflective light, in much the same way and for the same purposes that eyeglasses and camera lenses are coated. TARC depends on good coating properties, water solubility, and an extreme refractive index. PFOS is present in TARC at a total of about 3% by weight.

2.9 Hydraulic Fluids for the Aviation Industry

Hydraulic fluids were initially used in aircraft to apply brake pressure. As larger and faster aircraft were designed, greater use of hydraulic fluids became necessary. An increase in the number of hydraulic fluid fires in the 1940s necessitated work towards developing fire resistant fluids. The first of these fluids was developed around 1948, when fire resistant hydraulic fluids based on phosphate ester chemistry were developed. The development of this phosphate ester technology is said to have been instrumental in achieving a step change in aircraft safety, with the virtual elimination of hydraulic fluid fires in commercial aircraft.

Technological advances in the aviation industry required continuous modifications to the hydraulic fluids to meet the specifications of the aircraft manufacturers. For instance, servo valves containing phosphate ester-based fluids were found to experience corrosion on the high pressure side of the valve metering edge. It was found that certain additives (such as the perfluorinated anionic surfactants) could alter the electrical potential at the metal surface and prevent its electrochemical oxidation.

As a result, hydraulic fluids based on phosphate ester technology and incorporating additives based on perfluorinated anions are used in all commercial aircraft, and in many military and general aviation aircraft throughout the world, as well as by every airframe manufacturer.

In the past, structural/mechanical parts in aircraft hydraulic systems (e.g. pumps and valves) have been reported to exhibit a marked decrease in strength and an alteration in the geometry of the parts. Valves were also found to experience corrosion on the high pressure side of the valve metering edge, causing internal valve leakage, which resulted in decreased pressure and premature valve failure.

Valves control the flow of hydraulic fluid to actuate moving parts of the aircraft such as wing flaps, ailerons, the rudder and landing gear. These valves often contain passages or orifices having clearances of the order of a few thousands of an inch or less through which the hydraulic fluid must pass. Erosion increases the size of the passage and can reduce below tolerable limits the ability of the valve to serve as a precise control device. Corrosion in valves can thus result in the faulty operation of aircraft, excessive leakage of fluids or even hazardous conditions.

In the case of pumps, erosion can result in a decrease in the efficiency of operation and damage, which necessitate a premature overhaul of mechanical parts (with both cost and time implications). This is in addition to increased risks to the environment resulting from the premature draining of the contaminated fluids from the system, filter clogging and filter replacement.

It was discovered that the localised corrosion (referred to as erosion) was a result of a unique combination of factors including:

- A very high fluid velocity at the upstream edge of the valve metering edge
- The slight ionic character of phosphate esters
- The steel metallurgy of the slide and sleeve construction

Tests showed that perfluorinated anionic surfactants (such as PFOS) could inhibit erosion (and control damage) of mechanical parts of hydraulic systems that are used in all aircraft. These perfluorinated anions act by altering the electrical potential at the metal surface, thereby preventing the electrochemical oxidation of the metal surface under high fluid flow conditions. (UK Stage 4 Final Report)

2.10 Other uses

There is information on other historical or current PFOS applications such as in Pesticides, medical applications, mining and oil surfactants, flame retardants and in adhesives. These applications represent a minor part of known PFOS applications and are therefore not further elaborated in this dossier.

3. Emissions and pathways to the environment

There is to date very limited information regarding the emissions and pathways of PFOS to the environment. The occurrence of PFOS in the environment is a result of anthropogenic manufacturing and use, since PFOS is not a naturally occurring substance.

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 (3M, 2000).

Manufacturing processes constitute a major source for PFOS to the local environment. During these processes volatile PFOS-related substances may be released to the atmosphere. PFOS and PFOS-related substances could also be released via sewage effluents (3M, 2000). High local emissions are supported by one study that has showed extremely high concentrations of PFOS in wood mice collected in the immediate vicinity to 3M’s fluorochemical plant in Antwerpen, Belgium (Hoff et al., 2004).

Fire training areas have also revealed to constitute a source of PFOS-emissions due to the presence of PFOS in fire-fighting foams. High levels of PFOS have been detected in neighbouring wetlands of such an area in Sweden (Swedish EPA, 2004) as well as elevated groundwater levels in the US close to a fire-training area (Moody et al., 2003).

One route for PFOS and PFOS-related substances to the environment seem to be through sewage treatment plants (STPs) and landfills, where elevated concentrations have been observed compared to background concentrations.

Once released from STPs, PFOS will partially adsorb to sediment and organic matter and bioaccumulate in living organisms. A substantial amount of PFOS will also end up in agricultural soil, due to the application of sewage sludge. The primary compartments for PFOS are therefore believed to be water, sediment and soil (RIKZ, 2002).

Dispersion of PFOS in the environment is thought to occur through transport in surface water, transport in air (volatile PFOS-related substances), adsorption to particles (in water, sediment or air) and through living organisms (3M, 2003).

One major obstacle when trying to estimate the releases of PFOS to the environment is that PFOS can be formed through degradation of PFOS-related substances. The rate and the extent of that formation is presently not known. In a study on Swedish STPs, higher concentrations of PFOS were found in the effluents compared to incoming sewage water, which could indicate that a formation of PFOS through PFOS-related substances has occurred (Posner and Järnberg, 2004).

B. Environmental levels and bioavailability

Levels of PFOS have been measured in various environmental matrices in countries such as Sweden, the US and the Netherlands.

Measured environmental levels

A screening study have been made assigned by the Swedish EPA and performed by ITM, Institute of Applied Environmental Research, on the levels of PFOS in the Swedish environment (Swedish EPA, 2004). The results showed highly elevated levels of PFOS in a wetland in the vicinity of a fire drill area with a declining gradient out in the adjacent bay (2.2 – 0.2µg/L). Elevated levels were also detected outside STPs and landfills. Effluents from STPs contained levels of PFOS up to 0.020 µg/L and leakage water from landfills between 0.038 – 0.152 µg/L.

The occurrence of PFOS and other PFAS in open ocean waters such as the Atlantic and the Pacific Ocean have been investigated. The results showed that PFOS is present in central to western Pacific Ocean on concentrations ranging from 15 – 56 pg/L, and were comparable to the concentrations in the mid-Atlantic ocean. These values appear to be the background values for remote marine waters far from local sources (Taniyasu et al., 2004).

