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Item 5 (e) of the provisional agenda*

Consideration of draft risk profiles:
perfluorooctane sulfonate

Draft risk profile: perfluorooctane sulfonate (PFOS)

Note by the Secretariat

1. At its first meeting, the Persistent Organic Pollutants Review Committee adopted decision POPRC-1/7 on perfluorooctane sulfonate (PFOS).[1] In paragraph 2 of the decision, the Committee decided to establish an ad hoc working group to review further the proposal to list PFOS in Annex A to the Convention (UNEP/POPS/POPRC.1/9 and UNEP/POPS/POPRC.1/INF/9) and to prepare a draft risk profile in accordance with Annex E. In paragraph 3 of the decision, the Committee decided further that issues related to the inclusion of potential perfluorooctane sulfonate precursors should be dealt with in developing the draft risk profile.

2. The members of the ad hoc working group on PFOS and its observers are listed in annex VI of document UNEP/POPS/POPRC.1/10.

3. A standard workplan for the preparation of a draft risk profile was adopted by the Committee at its first meeting.[2]

4. The process for developing draft risk profiles is summarized in document UNEP/POPS/POPRC.2/INF/14.

5. In accordance with decision POPRC-1/7 and the standard workplan adopted by the Committee, the ad hoc working group on PFOS prepared the draft risk profile set forth in the annex to the present note. The draft risk profile has not been formally edited.

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* UNEP/POPS/POPRC.2/1.

[1] UNEP/POPS/POPRC.1/10, annex I.

[2] Ibid., para. 42 and annex II.

Possible action by the Committee

6. The Committee may wish:

(a) To adopt, with any amendments, the draft risk profile set forth in the annex to the present note;

(b) To decide, in accordance with paragraph 7 of Article 8 of the Convention and on the basis of the risk profile, whether the chemical is likely as a result of its long-range transport to lead to significant adverse human health and/or environmental effects such that global action is warranted and that the proposal shall proceed;

(c) To agree, depending on the decision taken under (b) above:

   (i) To invite all Parties and observers to provide information pursuant to Annex F of the Convention, to establish an ad hoc working group to develop a draft risk management evaluation and to agree on a workplan for completing the draft; or

   (ii) To make the risk profile available to all Parties and observers and set it aside.

Annex

PERFLUOROOCTANE SULFONATE (PFOS)

WORKING DRAFT RISK PROFILE

Draft prepared for the ad hoc working group on PFOS under the POP Review Committee of the Stockholm Convention

This revised draft profile has been prepared by Swedish Chemicals Inspectorate (KemI)

July 2006

EXECUTIVE SUMMARY

1 INTRODUCTION

1.1 Chemical Identity of the proposed substance

On 14th of July 2005, the government of Sweden made a proposal for listing perfluorooctane sulfonate (PFOS) and 96 PFOS-related substances in Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs).

Chemical name: Perfluorooctane Sulfonate (PFOS)

Molecular formula: $C_8F_{17}SO_3^-$

PFOS, as an anion, does not have a specific CAS number. The parent sulfonic acid and some of its commercially important salts are listed below:

Perfluorooctane sulfonic acid (CAS No. 1763-23-1)

Potassium salt (CAS No. 2795-39-3)

Diethanolamine salt (CAS No. 70225-14-8)

Ammonium salt (CAS No. 29081-56-9)

Lithium salt (CAS No. 29457-72-5)

Structural formula:

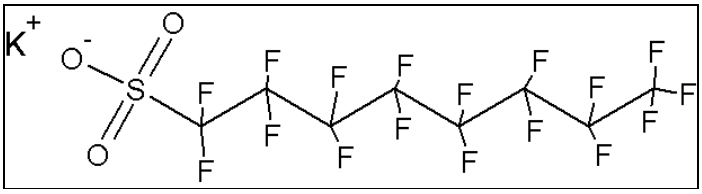

Figure 1. Structural formula of PFOS shown as its potassium salt

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 substances which can give rise to PFOS, are members of the large family of perfluoroalkyl sulfonate 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	< 2 x 10^{-6} (3M, 2003)
Henry's Law Constant	3,09 x 10^{-9} atm m^3/mol pure water

PFOS can be formed (by environmental microbial degradation or by metabolism in larger organisms) from PFOS-related substances, i.e., molecules containing the PFOS-moiety depicted in Figure 1. Although the ultimate net contribution of individual PFOS-related substances to the environmental loadings of PFOS cannot be predicted readily, it is considered here that any molecule containing the PFOS moiety can be a precursor to PFOS.

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 extents depending on the substances under consideration and the overlap between national lists of existing chemicals.

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

Source	Number of PFOS-related substances
UK – DEFRA (2004)	96
US - EPA (2002, 2006)	88[1] + 183[1]
OECD (2002)	172[1] (22 classes of perfluoroalkyl sulfonate substances)
OSPAR (2002)	48
Canada (2004)	57

1 Perfluorinated substances with different carbon chain lengths are included in the list.

A large number of substances may give rise to PFOS and thus contribute to the contamination problem. DEFRA, UK (2004) has recently proposed a list of 96 PFOS-related substances. However, the properties of the 96 substances have not generally been determined. According to 3M, (submission to the secretariat of Stockholm Convention (SC), 2006), they may have very different environmental characteristics such as solubility, stability and ability to be absorbed or metabolised. Nevertheless, it is expected that all of these substances would give rise to the final degradation product of PFOS.

Environment Canada's ecological risk assessment defines PFOS precursors as substances containing the perfluorooctylsulfonyl ($C_8F_{17}SO_2$, $C_8F_{17}SO_3$,, or $C_8F_{17}SO_2N$) moiety that have the potential to transform or degrade to PFOS. The term "precursor" applies to, but is not limited to, some 50 substances identified in the ecological assessment. However, this list is not considered exhaustive, as there may be other perfluorinated alkyl compounds that are also PFOS precursors. This information was compiled based on a survey to industry, expert judgement and CATABOL modelling, in which 256 perfluorinated alkyl compounds were examined to determine whether non-fluorinated components of each substance were expected to degrade chemically and/or biochemically and whether the final perfluorinated degradation product was predicted to be PFOS. While the assessment did not consider the additive effects of PFOS and its precursors, it is recognized that the precursors to PFOS contribute to the ultimate environmental loading of PFOS. Precursors may also play a key role in the long-range transport and subsequent degradation to PFOS in remote areas, such as the Canadian Arctic.

