## Perfluorooctane Sulphonate (PFOS)



OSPAR Commission 2005 (2006 Update) The Convention for the Protection of the Marine Environment of the North-East Atlantic (the "OSPAR Convention") was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. It has been ratified by Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland and the United Kingdom and approved by the European Community and Spain.

La Convention pour la protection du milieu marin de l'Atlantique du Nord-Est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. La Convention a été ratifiée par l'Allemagne, la Belgique, le Danemark, la Finlande, la France, l'Irlande, l'Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d'Irlande du Nord, la Suède et la Suisse et approuvée par la Communauté européenne et l'Espagne.

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## EXECUTIVE SUMMARY/RÉCAPITULATIF

Perfluorooctane sulphonate (PFOS) is a group of organic substances which contain the particular perfluorooctance sulphonyl arrangement of atoms. PFOS-related substances are members of the large family of perfluoroalkyl sulphonate substances (PFAS). PFOS-related substances are used in a number of industries and products, namely in providing water and oil resistance to textiles, carpets and papers. They are used in the metal plating, photographic and semiconductor industries, in hydraulic fluids of aircrafts, in fire fighter foams, in flame retardants, for photographic processes, as active ingredient in pesticides and insecticides, in industrial and household cleaning products, in medical applications or mining and oil surfactants. PFOS was added to the OSPAR List of Chemicals for Priority Action in 2003.

Le sulfonate de perfluoro-octane (PFOS) est un groupe de substances organiques ayant la structure atomique propre au sulfurile de perfluoro-octane. Les substances connexes au PFOS sont des membres de la grande famille des substances constituées de sulfonate perfluoroalkyle (PFAS). Les substances connexes au PFOS sont utilisées dans plusieurs industries et sont présentes dans divers produits ; elles permettent d'imperméabiliser les textiles, les moquettes et les papiers contre l'eau et l'huile. Elles sont utilisées dans les industries de la galvanoplastie, de la photographie et des semi-conducteurs, dans les fluides hydrauliques des aéronefs, dans les mousses anti-incendie, dans les retardateurs de flammes, dans les procédés photographiques, comme ingrédients actifs dans les pesticides et les insecticides, dans des produits de nettoyage industriels et domestiques, dans des applications médicales ou dans les mines et comme agents tensioactifs de l'huile. Le PFOS a été inscrit en 2003 sur la Liste OSPAR des produits chimiques devant faire l'objet de mesures prioritaires.

There is limited information on the manufacture and quantification of uses of PFOS in the European Union. In 2000, the total global PFOS production by the US company 3M, which phased out its production since 2001, was estimated as being around 3 665 metric tonnes. Production plants are indicated to be located in Germany, Switzerland, Russia and Japan. Production volumes from these facilities have not been provided. The current demand for PFOS-related substances in the EU in the metal plating, photographic and semiconductor industries is estimated to be about 12 200 kg/year in addition to a total of 122 000 kg for fire fighting foam storage for emergency use. Data suggest that, at present, other uses have ceased in the EU following suspension of PFOS production by 3M.

L'on ne dispose que de peu d'informations sur la fabrication et sur la quantification des utilisations du PFOS dans l'Union européenne. En 2000, la production globale de PFOS de la société américaine 3M, qui a cessé sa fabrication en 2001, était estimée à 3 665 tonnes métriques à peu près. Il est signalé que des installations de fabrication sont implantées en Allemagne, en Suisse, en Russie et au Japon. Les volumes de la production de ces installations n'ont pas été communiqués. La demande actuelle de substances connexes au PFOS dans l'Union européenne, dans les industries de la galvanoplastie, de la photographie et des semiconducteurs est estimée être de l'ordre de 12 200 kg/an, ceci s'ajoutant aux 122 000 kg dans le cas du stock de mousse anti-incendie utilisable en cas d'urgence. Les données donnent à penser qu'à l'heure actuelle, d'autres applications ont cessé dans l'Union européenne par suite de la suspension de la production de PFOS par 3M.

Given the wide range of applications and products in which PFOS compounds are used, pathways to the marine environment include wastewater treatment plant effluents, leachates from landfills, atmospheric losses during combustion and from certain domestic and commercial uses, wash-off from various applications such as in fire fighting foam applications, or emissions from wearing PFOS treated materials. PFOS has been detected in samples of rainwater, lakes, coastal water, sewage effluent and sludge, landfill effluent, sediments, freshwater and marine fish, marine mammals, polar bears, birds, reptiles and amphibians from around the world, including remote marine areas such as the polar region. PFOS is considered to be very persistent, bioaccumulative and secondary toxic through the food chain and therefore to be a PBT substance according to the criteria of the EC Technical Guidance Document on risk assessment.