Studies in the US have identified the presence of PFOS in surface water and sediment downstream of a production facility, as well as in wastewater treatment plant effluent, sewage sludge and landfill leachate at a number of urban centres in the US (3M Multi City study, reviewed in OECD (2002) and 3M (2003)). Four of the cities (Decatur (AL), Mobile, Columbus (GA), Pensacola) were cities that have manufacturing or industrial use of fluorochemicals; two of the cities (Cleveland (TN), Port St. Lucie) were control cities that do not have significant fluorochemical activities. The ranges of PFOS levels in these cities are provided in Table 5.

Table 5. Environmental Levels of PFOS in Six US Urban Centres in the US (from OECD, 2002)

Medium	Range of PFOS levels (µg/L or µg/kg)
Municipal wastewater treatment plant effluent	0.041 - 5.29
Municipal wastewater treatment plant sludge	0.2 - 3,120 (dry weight)
Drinking water	ND - 0.063
Sediment	ND - 53.1 (dry weight)
Surface water	ND - 0.138
‘Quiet’ water	ND - 2.93

Note: ND: not detected

The control cities’ samples generally inhabited the lower end of the above ranges, except for the municipal wastewater treatment plant effluent and sludge findings for one of the control cities (Cleveland), which were intermediate in their ranges, and the ‘quiet’ water samples at control city (Port St. Lucie), which were the highest.

Samples of effluent from fifteen representative industrial branches have been analysed for PFOS (Hohenblum et al, 2003). The industry branches were printing (1 site), electronics (3), leather, metals, paper (6), photographic and textiles (2). The PFOS levels found ranged from zero to 2.5 µg/L (2.5 µg/L for leather, 0.120 µg/l for metal, 0.140-1.2 µg/l at four paper sites, 1.2 µg/l for photographic, not found in textiles or electronic).

Groundwater from below an air force base in Michigan, US, has been sampled (Moody et al, 2003). Fire fighting foams containing PFOS had been used there in training exercises from the 1950s to 1993 when the base was decommissioned. The groundwater was found to contain PFOS, at levels from 4 to 110 µg/l.

Environmental levels in biota

PFOS and related fluorochemicals have been traced in animals in a number of studies in a variety of locations around the globe. Generally the highest concentrations are found in top predators in food chains containing fish.

Martin et al (2004) measured the levels of PFOS in liver samples from biota in the Canadian Arctic. PFOS was found in the vast majority of the samples and higher levels were found in animals at the top of the food chain. The highest levels were found in polar bear, with a mean level of 3.100 ng/g from seven animals (maximum value > 4.000 ng/g). These levels PFOS in the liver exceeds the levels of all other known individual organohalogens. High levels of PFOS were also found in the arctic fox. The sulphonamide FOSA, that is a precursor to PFOS, was also found in most of the samples. The concentration of FOSA was higher than that of PFOS in fish, but not in mammals. This could indicate that FOSA has been metabolised to PFOS in mammals and the high concentrations may be the result of both direct exposure to PFOS and metabolism from FOSA.

Kannan and Giesy (2002) have summarised results of analyses on archived samples. The tissues analysed came from marine mammals, birds, fish, reptiles and amphibians from around the worlds, including the Arctic and Antarctic Oceans. Samples collected in the 1990s were used. Around 1.700 samples were analysed, with concentrations in liver, egg yolk, muscle or blood plasma determined. The detection limit varied from 1 to 35 ppb wet weight. A summary of the results is in Table 6.

Table 6. Maximum concentrations of PFOS in various species as well as frequency of detection. Based on Kannan and Giesy (2002)

Species	Maximum concentration ng/g wwt	Frequency of detection
Marine mammals	1520	77%
Mink and otter	4900	100%
Birds	2570	60%
Fish	1000	38%

PFOS was detectable in most of the samples, including those from remote marine locations, at concentrations >1 ng/g. The authors compared the results from remote areas with those from more industrial locations. They comment that PFOS is widely distributed in remote regions, including the Polar Regions, but that the levels found in more urban and industrial areas (e.g. the Baltic, Great Lakes) are several times higher. The tissues of fish-eating birds in Canada, Italy, Japan and Korea all contained detectable levels of PFOS, suggesting that they are exposed through the fish they consume.

A summary of a number of studies is given in Table 7.

Table 7. Monitored Levels of PFOS in Animals (data from selected studies, based on OECD, 2002)

Description	Ref	Reported Highest Concentrations (Max, Mean)	Location of Concentrations
Global monitoring survey of marine mammals (Florida, California, Alaska, northern Baltic Sea, Mediterranean Sea, Arctic, Sable Island (Canada))	A	Bottlenose dolphin (liver, n = 26): Max: 1520 ng/g wet wt. Mean: 420 ng/g wet wt.	Florida
		Ringed seal (liver, n = 81): Max: 1100 ng/g wet wt. Mean: 240 ng/g wet wt.	Northern Baltic Sea
Survey of mammals, birds and fish in the Canadian Arctic	B	Polar bear (liver, n = 7): Max: > 4000 ng/g wet wt. Mean: 3100 ng/g wet wt.	Canadian Arctic
		Arctic fox (liver, n = 10): Max: 1400 ng/g wet wt. Mean: 250 ng/g wet wt.	
Survey of fish (US, Europe, North Pacific Ocean, Antarctic)	C	Fish (muscle, n = 172): Max: 923 ng/g wet wt. Mean. 40 ng/g wet wt.	Belgian estuary
		Carp (muscle, n = 10): Max: 296 ng/g wet wt. Mean: 120 ng/g wet wt.	US Great Lakes
Survey of fish-eating birds (US, Baltic Sea, Mediterranean Sea, Japanese coast, Korean coast)	D	Bald eagle (plasma, n = 42): Max: 2570 ng/mL Mean: 520 ng/mL	Midwest US
Survey of mink and river otter in the US	E	Mink (liver, n = 77): Max: 4870 ng/g wet wt. Mean: 1220 ng/g wet wt.	US
		River otter (liver, n = 5): Max: 994 ng/g wet wt. Mean: 330 ng/g wet wt.	US
Survey of oysters in the US (Chesapeake Bay & Gulf of Mexico)	F	Oyster (Whole body, n =77) Max: 100 ng/g wet wt. Mean: 60 ng/g wet wt.	US
Fish samples upstream and downstream of 3M facility in Decatur, Alabama, US	G	Fish (whole body): Mean (upstream): 59.1 µg/kg wet wt. Mean (downstream): 1,332 µg/kg wet wt.	Decatur, US
Swedish urban and background fish samples	H	Perch: 3 - 8 ng/g (urban sites in the vicinity of municipal STPs); 20-44 ng/g in Lake Mälaren and near Stockholm	Sweden (Lake Mälaren)

Sources: A: 3M (2003), B: Martin et al (2004); C: Giesy and Kannan (2001c) in 3M (2003); D: Giesy and Kannan (2001b) in 3M (2003); E: Giesy and Kannan (2001d) in 3M (2003); F: Giesy and Kannan (2001e) in 3M (2003); G: Giesy and Newsted (2001) in OECD (2002); H: Holmström et al (2003).