In order to avoid excluding substances that may be PFOS precursors, PFOS-related substances/potential PFOS precursors are defined in this document as all molecules having the following molecular formula: $C_8F_{17}SO_2Y$, where Y = OH, metal salt, halide, amide and other derivatives including polymers. This definition has been proposed by the EU (EU COM 2005).

1.2 Conclusion of the POP Review Committee of Annex D information

The Persistent Organic Pollutants Review Committee (POPRC) has evaluated Annex D at the First meeting of the POPRC, Geneva, 7-11 November 2005, and has concluded that PFOS meets the screening criteria specified in Annex D (decision POPRC-1/7: Perfluorooctane sulfonate).

1.3 Data sources

This document on PFOS mainly builds on information that has been gathered in the hazard assessment report prepared by the UK and the USA for the OECD, and in the UK risk reduction strategy:

OECD (2002) Co-operation on Existing Chemicals - Hazard Assessment of Perfluorooctane Sulfonate and its Salts, Environment Directorate Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology, Organisation for Economic Co-operation and Development, Paris, 21 November 2002.

Risk & Policy Analysts Limited (RPA & BRE, 2004) in association with BRE Environment, Perfluorooctane Sulfonate – Risk reduction strategy and analysis of advantages and drawbacks, Final Report prepared for Department for Environment, Food and Rural Affairs and the Environment Agency for England and Wales.

Recent relevant information from the open scientific literature (up to May 2006) is also included. Data submitted by Parties and observers, which have been considered, are also included in this report when they add new information.

1.4 Summary of available risk information

The hazard assessment of PFOS, prepared by the 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.

An environmental risk assessment, 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) shows that PFOS is of concern.

The Environment Canada/Health Canada Draft Assessments of PFOS, its Salts and its Precursors were released for public comment in October 2004. The ecological and human health assessments have been subsequently revised and should be publicly available soon. The ecological risk assessment has concluded that PFOS is persistent, bioaccumulative, and may have immediate or long-term harmful effects on the environment.

Sweden has made a notification to the European Commission concerning proposed restrictions on marketing and use of PFOS and their 96 known derivatives. The proposed Swedish regulation prohibits products that 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 UK has notified a national regulation of PFOS and substances that degrade to it. The proposed UK regulation prohibits the import into the United Kingdom of fire fighting foams containing perfluorooctane sulfonate. The regulation also prohibits the supply, storage and use of perfluorooctane sulfonate for any uses and time limited derogations for certain uses.

The UK and Sweden have proposed the following classification for PFOS in EU (2005):

T Toxic

R40 Carcinogen category 3; limited evidence of carcinogenic effect

R48/25 Toxic; danger of serious damage to health by prolonged exposure if swallowed

R61 May cause harm to the unborn child

R51/53 Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

The EU is now considering a proposal on the prohibition of PFOS and PFOS-related compounds in some products and chemical mixtures.

Norway is now considering a proposal to prohibit the use of fire fighting foams containing PFOS and PFOS-related compounds, which is the major use of these compounds today in Norway.

The Environmental Protection Agency (EPA) in the USA finalized two Significant New Use Rules (SNURs) in 2002, requiring companies to inform the EPA before manufacturing or importing 88 listed PFOS-related substances. The EPA proposed an additional SNUR under section 5(a)(2) of the Toxic Substances Control Act (TSCA) in March 2006 to include within the scope of this regulation another 183 perfluoroalkyl sulfonates with carbon chain lengths of five carbons and higher. The EPA further proposed an amendment to the Polymer Exemption rule in March 2006 which would remove from exemption polymers containing certain perfluoroalkyl moieties consisting of CF3- or longer chains, and would require that new chemical notifications be submitted on such polymers.

1.5 Status of the chemical under international conventions

OSPAR: PFOS was added to the list of Chemicals for Priority Action in June 2003.

Persistent Organic Pollutants Protocol to the Long-Range Transboundary Air Pollution Convention ("LRTAP"): Perfluorooctane sulfonate and its precursors were approved under Track A and are currently under Track B review.

2 SUMMARY INFORMATION RELEVANT FOR THE RISK PROFILE

2.1 Sources

2.1.1 Production and trade

The main production process of PFOS and PFOS-related substances is electro-chemical fluorination (ECF) and utilized by 3M, the major global producer of PFOS and PFOS-related substances prior to 2000.

- *Direct fluorination, electro-chemical fluorination (ECF):*

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

The reaction product, perfluorooctanesulfonyl fluoride (PFOSF)[1] is the primary intermediate for synthesis of PFOS and PFOS-related substances. The ECF method results in a mixture of isomers and homologues with about 35-40% 8-carbon straight chain PFOSF. However, the commercial PFOSF products were a mixture of approximately 70% linear and 30% branched PFOSF derivate impurities. The global production of PFOSF by 3M until the production ceased is estimated to have been 13,670 metric tonnes (1985 to 2002), with the largest yearly production volume, 3500 metric tonnes, in 2000 (3M, Submission to SC, 2006). PFOSF may be further reacted with methyl- or ethylamine to form *N*-ethyl- and *N*-methyl perfluorooctane sulfamide and subsequently with ethylene carbonate resulting in *N*-ethyl- and -methyl- perfluorooctane sulfamidoethanol (*N*-EtFOSE and *N*-MeFOSE). *N*-EtFOSE and *N*-MeFOSE were the principal building blocks of 3M's product lines. PFOS is formed after the chemical or enzymatic hydrolysis of PFOSF (3M, 1999).

Other production methods for perfluoroalkylated substances are telomerisation and oligomerisation. However, to which extent these methods are applied for production of PFOS and PFOS-related substances is not evident.

On 16 May 2000, 3M announced that the company would phase-out the manufacture of PFOS and PFOS-related substances voluntarily from 2001 onwards. The 3M global production of PFOS and PFOS-related substances in year 2000 was approximately 3,700 metric tonnes. By the end of 2000 about 90 % of 3M's production of these substances had stopped and in the beginning of 2003 the production ceased completely.

3M´s voluntary phase-out of PFOS production has led to a 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 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). However, this list may not be exhaustive or current.

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[1] In the OECD report, 2002, perfluorooctanesulfonyl fluoride is abbreviated POSF.