Concentrations of PFOS in guillemot (*Uria aalge*) eggs from Stora Karlsö in the Baltic Sea have been measured retrospectively from 1968 to 2003 in a study by the Institute of Applied Environmental Research assigned by the Swedish EPA. The results shown in Figure 2 displays a trend of increasing concentrations since 1968 (17 – 623 ng/g).

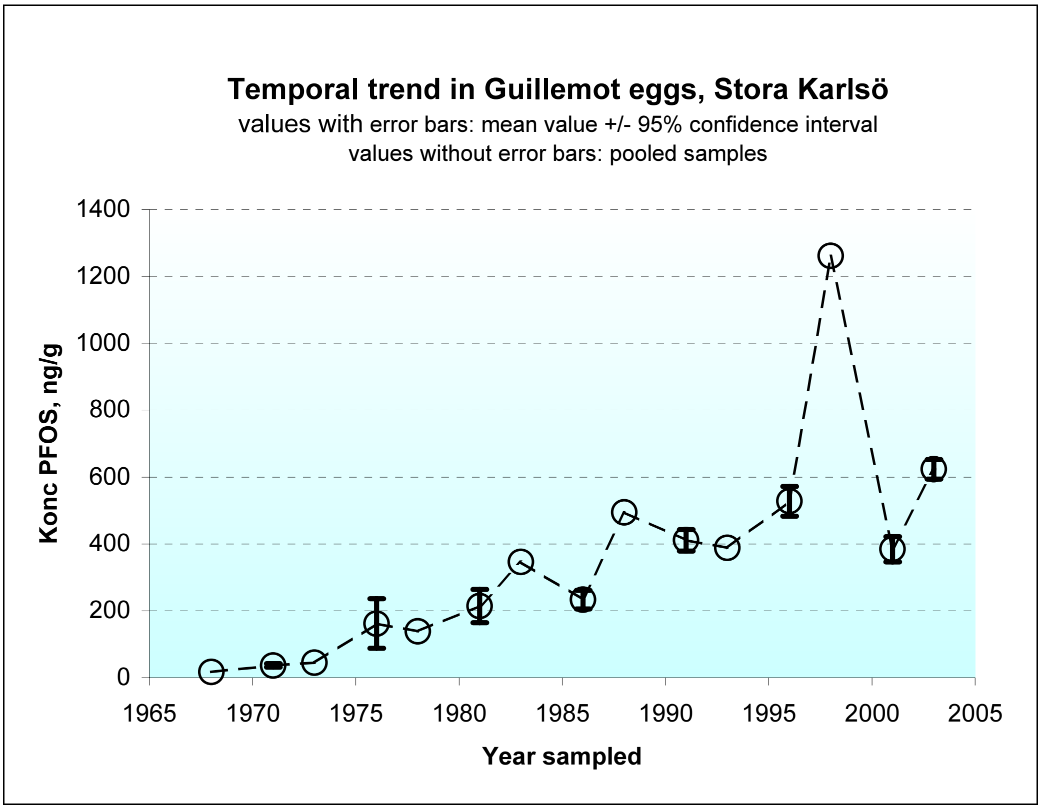


Figure 2. Measured concentrations of PFOS in Guillemot (Uria aalge) eggs sampled at Stora Karlsö in the Baltic Sea between the years 1968 – 2003. The graph is taken from the report "Screening av perfluorerade ämnen" by the Swedish EPA, Environmental Assessment Department (2004).

Bioavailability

Studies on fish have shown that PFOS has bioconcentrating properties. In studies on bluegill sunfish (*Lepomis macrochirus*) and rainbow trout (*Oncorhynchus mykiss*) bioconcentration factors (BCFs) have been estimated to 2796 (whole fish) as well as 2900 (liver) and 3100 (plasma) respectively. The major route of uptake is believed to be through the gills (Martin et al., 2003)

Since PFOS is believed to be released to the environment mainly through water from STPs one major route for PFOS into food chains could be through fish. PFOS have shown a high oral uptake (95%) within 24 hours in the gastro-intestinal (GI) tract in studies on rats (OECD, 2002). Taken together, this could constitute the basis of the highly elevated levels that have been observed in top predators in food chains containing fish.

This could also be confirmed by two separate studies on the Swedish population where the levels of PFOS in whole blood was higher (27.2 ppb, 3.0 – 67, n = 10) in females with a high consumption of fish (Berglund, 2004) compared to samples from females in the general population (17.8 ppb, 4.6 – 33, n = 26) (Kärrman et al., 2004).

In humans, the highest concentrations of PFOS have been detected in workers at 3M's manufacturing plant for perfluorochemicals in Decatur, US, where the levels in serum in the last measurement (2000) ranged between 0.06 – 10.06 ppm (OECD, 2002).

C Socio-economic factors

1 National and International Regulation

1.1 Voluntary Phase Out of Production by 3M

As discussed above the main producer of PFOS compounds voluntarily decided to phase-out the production in 2000. Production ceased completely by the beginning of 2003. Although it is recognised that 3M was the largest global producer of PFOS, other producers do exist.

1.2 EU

There is currently no legislation on the use of PFOS related substances in the EU that is related with their (potential) environmental and/or human health effects.

It should however be noted that some legislation which generally applies to the release of substances to the environment may be relevant to the release of PFOS to the environment (for instance, the IPPC Directive 96/61/EC includes fluorine and its compounds in the indicative list of the main polluting substances to be taken into account if they are relevant for fixing emission limit values (Annex III to the Directive)). (UK Stage 4 Final Report)

1.3 USA

Following the announcement by 3M in May 2000 to phase out the production of PFOS, the US EPA proposed a significant new use rule (SNUR) under section 5(a)(2) of the TSCA for 88 PFOS related substances on October 2000 (US EPA, 2000).