According to the recent submission from Japan to the secretariat of the Stockholm Convention, 2006, there is one manufacturer in Japan still producing PFOS and with a production amount of 1-10 tonnes (2005). The submission from Brazil states that lithium salt of PFOS is produced but that no quantitative data is available.

2.1.2 Uses

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 makes them suitable for high temperature applications and for applications in contact with strong acids or bases. It is the very strong carbon-fluorine binding property that causes the persistence of perfluorinated substances.

The historical use of PFOS-related substances in the following applications has been confirmed in the US and the EU.

- 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 (RPA & BRE, 2004), 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 semiconductor
- Hydraulic fluids
- Metal plating

The sectors presented above account for the UK but are considered to be representative for EU. However, deviation in the current use pattern between EU countries can not be excluded.

PFOS and its precursors are not manufactured in Canada but rather are imported as chemicals or products for Canadian uses. They may also be components in imported manufactured articles. It is estimated that the majority of PFOS has been used as water, oil, soil and grease repellents (e.g. on fabric, leather, paper, packaging, rugs and carpets) and as surfactants (e.g. in fire fighting foams and coating additives) (Environment Canada, 2004).

PFOS and its precursors are not manufactured in the US, but can be imported either as chemicals or in products for the specific limited uses that were excluded from regulation. These comprise use as an anti-erosion additive in aviation hydraulic fluids; use as a component of a photoresist substance, including a photo acid generator or surfactant, or as a component of an anti-reflective coating, used in a photomicrolithography process to produce semiconductors or similar components of electronic or other miniaturized devices; use in coatings for surface tension, static discharge, and adhesion control for analog and digital imaging films, papers, and printing plates, or as a surfactant in mixtures used to process imaging films; and use as an intermediate only to produce other chemical substances to be used solely for these uses. Historically, PFOS and its precursors were also used as surfactants in fire fighting foams and in industrial and household cleaning products; in carpet, textile, leather, and paper coatings; and in termite and ant bait insecticide products. Stocks of PFOS and PFOS-containing products that were in existence at the time the US regulations were promulgated in 2002 could continue to be used in any application until they were consumed without violating the regulation, except that the PFOS-related insecticide products are subject to a phaseout agreement prohibiting their use after 2015.

The table below outlines the estimated current demand for PFOS-related substances in these applications in the EU (RPA & BRE, 2004).

Estimated Current (2004) Demand for PFOS Related Substances in the EU	
Industry Sector	Quantity (kg/year)
Photographic industry	1,000
Photolithographic and semi-conductors	470
Hydraulic fluids	730
Metal plating	10,000

In the survey on production and use of PFOS and related substances performed by OECD in 2004 (published 2005), data concerning PFOS were difficult to separate from data on other perfluoroalkyl sulfonates.

Fire Fighting Foams

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

- Fluorine containing foam types (some of them consist 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 (RPA & BRE, 2004). Historically, in Canada, the most significant imports of PFOS, itself, were in the form of the potassium salt, used for fire-fighting foams (Environment Canada, 2004). Canada has also identified that existing stocks of PFOS-containing fire fighting foams could be a continued significant source of releases.

An industry survey conducted in the US by the Fire Fighting Foam Coalition in 2004 reported that the total inventory of aqueous film-forming foam in the US was approximately 9.9 million gallons, of which about 45% was PFOS-based stocks produced before 2003, with the other 55% comprised of telomere-based foams.

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. Since 3M´s withdrawal from the market, PFOS-related substances are used to a much smaller extent for these applications (RPA & BRE, 2004).

Paper and Packaging Protection

FOS-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 used to a much smaller extent for these applications (RPA & BRE, 2004).

Coatings and Coating Additives

3M indicates that prior to its 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) (RPA & BRE, 2004).These polymers contained fluorocarbon residuals at a concentration of 4% or less. Other applications for aqueous coatings are to protect tile, marble and concrete. It is unclear which of these products were actually based on PFOS-related substances.

A survey in the UK among members of the British Coatings Federation (BCF) showed that the use of PFOS-related substances for these purposes is very limited (RPA & BRE, 2004).

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 (specify what survey and year) do 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 (RPA & BRE, 2004).

Photographic Industry

PFOS-based chemicals are used for the following purposes in mixtures, in coatings applied to photographic films, papers, and printing plates (RPA & BRE, 2004):

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

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. Photolithography is also integral to the miniaturization of semiconductors. (RPA & BRE, 2004).

.PFOS is used as a photoacid generator (PAG) in a mechanism called chemical amplification that increases the sensitivity of photoresist to allow etching images smaller than wavelength of light.

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.

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.

Perfluorinated anions acts by altering the electrical potential at the metal surface, thereby preventing the electrochemical oxidation of the metal surface under high fluid flow conditions (RPA & BRE, 2004). 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 (RPA & BRE, 2004).

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 (RPA & BRE, 2004).

Other

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. Based on current understanding, these applications represent a minor part of known PFOS applications and are therefore not further elaborated in this dossier.

2.1.3 Releases 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 and sewage treatment plants after the use of the products (3M, 2000).

Manufacturing processes constitute a major source of 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 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). High concentrations of PFOS were also found in liver and blood from fish collected in the Mississippi River at the immediate vicinity of another of 3M's fluorochemical plant, Cottage Grove in Minnesota (MPCA, 2006).

Fire training areas have also been 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 in groundwater in the US close to a fire-training area (Moody et al., 2003).

An investigation on the uses of PFOS and PFOS-related compounds in Norway in 2005 shows that approximately 90% of the total use is in fire extinguishers (Submission to SC, 2006). Estimated releases of PFOS related to fire extinguishers are at least 57 tonnes since 1980 to 2003 (2002; 13-15 tonnes). Remaining quantities of fire extinguisher foam in Norway are estimated to be a minimum of 1.4 million litres, which corresponds to an amount of approximately 22 tonnes PFOS. Releases from the municipal sector in Norway, 2002, were estimated to be 5-7 tonnes (Submission to SC, 2006).

The use of PFOS in semiconductors is estimated to result in a release of 43 kg per year in the EU, according to the Semiconductur Industry Association (SIA) (SIA, Submission to SC, 2006). This corresponds to 12 % of the total PFOS use in this application. PFOS released in the USA from semiconductors is estimated to be in the same range (SIA, 2006).

The releases of sulfonated perfluorochemicals, including PFOS or PFOS-related substances, from different product usages have been estimated (3M Speciality Materials, 2002). For example, garments treated with home-applied products, are expected to lose 73 % of the treatment during cleaning over a 2-year life span. A loss of 34 % to air is expected from spray can products during use, while up to 12.5 % of the original content may be remaining in the cans at the time of disposal.

One route for PFOS and PFOS-related substances to the environment may 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. A substantial amount of PFOS may 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, or oceanic currents (Yamashita *et al.*, 2005, Caliebe *et al.*, 2004), transport in air (volatile PFOS-related substances), adsorption to particles (in water, sediment or air) and through living organisms (3M, 2003a).

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 are presently unknown. In a study on Swedish STPs, higher concentrations of PFOS were found in the effluents compared to incoming sewage water, which could indicate that PFOS was formed through PFOS-related substances (Posner and Järnberg, 2004).

2.2 Environmental fate

2.2.1 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 be 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. None of the studies demonstrated any signs of biodegradation.

Modelling with a simulator program of microbial degradation, the CATABOL system, and expert judgment predicted that of 171 studied perfluorinated substances over 99% would biodegrade to extremely persistent perfluorinated acids. Of them, 109 substances were predicted to end up as perfluorinated sulfonic acids, including PFOS, and 61 as perfluorinated carboxylic acids (Dimitrov et al., 2004).

The only known condition whereby PFOS is degraded is through high temperature incineration under correct operating conditions (3M, 2003a). Potential degradation at low temperature incineration is unknown.

2.2.2 Bioaccumulation

It should be noted that PFOS does not follow the “classical” pattern of partitioning into fatty tissues followed by accumulation, which is typical of many persistent organic pollutants. This is because PFOS is both hydrophobic and lipophobic. Instead, PFOS binds preferentially to proteins in the plasma, such as albumin and β-lipoproteins (Kerstner-Wood et al., 2003), and in the liver, such as liver fatty acid binding protein (L-FABP; Luebker et al., 2002). Because of the unusual physical-chemical characteristics of PFOS, the mechanism of bioaccumulation probably differs from other POPs.

In a study following OECD protocol 305, the bioaccumulation of PFOS in bluegill sunfish (*Lepomis macrochirus*) has been tested. The whole-fish kinetic bioconcentration factor (BCFK) was determined to be 2796 (3M, 2002).

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

When strictly looking at the BCF values, it is clear that these values are below the numeric BCF criteria in Stockholm Convention Annex D (the reported BCF values are below 5000) but, in this particular case, as noted above, the BCF numeric criteria may not adequately represent the bioaccumulation potential of the substance. Monitoring data from top predators at various locations show highly elevated levels of PFOS and demonstrate substantial bioaccumulation and biomagnification (BMF) properties of PFOS. It is notable that the concentrations of PFOS found in livers of Arctic polar bears exceed the concentrations of all other known individual organohalogens (Martin et al., 2004a). 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., 2004a.
• Arctic fox, Canadian Arctic	- Very high concentrations of PFOS in liver (6.1 - 1400 ng/g)	Martin et al., 2004a.
• Mink, US	- Very high concentrations of PFOS in liver (40 - 4870 ng/g). - BMF = 22 based on data from fish in the same area. - Another mink study also show very high concentrations of PFOS in liver (1280 - 59 500 ng/g, mean 18 000 ng/g,) - BMF ~145 to ~4000 based on data from their prey such as crayfish (whole body), carp (muscle) and turtles (liver	Giesy and Kannan, 2001 Kannan et al., 2005
• Bald Eagle, US	- Very high concentrations of PFOS in plasma (1 – 2570 ng/g).	Giesy and Kannan 2001.
• Dolphin, US	- Very high concentrations of PFOS in liver (10 – 1520 ng/g).	3M, 2003a.
• Seal in the Bothnian Sea, Finland	- Very high concentrations of PFOS in liver (130 – 1100 ng/g). - BMF > 60 based on data from salmon in the same area.	Kannan et al., 2002

In a study by Kannan et al. (2005), the whole body BCF for round gobies (*Neogobius* *melanostomus)* was calculated to be approximately 2400, which is comparable with laboratory data. PFOS concentrations in fish (whole body of round gobies) compared to concentrations in liver of salmon results in BMFs of approximately 10-20. In bald eagles, the mean PFOS concentration in the livers, 400 ng/g ww, gives a BMF of four to five when compared to fish at higher trophic levels in the study. For mink, BMFs from 145 to 4000 can be calculated when based on the mean liver concentration, 18 000 ng/g ww, compared to their prey items such as crayfish (whole body), carp (muscles) and turtles (liver).

In general, data show that animals at higher trophic levels have higher concentrations of PFOS than animals at lower trophic levels, indicating that biomagnification is taking place. For instance, a trophic magnification factor (TMF) of 5,9 was calculated for PFOS based on a pelagic food web including: one invertebrate species, Mysis; two forage fish species, rainbow smelt and alewife; and a top predator fish species, lake trout. A diet-weighted bioaccumulation factor of approximately 3 was determined for the trout (Martin et al., (2004b).

Morikawa *et al.* (2005) showed a high bioaccumulation in turtles. Results from a study performed by Tomy *et al.* (2004a) indicated that PFOS biomagnified in an eastern Arctic marine food web (liver concentrations of PFOS were used for seabirds and marine mammals). Houde *et al* (2006) showed PFOS biomagnification in the Atlantic Ocean bottlenose dolphin food web.

A study by Bossi *et al.* (2005a) further supports that biomagnification is taking place. In this study, a preliminary screening of PFOS and related compounds has been performed in liver samples of fish, birds and marine mammals from Greenland and the Faroe Islands. PFOS was the predominant fluorochemical in the biota analyzed, followed by perfluorooctane sulfonamide (PFOSA). The results from Greenland showed a biomagnification of PFOS along the marine food chain (shorthorn sculpin < ringed seal < polar bear).