A SNUR is not a ban. It requires companies to file a notice (a SNUN) with US EPA 90 days before beginning the new manufacture or import of listed PFOS chemicals. The US EPA could grant, deny or impose restrictions on the intended use. The required notice is intended to provide the US EPA with the opportunity to evaluate any intended new use and associated activities and if necessary, to prohibit or limit that activity before it occurs. (UK Stage 4 Final Report)

1.4 OECD

PFOS and related substances have been on the agenda within OECD since year 2000. At the 34th Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology (5-8 November 2002) it was agreed that OECD countries with production of these substances (Italy, Japan, Switzerland and UK) should ask their industry if they were planning to phase-out the production of PFOS. The result of this investigation was then reported to the 35th Joint Meeting in June 2003. It was also agreed that there will be continuous reporting on the production and use and exposure of PFOS related substances to the Joint Meeting every second year. To facilitate this exchange of information an electronic Clearing House on PFOS and related substances has been established. (UK Stage 4 Final Report)

1.5 OSPAR Convention

At a ministerial meeting of the Contracting Parties to the OSPAR Convention in Sintra in 1998, it was agreed that man-made hazardous substances should not occur in the marine environment and that naturally occurring hazardous substances should not exceed natural background concentrations. To this end, it was agreed to make every endeavour to cease all discharges, emissions and losses of hazardous substances that could reach the marine environment by the year 2020 (UK Stage 4 Final Report)

Within the framework of the above strategy on hazardous substances, perfluorinated compounds have been under consideration by OSPAR. A considerable amount of data has been generated that show that PFOS meets the OSPAR selection criteria as a hazardous substance. Following a number of earlier meetings of the Hazardous Substances Committee at the Hague on PFOS, the UK and Sweden in April 2003 presented a proposal on the best way to proceed with the prioritisation of PFOS type substances and how to establish fact sheets for produced and marketed substances. (UK Stage 4 Final Report)

2. Alternatives / Substitutes

A significant proportion of previous users of PFOS related substances have moved to other fluorochemical products (fluorinated telomers). Fluorinated telomers cannot degrade to PFOS but under certain circumstances may degrade to perfluorooctanoic acid (PFOA). It is important to note that, while there is little information currently available to assess the environmental and health impacts of fluorinated telomers, extensive work is currently on-going in the US and other countries where there is some concern over the fate and behaviour of these substances. Until these and other studies are concluded, it will not be possible to draw any firm conclusion concerning the environmental/human health advantages of telomers over the PFOS related substances that they have substituted. The US EPA released a Preliminary Risk Assessment on the developmental toxicity of PFOA in April 2003, and is currently working to develop information on the sources and pathways leading to environmental and human exposure to PFOA in the environment (UK Stage 4 Final Report)

2.1 Metal Plating Applications

PFOS related substances are used in the following applications:

- Decorative chromium plating
- Hard chromium plating

Information received indicates the there are currently no known alternative chemical mist suppressants to PFOS related substance for these applications; previous generations of chemical mist suppressants having failed due to excessive pitting of coatings and rapid breakdown during electrolysis.

However, information received from a number of industry and regulatory authorities indicates that the substitution of Cr (VI) with the less hazardous Cr (III) in decorative plating application would eliminate the need for the use of PFOS related substances in this application. Such substitution has potentially significant cost savings, health and safety and environmental benefits for the metal plating sector.

For hard chromium platers, the direct substitution of Cr (VI) is not currently a viable option as Cr (III) is not suitable for the deposition of thick chromium layers, as used in hard chrome applications. Substitutes such as the nickel-tungsten-silicon carbide composites are still in the research phase, although there exist the possibility of other substitutes such as electroless nickel coating in specific applications. These alternatives need to be explored in more detail.
(UK Stage 4 Final Report)

2.2 Fire Fighting Foams

A number of alternatives to the use of PFOS based fluorosurfactants in fire fighting foams are now available/under development. These alternatives include:

- Non-PFOS based fluorosurfactants
- Silicone based surfactants
- Hydrocarbon based surfactants
- Fluorine-free fire fighting foams
- Other developing fire fighting foam technologies that avoid use of fluorine

In UK, most of the fluorocarbon surfactants currently marketed are produced using the telomerisation process (see production) based on C_6 telomer fluorocarbon surfactants.

As a result of many years of continuous development, telomer based fluorosurfactants have been indicated as providing an equal and comparable performance to the PFOS based fire fighting foams and are reported to be highly reliable.

These telomer based fire-fighting foams are not likely to be a source of PFOA in the environment because they predominantly contain the C_6 fluorosurfactants.

Fluorine-free foams are a relative new technology (compared with the fluorosurfactant technology), particularly fluorine free foams for use on Class B fires. These newly developed foams for use on Class B fires do not contain any fluorosurfactants (UK Stage 4 Final Report).

2.3 Photographic Industry

Efforts to substitute PFOS related substances have resulted in a reduction of 83% in the total amount of PFOS related substances used in imaging products since 2000. This has involved the elimination of the following uses of PFOS related substances as:

- Defoamer used in the production of processing chemicals for films, papers, and printing plates
- Photo acid generators in photolithographic processing solutions used in the manufacture of printing plates
- Surfactants in photolithographic processing solutions used in the manufacture of printing plates

However, while work is ongoing to identify substitutes, there are currently no alternatives to PFOS related substances in the following applications:

- Surfactants for mixtures used in coatings applied to films, papers, and printing plates
- Electrostatic charge control agents for mixtures used in coatings applied to films, papers, and printing plates
- Friction control and dirt repellent agent for mixtures used in coatings applied to films papers, and printing plates
- Adhesion control agents for mixtures used in coatings

The market for photography products, although in decline following the rapid uptake of digital technology, still represents an important EU market with essential applications across a number of sectors (including defence and healthcare) (UK Stage 4 Final Report).

2.4 Photolithography and Semiconductors

PFOS based material are reported as being critical in two applications within the photolithography process: photoresist and anti-reflective coatings (ARC´s).

Photoresist

The operation of PFOS based PAGS is critical to the semiconductor industry in the photolithography process.
In limited cases, resist suppliers can formulate chemically amplified resist without PFOS PAG. This is the case with photoresist designed for 248 nm wavelength.