It is assumed that the main and most relevant route of exposure to PFOS for birds is through the diet as biomagnification in bird tissues can occur this way. BMFs above one are reported for several bird species collected in the Gulf of Gdansk (Gulkowska *et. al.* 2005). Kannan *et al.*, (2005) reported a BMF of 10 to 20 in bald eagles (relative to prey items). Tomy *et al.*, (2004a) calculated a trophic level BMF for black-legged kittiwake:cod of 5.1 and a BMF for glaucous gull:cod of 9.0. Newsted *et al* (2005) indicated that PFOS has relatively shorter half-lives in blood and liver tissue in birds compared to mammals. For example, the estimated elimination half-life for PFOS from serum is 13.6 days in male mallards whereas in male rats, it is greater than 90 days. A recent study has suggested that PFOS is excreted relatively rapidly from birds (Kannan *et al.*, 2005). However, if birds are chronically exposed to PFOS in their diet, biomagnification can still occur. Environmental monitoring of birds in northern parts of their range in fact indicates accumulation of PFOS.

The fact that PFOS binds to proteins leads to the relevant question -- *at what concentrations of PFOS will the binding sites on these proteins be saturated?* Serum albumin is most likely the binding pool of PFOS (Jones *et al.*, 2003) and several studies have been carried out with regard to bioconcentration in plasma. In Ankley *et al.* (2005), the bioconcentration in fish was studied at concentrations of PFOS in water up to 1 mg /L; the concentration of PFOS in water and plasma followed an almost linear relationship in the doses tested up to 0.3 mg/l without any signs of saturation (1 mg/l was not tested due to mortality at that dose). This is far above environmentally relevant concentrations.

In a study by 3M (2003a), the bioconcentration factor (BCF) in whole fish was determined to be approximately 2800 at a PFOS concentration of 86 µg/l, based on calculations of uptake and depuration of PFOS. Steady-state levels were attained after 49 days of exposure. Depuration occurred slowly and 50% clearance for whole fish tissues was estimated to be 152 days. Due to mortality, a BCF could not be calculated for the other concentration used, 870 µg/l. Thus, it is not likely that saturation of serum protein binding sites will limit the bioconcentration of PFOS in fish. In Cynomolgus monkeys, cumulative doses of PFOS (0,03, 0,15, or 0,75 mg/kg/day, orally, for 182 days) showed a linear increase in plasma at the low- and mid-dose groups while a nonlinear response was showed in the high-dose group (Covance Laboratories, Inc. 2002a). We are not aware of similar data in other mammals, but considering the high level of bioaccumulation observed in mammals, and that mammalian serum contains high concentrations of protein, binding sites are not likely to limit the bioaccumulation of PFOS in environmentally exposed mammals.

2.2.3 Long range environmental 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.

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. The vapour pressures of precursors, such as N-EtFOSEA and N-MeFOSEA, may exceed 0.5 Pa (1000 times greater than that of PFOS) (Giesy and Kannan 2002). Other PFOS precursors considered volatile include N-EtFOSE alcohol, N-MeFOSE alcohol, N-MeFOSA and N-EtFOSA (3M, 2000). These precursors to PFOS could evaporate into the atmosphere and be wider transported through air than is possible for PFOS itself. 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). Martin *et al*. (2002) measured the air in Toronto and Long Point, Ontario for some precursors of PFOS. They found an average N-MeFOSE alcohol concentration of 101 pg/m^3 in Toronto and 35 pg/m^3 at Long Point. The average concentrations of N-EtFOSE alcohol were 205 pg/m^3 in Toronto and 76 pg/m^3 in Long Point.

For precursors released to water, the vapour pressure may be significant enough to allow the substance to enter into the atmosphere. For N-EtFOSE alcohol, the tendency to leave the water phase is indicated by its relatively high Henry's law constant (1.9×10^3 $Pa \cdot m^3 \cdot mol^{-1}$) (Hekster *et al*. 2002). It has been reported that when these PFOS precursors are present as residuals in products, they could evaporate into the atmosphere when the products containing them are sprayed and dried (3M, 2000).

PFOS has been detected in rainwater from an urban center in Canada with a concentration of 0.59 ng/L. Whether or not PFOS originates from precursors either being transported and subsequently wet deposited and degraded to PFOS, or atmospherically degraded and then wet deposited, is unclear. Measurements of potential precursors for PFOS were not performed in this study (Loewen *et al*, 2005)

The atmospheric half-life of PFOS is expected to be greater than two days. This statement, while not specifically tested, is based on the fact that PFOS has exhibited extreme resistance to degradation in all tests performed. However, an atmospheric half-life of 114 days has been calculated for PFOS using an AOP computer modeling program v1.91 (Environment Agency,, 2004). The indirect photolytic half-life of PFOS at 25°C has been estimated to be more than 3.7 years (OECD, 2002).

PFOS has been measured 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* (2004a), the levels of PFOS were measured in liver samples from biota in the Canadian Arctic and were found in the vast majority of the species examined. The presence of PFOS in Arctic biota, far from anthropogenic sources, demonstrates the potential of PFOS for long-range transport. The mechanisms of this transport are not known, but it could be due to the transport of volatile PFOS-related substances that eventually degrade to PFOS.

While precursors will undergo degradation once released to the environment, transformation rates may vary widely. Precursors that reach a remote region through the atmosphere or other media may be subject to both abiotic and biotic degradation routes to PFOS (Giesy and Kannan 2002a; Hekster *et al.* 2002). The mechanisms of this degradation are not well understood. When rats metabolize N-MeFOSE-based compounds, several metabolites have been confirmed in tissue samples, including PFOS and N-MeFOSE alcohol (3M Environmental Laboratory 2001a, 2001b). PFOS appears to be the final product of rat and probably other vertebrate metabolism of POSF-based substances.

A recent study performed with rainbow trout (*Onchorhynchus mykiss)* liver microsomes has demonstrated that *N*-ethyl perfluorooctanesulfonamide (N-EtPFOSA) is a precursor of PFOS in fish (Tomy et al., 2004b). 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 (Tomy et al., 2004a) strengthen the hypothesis that perfluorinated sulfonamides 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 (Bossi et al., 2005b)

2.3 Exposure

Measured environmental levels

A screening study was assigned by the Swedish Environmental Protection Agency (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 sewage treatment plants (STPs) and landfills. Effluents from STPs contained levels of PFOS up to 0.020 µg/L and leachate levels from landfills were between 0.038 – 0.152 µg/L.