It should be noted that the semiconductor industry continues to make many products with 436nm and 365nm photolithography for which further miniaturisation is no longer cost effective. These products do not require PFOS PAG (ESIA, 2003)

The semiconductor industry is just beginning to introduce 193nm photolithography. It is expected to be the photolithography technology that drives the next round of miniaturization, the so-called 100nm technology node, in 2003-4. Photolithography with 157nm is still in development. However, formulation for 193nm and 157nm wavelength is currently not feasible without PFOS PAG. This is because of the technical difficulties encountered in designing the chemical sensitivity to photo acids used in 248nm resists into 193nm and 157nm resist. The chemical sensitivities used in the 248nm resist make the resist absorb light too strongly to be used at the lower wavelength. (UK Stage 4 Final Report)

Anti-reflective Coatings

For anti-reflective coatings used in combination with deep ultra violet (DUV) photoresists, EISA indicates that there is no alternative available which fulfils the critical technical requirements necessary (UK Stage 4 Final Report).

For uses of PFOS related substances in top (TARC) and bottom (BARC) resist coatings, suppliers are said to be working on polymeric replacements. However, high fluorine content and polymeric nature are relatively incompatible properties. The semiconductors industry indicates that replacement could take up to five years, if it can be done at all (UK Stage 4 Final Report)

2.5 Hydraulic Fluids

According to information received from one of the major producers of hydraulic fluids, there are no alternatives to the PFOS substances currently being used in aircraft systems. There is also no known alternative chemistry that will provide adequately protection to aircraft.

According to this manufacturer, there have been attempts over the last 30 years to find acceptable alternatives to PFOS, and efforts have been accelerated since 3M announced its withdrawal from the market. The company estimates that they have screened up to 2,500 formulations looking for the best erosion resistance additive package. There are currently no promising leads for a substitute for the PFOS related substances now in use, and there are no assurance that an acceptable alternative will ever be identified.

To date, alkali metal salts of perfluoroalkyl sulfonic acids are the only available additives that have been found to provide effective erosion resistance for hydraulic fluids marketed for aircraft use. The incorporation of small amounts of these perfluorinated anionic surfactants into fire resistant phosphate esters based hydraulic fluids improves the ability to inhibit erosion of metal parts without adversely affecting the other properties of the fluid, such as viscosity, oxidative and thermal stability, corrosion resistance to the metal parts, and lubrication qualities for hydraulic system parts (UK Stage 4 Final Report).

3 Emission Control Techniques

Executive Body Decision 1998/2 indicates that this section could consider process changes, control technologies, operating practices and other pollution prevention techniques which may be used to reduce emissions; along with comment on their applicability and effectiveness.

In the UK Stage 4 final report, the following measures that could be applied to reduce or eliminate the emissions of PFOS to the environment are identified:

- Process controls are applicable to the chromium plating industry, where these process changes are associated with the use of improved extraction and enclosure methods in hard chromium (VI) plating and a shift to chromium (III) processes in decorative plating.

- Emission controls are applicable to all existing and professional uses, and in some industry sectors sophisticated environmental emission control is already applied.

- Conditions on use might include the use of fire fighting foams in contained situations with accompanying fire water collection, treatment and disposal requirements and the use of containment and disposal technologies in aircraft maintenance.

However, due to the end use of PFOS related substances in articles, emission control techniques cannot eliminate the diffuse sources, which are considerable.

4 Cost and Benefits of Control

In general, the benefits of identifying alternatives of substitutes for persistent organic pollutants, or of identifying process changes that decrease their use, include:

- Lower emission to the environment
- Lower worker exposure to the substance
- Products that do not contain the substance will not release the substance either during their use or during subsequent recycling or disposal

Generally, costs of alternatives or substitutes will include research and development and actual costs associated with use of substitutes. These costs are sometimes hard to distinguish from normal costs related to product development.

Some examples of calculated costs
The annualised costs per company, in the *Metal Plating industry*, of adopting improved ventilation extraction/tank enclosure have been calculated as being of order of £3,400 per year (15 years at discount rate of 3.5%)

Decorative platers are likely to switch to the use of Cr (III) to avoid these costs and take up the potential net financial benefits from moving to the Cr (III) process.

As indicated, efforts to replace PFOS related substances in *Photographic Industry* have resulted in a reduction of 83% in the total amount of PFOS related substances used in imaging products since 2000. The costs of achieving this 83% reduction across the EU since 2000 have been estimated as £12-24 million. (UK Stage 4 Final Report)

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ANNEX 1

UK Draft List of Compounds Potentially Degrading to PFOS in the Environment

Table A1.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

Ref No.	CAS Number	PFOS related substance
1	307-35-7	1-Octanesulphonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
2	376-14-7	2-Propenoic acid, 2-methyl-, 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester
3	383-07-3	2-Propenoic acid, 2-[butyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester
4	423-82-5	2-Propenoic acid, 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester
5	423-86-9	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-2-propenyl-
6	754-91-6	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
7	1652-63-7	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl]amino]-*N*,*N*,*N*-trimethyl-, iodide
8	1691-99-2	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-
9	1763-23-1	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
10	1869-77-8	Glycine, *N*-ethyl-*N*-[(heptadecafluorooctyl)sulphonyl]-, ethyl ester
11	2250-98-8	1-Octanesulphonamide, *N*,*N*',*N*''- [phosphinylidynetris(oxy-2,1-ethanediyl)]tris[*N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
12	2263-09-4	1-Octanesulphonamide, *N*-butyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-
13	2795-39-3	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt
14	2991-50-6	Glycine, *N*-ethyl-*N*-[(heptadecafluorooctyl)sulphonyl]-
15	2991-51-7	Glycine, *N*-ethyl-*N*-[(heptadecafluorooctyl)sulphonyl]-, potassium salt
16	3820-83-5	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[2-(phosphonooxy)ethyl]-
17	3871-50-9	Glycine, *N*-ethyl-*N*-[(heptadecafluorooctyl)sulphonyl]-, sodium salt
18	4151-50-2	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
19	13417-01-1	1-Octanesulphonamide, *N*-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
20	14650-24-9	2-Propenoic acid, 2-methyl-, 2- [[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester
21	24448-09-7	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-*N*-methyl-
22	24924-36-5	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-2-propenyl-
23	25268-77-3	2-Propenoic acid, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester

Table A1.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

Ref No.	CAS Number	PFOS related substance
24	29081-56-9	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt
25	29117-08-6	Poly(oxy-1,2-ethanediyl), .alpha.-[2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl]-.omega.-hydroxy-
26	29457-72-5	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt
27	30295-51-3	1-Octanesulphonamide, N-[3-(dimethyloxidoamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
28	30381-98-7	1-Octanesulphonamide, *N*,*N*'-[phosphinicobis(oxy-2,1-ethanediyl)]bis[*N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt
29	31506-32-8	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-methyl-
30	38006-74-5	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl]amino]-*N*,*N*',*N*''-trimethyl-, chloride
31	50598-29-3	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(phenylmethyl)-
32	52550-45-5	Poly(oxy-1,2-ethanediyl), α-[2-[[(heptadecafluorooctyl)sulphonyl]propylamino]ethyl]-ω -hydroxy-
33	56773-42-3	Ethanaminium, *N,N',N''*-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulphonic acid (1:1)
34	57589-85-2	Benzoic acid, 2,3,4,5-tetrachloro-6-[[[3- [[(heptadecafluorooctyl)sulphonyl]oxy]phenyl]amino]carbonyl]-, monopotassium salt
35	58920-31-3	2-Propenoic acid, 4-[[(heptadecafluorooctyl)sulphonyl]methylamino]butyl ester
36	61577-14-8	2-Propenoic acid, 2-methyl-, 4-[[(heptadecafluorooctyl)sulphonyl]methylamino]butyl ester
37	61660-12-6	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[3-(trimethoxysilyl)propyl]-
38	67939-42-8	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[3-(trichlorosilyl)propyl]-
39	67969-69-1	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[2-(phosphonooxy)ethyl]-, diammonium salt
40	67939-88-2	1-Octanesulphonamide, *N*-[3-(dimethylamino)propyl]- 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, monohydrochloride
41	68081-83-4	Carbamic acid, (4-methyl-1,3-phenylene)bis-, bis[2-[ethyl[(perfluoro-C4-8-alkyl)sulphonyl]amino]ethyl] ester
42	68298-11-3	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl](3-sulphopropyl)amino]-*N*-(2-hydroxyethyl)-*N*,*N*-dimethyl-, hydroxide, inner salt
43	68329-56-6	2-Propenoic acid, eicosyl ester, polymer with 2-[[(heptadecafluorooctyl)sulphonyl] methylamino]ethyl 2-propenoate, hexadecyl 2-propenoate, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate and octadecyl 2-propenoate
44	68239-73-6	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(4-hydroxybutyl)-*N*-methyl-
45	68310-75-8	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl]amino]-*N*,*N'*,*N''*-trimethyl-, iodide, ammonium salt
46	68541-80-0	2-Propenoic acid, polymer with 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and octadecyl 2-propenoate

Table A1.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

Ref No.	CAS Number	PFOS related substance
47	68555-90-8	2-Propenoic acid, butyl ester,polymer with 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl 2-propenoate, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate and 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate
48	68555-91-9	2-Propenoic acid, 2-methyl-, 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester, polymer with 2-[ethyl[(nonafluorobutyl)sulphonyl]amino] ethyl 2-methyl-2-propenoate, 2-[ethyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [ethyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and octadecyl 2-methyl-2-propenoate
49	68555-92-0	2-Propenoic acid, 2-methyl-, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester, polymer with 2- [methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and octadecyl 2-methyl-2-propenoate
50	68608-14-0	Sulphonamides, C4-8-alkane, perfluoro, *N*-ethyl-*N*-(hydroxyethyl), reaction products with 1,1'-methylenebis[4-isocyanatobenzene]
51	68649-26-3	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-, reaction products with *N*-ethyl-1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-1-butanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-*N*-(2-hydroxyethyl)- 1-heptanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-(2-hydroxyethyl)-1-hexanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,5-undecafluoro-*N*-(2-hydroxyethyl)-1-pentanesulphonamide, polymethylenepolyphenyleneisocyanate and stearyl alc.
52	68867-60-7	2-Propenoic acid, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester, polymer with 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2- [methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate and.alpha.-(1-oxo-2-propenyl)-.omega.-methoxypoly(oxy-1,2-ethanediyl)
53	68877-32-7	2-Propenoic acid, 2-methyl-, 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester, polymer with 2-[ethyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(tridecafluoro-hexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(undecafluoro-pentyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and 2-methyl-1,3-butadiene
54	68891-96-3	Chromium, diaquatetrachloro[.mu.-[*N*-ethyl-*N*- [(heptadecafluorooctyl)sulphonyl] glycinato-.kappa.O:.kappa.O']]-.mu.-hydroxybis(2-methylpropanol)di-
55	68909-15-9	2-Propenoic acid, eicosyl ester, polymers with branched octylacrylate, 2- [[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl acrylate, 2-[methyl [(nonafluorobutyl)sulphonyl]amino]ethyl acrylate, 2- [methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl acrylate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl acrylate, 2- [methyl[(undecafluoropentyl)sulphonyl]amino]ethyl acrylate, polyethylene glycol acrylate Me ether and stearyl acrylate
56	68958-61-2	Poly(oxy-1,2-ethanediyl), .alpha.-[2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl]-.omega.-methoxy-
57	70225-14-8	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1)
58	70776-36-2	2-Propenoic acid, 2-methyl-, octadecyl ester, polymer with 1,1-dichloroethene, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl 2-propenoate, *N*-(hydroxymethyl)-2-propenamide, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate and 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate
59	71463-78-0	Phosphonic acid, [3-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]propyl]-
60	71463-80-4	Phosphonic acid, [3-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]propyl]-, diethyl ester

Table A1.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

Ref No.	CAS Number	PFOS related substance
61	71487-20-2	2-Propenoic acid, 2-methyl-, methyl ester, polymer with ethenylbenzene, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl 2-propenoate, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2- [methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate, 2- [methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate and 2-propenoic acid
62	91081-99-1	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-(hydroxyethyl)-*N*-methyl, reaction products with epichlorohydrin, adipates (esters)
63	92265-81-1	Ethanaminium, *N*,*N*,*N*-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]-, chloride, polymer with 2-ethoxyethyl 2-propenoate, 2-[[(heptadecafluorooctyl)sulphonyl] methylamino]ethyl 2-propenoate and oxiranylmethyl 2-methyl-2-propenoate
64	94133-90-1	1-Propanesulphonic acid, 3-[[3-(dimethylamino)propyl][(heptadecafluorooctyl) sulphonyl]amino]-2-hydroxy-, monosodium salt
65	94313-84-5	Carbamic acid, [5-[[[2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethoxy]carbonyl]amino]-2-methylphenyl]-, 9-octadecenyl ester, (Z)-
66	98999-57-6	Sulphonamides, C_{7-8}-alkane, perfluoro, *N*-methyl-*N*-[2-[(1-oxo-2-propenyl)oxy]ethyl], polymers with 2-ethoxyethyl acrylate, glycidyl methacrylate and *N*,*N*,*N*-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]ethanaminium chloride
67	127133-66-8	2-Propenoic acid, 2-methyl-, polymers with Bu methacrylate, lauryl methacrylate and 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl methacrylate
68	129813-71-4	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-methyl-*N*-(oxiranylmethyl)
69	148240-78-2	Fatty acids, C_{18}-unsatd., trimers, 2-[[heptadecafluorooctyl)sulphonyl]methylamino]ethyl esters
70	148684-79-1	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-(hydroxyethyl)-*N*-methyl, reaction products with 1,6-diisocyanatohexane homopolymer and ethylene glycol
71	160901-25-7	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-ethyl-*N*-(hydroxyethyl), reaction products with 2-ethyl-1-hexanol and polymethylenepolyphenylene isocyanate
72	178094-69-4	1-Octanesulphonamide, *N*-[3-(dimethyloxidoamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-,potassium salt
73	178535-22-3	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-ethyl-*N*-(hydroxyethyl)-, polymers with 1,1'-methylenebis[4-isocyanatobenzene] and polymethylenepolyphenylene isocyanate, 2-ethylhexyl esters, Me Et ketone oxime-blocked
74	182700-90-9	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-methyl-, reaction products with benzene-chlorine-sulphur chloride (S_2Cl_2) reaction products chlorides
75	L-92-0151 (US Pre-manufacture notice)	2-Propenoic acid, 2-methyl-, butyl ester, polymer with 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [ethyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and 2-propenoic acid
76	P-94-2205 (US Pre-manufacture notice)	Polymethylenepolyphenylene isocyanate and bis(4-NCO-phenyl)methane reaction products with 2-ethyl-1-hexanol, 2-butanone, oxime, *N*-ethyl-*N*-(2-hydroxyethyl)-1-C_4-C_8 perfluoroalkanesulphonamide
77	192662-29-6	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-[3-(dimethylamino)propyl], reaction products with acrylic acid
78	251099-16-8	1-Decanaminium, *N*-decyl-*N*,*N*-dimethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulphonic acid (1:1)
79	306973-46-6	Fatty acids, linseed-oil, dimers, 2- [[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl esters
80	306973-47-7	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-(hydroxyethyl)-*N*-methyl, reaction products with 12-hydroxystearic acid and 2,4-TDI, ammonium salts

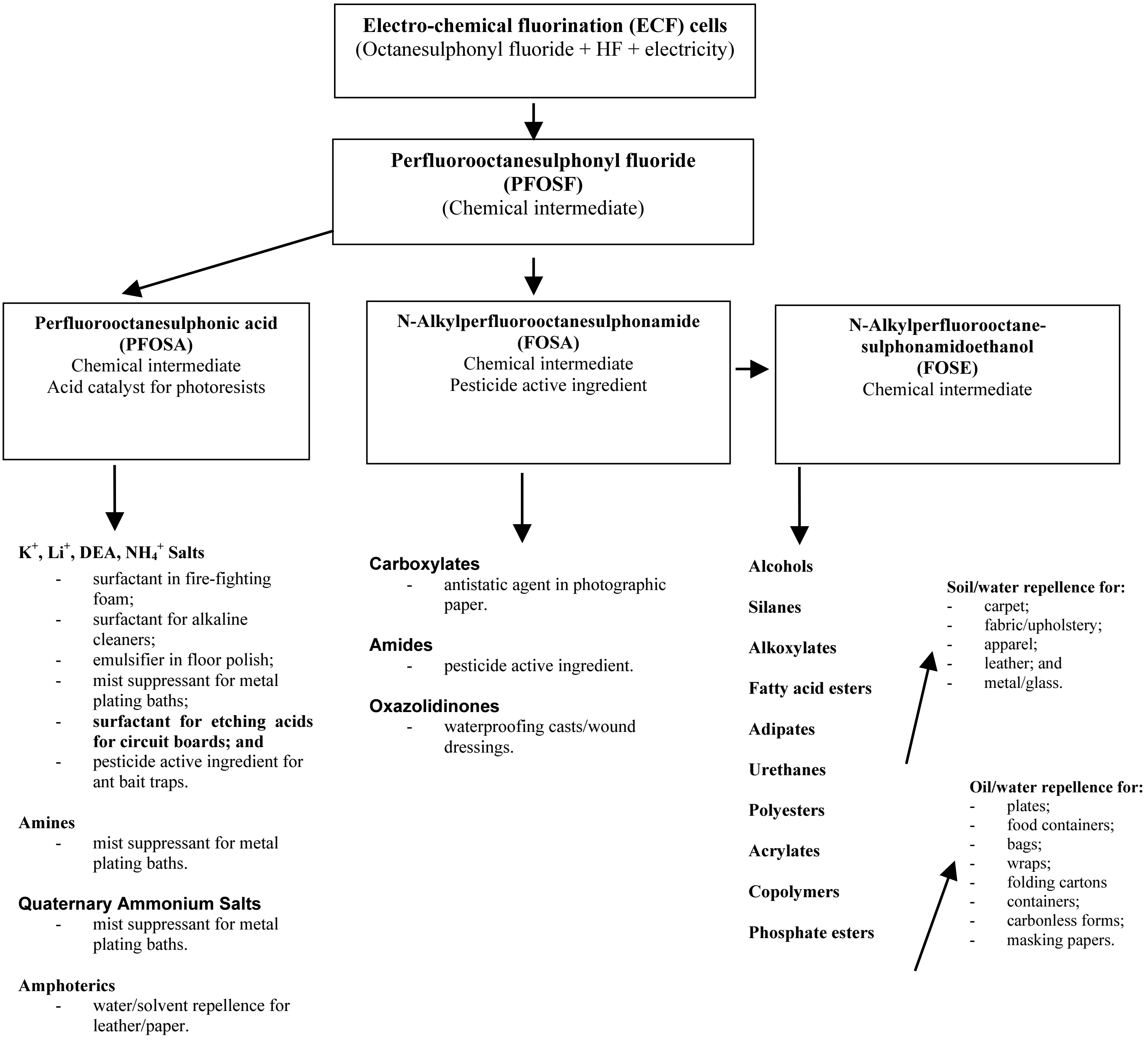
Table A1.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