The occurrence of PFOS and other perfluoroalkyl sulfonate substances in open ocean waters such as the Atlantic and the Pacific Ocean have been investigated. The detection of PFOS in oceanic waters suggests another potential long-range transport mechanism to remote locations such as the Arctic. The results showed that PFOS is present in central to western Pacific Ocean regions in concentrations ranging from 15 – 56 pg/L, 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). PFOS was also detected in oceanic waters in several coastal seawaters from Asian countries (Japan, Hong Kong, China, and Korea) at concentrations ranging from 1.1 - 57 700 pg.L^{-1} (Yamashita *et al*., 2005). PFOS was also observed in the North Sea (estuary of the river Elbe, German Bight, southern and eastern North Sea) (Caliebe *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 (2003a). 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. In Canada, suspended sediment samples were collected annually at Niagara-on-the-Lake in the Niagara River over a 22 year period (1980-2002). PFOS concentrations ranged from 5 to 1100 $pg.g^{-1}$ (Furdui *et al.,* 2005). Preliminary findings suggest that PFOS concentrations increased during the study period from < 400 $pg.g^{-1}$ in the early 1980s to > 1000 $pg.g^{-1}$ in 2002.

Samples of effluent from fifteen representative industry sectors have been analysed for PFOS (Hohenblum *et al*, 2003). The industry sectors were printing (1 site), electronics (3), leather, metals, paper (6), photographic and textiles (2). The PFOS levels ranged from 0-2.5 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 electronics).

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 - 110 µg/l.

Sixteen Great Lakes water samples (eight locations) were analysed for perfluorooctane surfactants. PFOS was present in all samples with a concentration range of 21-70 ng/L. Three PFOS precursors were also found in the water samples. N-EtFOSAA (4.2-11 ng/L) and PFOSA (0.6 -1.3 ng/L) were present in nearly all samples while PFOSulfinate was identified at six out of eight locations (2.2-17 ng/L) (Boulanger et al, 2004). PFOS was detected in surface water as a result of a spill of fire-fighting foam from the Toronto International Airport into nearby Etobicoke Creek. Concentrations of PFOS ranging from <0.017 to 2210 $\mu g.L^{-1}$ were detected in creek water samples over a 153-day sampling period. PFOS was not detected at the upstream sample site (Moody *et al*. 2003).

PFOS and related fluorochemicals have been detected 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. The highest North American or circumpolar concentration of PFOS in mammal tissue reported in the published literature is 59 500 $\mu g.kg^{-1}$ ww in mink liver from USA (Kannan *et al*., 2005a).

Martin *et al.* (2004a) 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 3100 ng/g from seven animals (maximum value > 4000 ng/g). The concentrations of PFOS in polar bear are 5-10 times higher than the concentration of all other perfluoroalkyl substances and were higher than any other previously reported concentrations of persistent organochlorine chemicals (e.g., PCBs, chlordane or hexachlorocyclohexane) in polar bear fat (Martin *et al.,* 2004a). PFOSA, a precursor to PFOS, was also found in most of the samples. The concentration of PFOSA was higher than that of PFOS in fish, but not in mammals. This could indicate that PFOSA 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.

PFOS is found in birds worldwide. In North America, PFOS has been found in eagles in the Great Lakes, mallards in the Niagara River, loons in northern Quebec, gulls in the arctic and in Canadian migratory species in the United States (e.g., common loon in North Carolina). In Canadian or Canada-US migratory species, concentrations have been measured in liver ranging from not detectable to 1780 ng/g mean liver PFOS concentration (loon, northern Quebec) and bald eagle, (Michigan), in blood plasma ranging from <1- 2220 ng/g blood plasma in bald eagles and in eggs and egg yolk ranging from 21-220 ng/g in double-crested cormorant in Manitoba. In several monitoring studies, piscivorous water birds were found to have some of the highest liver and serum PFOS concentrations compared to other species (Newsted *et al.,* 2005). In a study of birds in the Niagara River Region, piscivorous birds (common merganser, bufflehead) contained significantly greater PFOS concentrations than non-piscivorous birds (Sinclair *et al*., 2006). Preliminary data on temporal trends show an increase in bird PFOS concentrations, in two Canadian Arctic species (thick-billed murres and northern fulmars) from 1993 to 2004 (Butt *et al*., 2005). It is noted that concentrations of PFOS in plasma have been reported in eagle, gulls and cormorants around the Great Lakes and in the Norwegian Arctic ranging from <1 ng/g to 2220 ng/g .

Kannan and Giesy (2002b) have summarised results of analyses on archived tissue 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 1700 samples were analysed, with concentrations in liver, egg yolk, muscle or blood plasma determined. The detection limit varied from 1 ng/g to 35 ng/g wet weight. A summary of the results is shown in Table 6.

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

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 and noted 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 several studies is given in Table 7.

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

Description	Reference	Reported Highest Concentrations (Max, Mean)	Location
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

Description	Reference	Reported Highest Concentrations (Max, Mean)	Location
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 (2003a), B: Martin et al (2004a); C: Giesy and Kannan (2001c) in 3M (2003a); D: Giesy and Kannan (2001b) in 3M (2003); E: Giesy and Kannan (2001d) in 3M (2003a); 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 (Holmström et al, 2005). The results shown in Figure 2 display a trend of increasing concentrations since 1968 (17 – 623 ng/g).

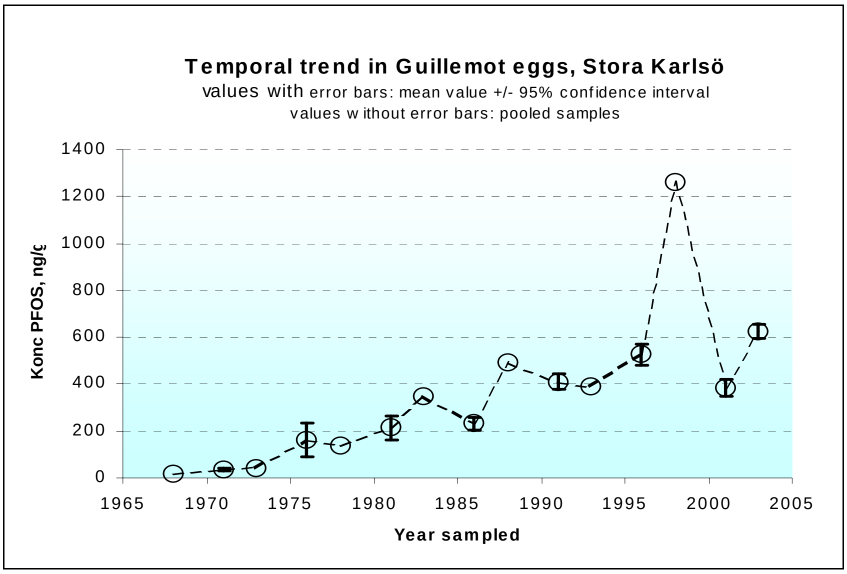

Figure 2. Measured concentrations of PFOS in Guillemot (Uria aalge) eggs sampled at Stora Karlsö in the Baltic Sea between the years 1968 – 2003. The graph is taken from the report "Screening av perfluorerade ämnen" by the Swedish EPA, Environmental Assessment Department (2004).

2.3.1 Bioavailability

Studies on fish have shown that PFOS has bioconcentration properties. In studies on bluegill sunfish (*Lepomis macrochirus*) and rainbow trout (*Oncorhynchus mykiss*) bioconcentration factors (BCFs) have been estimated to be 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 from sewage treatment plants to the environment i.a. through water, one major route for PFOS into local food chains could be through fish. PFOS has 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 corroborated by two separate human monitoring studies on the Swedish population where the levels of PFOS in whole blood was higher (27.2 ng/g, 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 (ng/g, 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 year of measurement (2000) ranged between 0.06 – 10.06 ug/g (n = 263, OECD, 2002).

In a study of the general population, blood samples from families including three generations living in 12 European countries were tested for a large number of chemicals including PFOS and PFOSA. PFOS was present in 37 of 38 samples with concentrations from 0.36 to 35.3 ng/g blood, while PFOSA was present in 36 of 38 samples with concentrations from 0.15 to 2.04 ng/g blood (WWF, 2005).

Pooled serum samples from 3802 Australian residents, collected 2002-2003 and divided in relation to age, gender and region were analysed for perfluoroalkylsulfonates, perfluoroalkylcarboxylates and PFOSA (Kärrman et al., 2006). PFOS and PFOSA were quantified in all pooled serum samples with a total range of 12.7-29.5 ng/ml (mean 7.2 ng/ml) and 0.36-2.4 ng/ml (mean 0.81 ng/ml), respectively. For PFOS, a significant correlation between age and increasing concentration was shown. No substantial difference was found in levels of perfluorinated compounds between the urban and rural regions. According to gender some differences were shown for some of the age groups.

2.4 Hazard assessment for endpoints of concern

2.4.1 Mammalian 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 data for this risk profile 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. A NOAEL could not be established since the lowest dose was a LOAEL (Goldenthal et al., 1978a).
- A 90-day oral repeated dose toxicity study in rats that were fed diets containing 0, 30, 100, 300, 1000 and 3000 mg PFOS potassium salt per kg diet. All rats died when fed diets containing 300 mg/kg PFOS and above (equivalent to 18 mg/kg bw/day and above). At 100 mg/kg (6 mg/kg bw/day), 50% (5/10) of the animals died. All rats receiving diets containing 30 mg/kg 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 (Goldenthal et al., 1978b).
- 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. The 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. (Christian et al., 1999). A new study by Luebker *et al.* (2005) supports these results.
- Cynomolgus monkeys administered PFOS for 26 weeks were observed to have thymic atrophy (females), and reduced high density lipoprotein, cholesterol, triiodothyronine, total bilirubin levels (males) (Covance Laboratories, Inc. 2002a). The LOEL dose was 0.03 $mg.kg^{-1}$ bw/day at which average mean female and male concentrations in sera and liver were 19.8 $\mu g.g^{-1}$ and 14.5 $\mu g.mL^{-1}$, respectively.
- A 2-year dietary rat study in which histopathological effects in the liver were seen in males and females at intakes as low as 0.06–0.23 mg PFOS/kg bw per day and 0.07–0.21 mg PFOS/kg bw per day, respectively (Covance Laboratories, Inc. 2002b). Average values were determined for males and females to establish LOELs of 40.8 ug/g in liver and 13.9 mg/L in serum.

A study by Grasty *et al.* (2003) concluded that exposure of pregnant rats to PFOS late in gestation, 25 mg/kg b.w. PFOS by oral gavage on gestation day (GD) 17-20 or 50 mg/kg PFOS on GD 19-20, is sufficient to induce 100% pup mortality and that the causative factor may be inhibition of lung maturation. However, in a subsequent study by Grasty *et al.* (2005) the mechanism behind pup mortality could not be established.

2.4.2 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 be 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). The lowest LC_{50} (96h) for aquatic invertebrates has been observed in the Mysid shrimp (*Mysidopsis bahia)* and was estimated to be 3.6 mg/l. The lowest NOEC value has been observed in *Mysidopsis bahia* at 0.25 mg/l (OECD, 2002).

A study by Macdonald *et al*. (2004) reported a 10 day NOEC of 0.0491 mg/L for the growth and survival of the aquatic midge (*Chironomous tentans*).

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).

Mallard and bobwhite quail were exposed to PFOS in feed for up to 21 weeks and a variety of endpoints examined including changes in adult body and organ weights, feed consumption rate, fertility, hatchability, and offspring survival. At a dose of 10 mg/kg diet PFOS, effects in male mallards (*Anas platyrhyncos)* included reduced testes size and decreased spermatogenesis (3M, 2003b). At this dose, the concentrations of PFOS in serum and liver were 87.3 ug/mL and 60.9 ug/g, respectively. (3M, 2004). For quail (*Colinus virginianus*), at 10 mg/kg in diet, minor effects were observed in adults, including an increase in liver weight (females), an increase in the incidence of small testes size (males), and reduction in survivability in quail chicks as a percentage of eggs set. Concentrations in serum and liver of adult quail females was 84 $\mu g.mL^{-1}$ serum (week 5, pre-reproductive phase), and 8.7 $\mu g.mL^{-1}$ serum (week 21) and 4.9 $\mu g.kg^{-1}$ wet weight liver; in adult quail males, concentrations were 141 $\mu g.mL^{-1}$ serum and 88.5 $\mu g.g^{-1}$ wet weight liver (3M, 2003c).