Ref No.	CAS Number	PFOS related substance
81	306974-19-6	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-methyl-*N*-[(3-octadecyl-2-oxo-5-oxazolidinyl)methyl]
82	306974-28-7	Siloxanes and Silicones, di-Me, mono[3-[(2-methyl-1-oxo-2-propenyl)oxy]propylgroup] -terminated, polymers with 2-[methyl[(perfluoro-C4-8-alkyl)sulphonyl]amino]ethyl acrylate and stearyl methacrylate
83	306974-45-8	Sulphonic acids, C_{6-8}-alkane, perfluoro, compounds with polyethylene-polypropylene glycol bis(2-aminopropyl) ether
84	306974-63-0	Fatty acids, C_{18}-unsatd.,dimers, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino] ethyl esters
85	306975-56-4	Propanoic acid, 3-hydroxy-2- (hydroxymethyl)-2-methyl-, polymer with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol and *N*,*N*',2-tris(6-isocyanatohexyl)imidodicarbonic diamide, reaction products with *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-1-octanesulphonamide and *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-*N*-(2-hydroxyethyl)-1-heptanesulphonamide, compounds with triethylamine
86	306975-57-5	Propanoic acid, 3-hydroxy-2-(hydroxymethyl)-2-methyl-, polymer with 1,1'-methylenebis[4- isocyanatobenzene] and 1,2,3-propanetriol, reaction products with *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-1-octanesulphonamide and *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-*N*-(2-hydroxyethyl)-1-heptanesulphonamide, compounds with morpholine
87	306975-62-2	2-Propenoic acid, 2-methyl-, dodecyl ester, polymers with 2- [methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate and vinylidene chloride
88	306975-84-8	Poly(oxy-1,2-ethanediyl), .alpha.-hydro-.omega.-hydroxy-, polymer with 1,6-diisocyanatohexane, *N*-(hydroxyethyl)-*N*-methyl perfluoro C_{4-8}-alkane sulphonamides-blocked
89	306975-85-9	2-Propenoic acid, 2-methyl-, dodecyl ester, polymers with *N*-(hydroxymethyl)-2-propenamide, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl methacrylate, stearyl methacrylate and vinylidene chloride
90	306976-25-0	1-Hexadecanaminium, *N*,*N*-dimethyl-*N*-[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]-, bromide, polymers with Bu acrylate, Bu methacrylate and 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate
91	306976-55-6	2-Propenoic acid, 2-methyl-, 2-methylpropyl ester, polymer with 2,4-diisocyanato-1-methylbenzene, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol and 2-propenoic acid, *N*-ethyl-*N*-(hydroxyethyl)perfluoro-C_{4-8}-alkanesulphonamides-blocked
92	306977-58-2	2-Propenoic acid, 2-methyl-, 3-(trimethoxysilyl)propyl ester, polymers with acrylic acid, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate and propylene glycol monoacrylate, hydrolysed, compounds with 2,2'-(methylimino)bis[ethanol]
93	306978-04-1	2-Propenoic acid, butyl ester, polymers with acrylamide, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate and vinylidene chloride
94	306978-65-4	Hexane, 1,6-diisocyanato-, homopolymer, *N*-(hydroxyethyl)-*N*-methyl perfluoro-C_{4-8}-alkane sulphonamides- and stearyl alc.-blocked
95	306979-40-8	Poly(oxy-1,2-ethanediyl), .alpha.-[2-(methylamino)ethyl]-.omega.-[(1,1,3,3-tetramethylbutyl)phenoxy]-, *N*-[(perfluoro-C_{4-8}-alkyl)sulphonyl]
96	306980-27-8	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*,*N*'-[1,6-hexanediylbis[(2-oxo-3,5-oxazolidinediyl)methylene]]bis[*N*-methyl-

Sources: US EPA (2002a); US EPA (2002b); Environment Agency (2001); Consultation with Environment Canada (note that RPA reviewed a confidential draft list of PFOS precursors that was provided by Environment Canada. This was developed from the 182 PFAS that were listed in a June 2000 survey to Canadian industry (Environment Canada, 2000). The draft list will be available as an appendix in the draft screening assessment report on PFOS and its Precursors that the Departments of Environment and Health Canada will release for public comment in early 2004 (Windle, 2003)).

Annex 2:

Major Product Categories and Applications for Perfluorooctylsulphonates (OECD, 2002)



Annex 3

Overview of Uses for PFOS and PFOS Related Substances (UK Stage 4 final report)

Group	Uses/Applications	End Product	Substances Used (if known)
Surface Treatment Applications	Treatment	Apparel/Textile	FOSE alcohols FOSE silanes FOSE alkoxylates FOSE fatty acid esters FOSE adipates FOSE urethanes FOSE acrylates FOSE polyesters FOSE copolymers
		Fabric/upholstery	
		Carpets	
		Automotive interiors	
	Treatment of metal and glass	Metal/glass	
	Leather treatment (water/oil/solvent repellence)	Leather	As above including PFOSA amphoterics
	Mist suppressant Corrosion inhibitors	Metal plating baths	PFOSA K^+, Li^+, DEA and NH_4^+ salts
Paper Protection Applications	Water/oil grease/solvent repellence	Plates and food containers	FOSE acrylates FOSE copolymers FOSE phosphate esters
		Bags and wraps	
		Folding cartons	
		Containers	
		Carbonless forms	
		Masking papers	
Performance Chemical Applications	Surfactants	Surfactant in fire fighting foams	PFOSA K^+, Li^+, DEA and NH_4^+ salts
		Surfactant in alkaline cleaners	
		Mine and oil well surfactants	
	Cleaning agents	Denture cleaners	
		Shampoos	
		Carpet spot cleaners	
		Mould release agents	
	Waxes and polishes	Emulsifier in wax and floor polishes	PFOSA K^+, Li^+, DEA and NH_4^+ salts
	Coatings	Coating additives	
	Photography	Antistatic agents; Surfactants for paper, films, photographic plates;	FOSA carboxylates
	Photolithography	Coatings for semiconductors anti-reflective coatings	
	Pesticides/insecticides	Pesticides active ingredient	FOSA amides
		Active ingredient for ant bait traps	PFOSA amines
	Chemical synthesis	Chemical intermediates	PFOSF, PFOSA, FOSA, FOSE
	Medical applications	Waterproofing casts/wound dressings	FOSA oxazolidones
	Hydraulic fluids	Hydraulic agents	

Sources: Danish EPA, 2002; OECD, 2002; Consultation

Notes: PFOSA: Perfluorooctanesulphonic acid; FOSA: N-Alkylperfuorooctanesulphoneamide; FOSE: N-Alkylperfluorooctanesulphonamidoethanol; PFOSF: Perfluorooctanesulphonyl fluoride; DEA: Diehanolamine