3 SYNTHESIS OF THE INFORMATION

Perfluorooctane sulfonate (PFOS) is a fully fluorinated anion, which is commonly used as a salt in some applications or incorporated into larger polymers. Due to its surface-active properties it has historically been used in a wide variety of applications, typically including fire fighting foams and surface resistance/repellency to oil, water, grease or soil. PFOS can be formed by degradation from a large group of related substances, referred to as PFOS-related substances (see definition on page 3).

Due to their intrinsic properties, PFOS and its related substances have been used in a wide variety of applications. While historically, PFOS and PFOS-related substances have been used in eight different sectors as shown in Section 2.1.2. above, the present use in industrialized countries seems to be limited to five sectors, see 2.1.2. It is not known whether this also refers to the global use.

PFOS and PFOS-related substances can be released to the environment at their manufacture, during their use in industrial and consumer applications and from disposal of the chemicals or of products or articles containing them after their use.

The rate and the extent of the formation of PFOS from its related chemicals are largely unknown. Lack of data makes it very difficult to estimate the net contribution of the transformation of each of the PFOS-related substances to the environmental loadings of PFOS. However, based on its extreme stability it is expected that PFOS will be the final degradation product of all PFOS-related substances.

PFOS is extremely persistent. It has not showed any degradation in tests of hydrolysis, photolysis 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 given the highly elevated concentrations that have 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 for these predators. BCF values in fish, although (rather) high do not in themselves meet the specific numeric criteria. However, due to the properties of PFOS, which binds preferentially to proteins in non-lipid tissues, application of numeric criteria for BCF or BAF, which are derived based on consideration of lipid-partitioning substances, may be inappropriate for PFOS. Most notable and alarming are the high concentrations of PFOS that have been found in Arctic animals, far from anthropogenic sources. PFOS has been detected in higher trophic level biota and predators such as fish, piscivorous birds, mink, and Arctic biota. Also, predator species, such as eagles, have been shown to accumulate higher PFOS concentrations than birds from lower trophic levels. Even with reductions in manufacturing of PFOS by some manufacturers, wildlife, such as birds, can continue to be exposed to persistent and bioaccumulative substances such as PFOS simply by virtue of its persistence and long-term accumulation.

According to available data, PFOS meets the criteria for the potential for long-range 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 atmospheric half-life.

PFOS fulfils the criteria for adverse effects. It has demonstrated toxicity towards mammals in sub-chronic repeated dose studies at low concentrations, as well as rat reproductive toxicity with mortality of pups occurring shortly after birth. PFOS is toxic to aquatic organisms with mysid shrimp and *Chironomus tentans* being the most sensitive organisms.

Table 8. POP characteristics of PFOS (Studies performed with the potassium salt of PFOS, unless otherwise noted).

Criterion	Meets the criterion (Yes/No)	Remark
Potential for Long-Range Environmental Transport	Yes	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 rat pups at 1.6 mg/kg bw/day.

		Acute toxicity to Mysid shrimp (*Mysidopsis bahia)*: LC_{50} (96h) = 3.6 mg/L Acute toxicity to fish, Fathead minnow (*Pimephales promelas*): LC_{50} = 4.7 mg/L[1]
Persistence	Yes	Extremely persistent. No degradation recorded in chemical or biological tests
Bioaccumulation	Yes	Found in highly elevated concentrations in top predators. Calculated hypothetical BMFs = 22 - 160. BCF in fish = 2796 - 3100.

1The study compound was the lithium salt of PFOS

A risk quotient analysis, where known or potential exposures are integrated with known or potential adverse environmental effects, have been performed on PFOS for the wildlife in Canada (Canadian Ecological Screening Assessment report, 2006). The results indicate that the higher trophic level mammals may be at risk at current environmental concentrations of PFOS.

In the risk quotient analyses for polar bear, the highest concentration was found in South Hudson Bay with a maximum concentration of 3.77 $\mu g.g^{-1}$ ww liver (range 2.00-3.77 $\mu g.g^{-1}$, mean 2.73 $\mu g.g^{-1}$ ww liver, Smithwick *et al*. 2005). In comparison of 3.77 $\mu g.g^{-1}$ ww liver of PFOS in polar bear with a critical toxicity value of 40.8 $\mu g.g^{-1}$ ww liver for histopathological effects in liver of rats (a 2-year study, Covance Laboratories, Inc. 2002), the difference is only about a factor 10. Using an application factor of 100[1], as was used in the Canadian Ecological Screening Assessment report, a risk quotient of 9.2 was calculated, where values above one indicate risk. Risk quotients were also calculated on toxicological endpoints from other studies in rats and monkeys but with the same maximum exposure concentration from the south Hudson Bay polar bear, showing risk quotients from 2.1 to 19.

Concentrations in Canadian Arctic polar bear are among the highest in polar bears worldwide but the exposure concentrations are not considered an anomaly given similar concentrations in polar bears in other North America and European Arctic locations and high concentrations in other wildlife globally as shown above.

Risk quotients were also calculated for a number of bird species that are native to Canada, including many piscivorous birds and migratory species. The range of risk quotients is either above or approaching one that indicates potential for harm at concentrations observed in native species, including migratory species (Canadian Ecological Screening Assessment report, 2006).

4 CONCLUDING STATEMENT

PFOS is a synthetic substance of anthropogenic origin with no known natural occurrence. It can be concluded therefore that the presence of PFOS and its precursors in the environment are the result of anthropogenic activities and that PFOS found in remote areas far from possible sources has been

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[1] An application factor of 100 applied for extrapolation from laboratory to field conditions and for intraspecies and interspecies variations in sensitivity, and extrapolation from the observed effects level to a no-effect level.

brought there through long-range environmental transport. While PFOS related substances may be degraded to PFOS, PFOS itself is extremely persistent in all media and can bioaccumulate and biomagnify in mammals and piscivorous birds.

The voluntary phase out of PFOS production by the major producer in the USA has led to a reduction in the current use of PFOS-related substances. However, it can be assumed that it is still produced in some countries and there is evidence that it continues to be used in many countries. Given the inherent properties of PFOS and its precursors, together with demonstrated or potential environmental concentrations that may exceed the effect levels for certain higher trophic level biota such as piscivorous birds and mammals; and given the widespread occurrence of PFOS in biota, including in remote areas; and given that PFOS precursors may contribute to the overall presence of PFOS in the environment, it is concluded that PFOS and its precursors may have immediate or long-term harmful effects on the environment such that global action is warranted.

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