Etant donné le large éventail des applications et des produits dans lesquels des composés de PFOS sont utilisés, les voies de pénétration dans le milieu marin sont notamment les effluents des stations d'épuration des eaux usées, la lixiviation des décharges à ordures, les pertes dans l'atmosphère pendant la combustion ainsi que du fait de certaines applications domestiques et industrielles, les pertes par lessivage de diverses applications telles que les applications dans les mousses anti-incendie, ou les émissions dues à l'usure des matières traitées au PFOS. Du PFOS a été décelé dans des échantillons d'eau de pluie, dans des lacs, dans des eaux côtières, dans les eaux et les boues des égouts, dans les effluents des décharges à ordures, dans des sédiments, chez le poisson d'eau douce et de mer, chez des mammifères marins, chez les ours polaires, chez des oiseaux, des reptiles et des amphibiens dans le monde entier, y compris dans des zones

marines lointaines telles que la région polaire. Le PFOS est considéré très persistant, bio-accumulatif et comme étant un toxique secondaire par le biais de la chaîne alimentaire, et par conséquent comme une substance PBT selon les critères du Document communautaire d'orientation technique sur l'évaluation des risques.

PFOS-related substances have neither been identified as priority substance under the Water Framework Directive nor are any of the 96 compounds listed in Annex 1 to this document included in Annex I of the Dangerous Substances Directive 67/548/EEC. So far, no EU measures exist to restrict the production, marketing and use of PFOS. The European Commission is presently considering taking action on PFOS at Community level.

Les substances connexes au PFOS n'ont pas été classées parmi les substances prioritaires dans la Directive cadre relative à l'eau ; d'autre part, aucun des 96 composés énumérés en annexe 1 au présent document n'est inscrit à l'annexe I à la Directive sur les substances dangereuses (67/548/CEE). A ce jour, il n'existe aucune mesure communautaire européenne qui restreindrait la production, la commercialisation et l'utilisation du PFOS. La Commission européenne envisage à l'heure actuelle de prendre des mesures visant le PFOS au niveau communautaire.

The actions recommended in this Background Document are: to support the process in the EU to take action at Community level; to encourage efforts to develop and test existing and future substitutes for PFOS in current activities; Contracting Parties to support substitution processes by establishing contacts with representatives of the industries using PFOS-related substances as a means of establishing status and use, and options for reduction within their own territories, and by preparing dossiers on use and practicality of reduction; to invite relevant industries to work with Contracting Parties to improve estimates of emissions where necessary and, if necessary, the estimation of PNEC values; to review current and future proposals made by individual Contracting Parties and overarching legal entities (such as the EU) to check that the needs identified by the OSPAR Background Document will be met and to identify any action that may be required on the part of these Parties; to consider whether a monitoring programme should be set up to track the progress towards the cessation of discharges, emissions and losses of PFOS; to communicate this Background Document to the European Commission and to other appropriate international organizations which deal with hazardous substances.

Les actions recommandées dans le présent document de fond sont les suivantes : apporter un soutien au processus de l'Union européenne visant à prendre des mesures au niveau de la Communauté ; encourager les efforts de création et de mise à l'épreuve des succédanés existants et futurs du PFOS dans les applications actuelles; que les Parties contractantes apportent leur soutien aux processus de substitution, ce en établissant des contacts avec des représentants des industries utilisant des substances connexes au PFOS, afin de définir le statut et la consommation ainsi que les options de réduction dans les limites de leurs propres territoires, de même qu'en établissant des dossiers sur l'utilisation et la faisabilité de la réduction; inviter les industries concernées à travailler avec les Parties contractantes afin d'améliorer les estimations des émissions lorsque nécessaire, et, s'il y a lieu, l'estimation des valeurs PNEC ; examiner les propositions actuelles et futures faites individuellement par les Parties contractantes et par les entités juridiques d'ensemble (telles que l'Union européenne) afin de s'assurer que les besoins énoncés dans le document de fond OSPAR seront satisfaits et déterminer toute action qui s'imposerait de la part de ces Parties; considérer s'il y aurait lieu de mettre sur pied un programme de surveillance afin de suivre les progrès accomplis dans le sens de la cessation des rejets, émissions et pertes de PFOS; communiquer le présent document de fond à la Commission européenne et à d'autres organisations internationales compétentes traitant des substances dangereuses.

A monitoring strategy for PFOS is annexed to this background document.

Une stratégie de surveillance relative au PFOS est annexée à ce document de fond.

## INTRODUCTION

Perfluorooctane sulphonate (PFOS) is a fully fluorinated anion, the related compounds of which, are members of the large family of perfluoroalkyl sulphonate substances (PFAS). The majority of PFOS-related substances<sup>1</sup> are polymers of high molecular weight, in which PFOS is only a fraction of the polymer and final product (OECD, 2002). Several PFOS precursors have been selected on the OSPAR List of Substances of Possible Concern and following examination in the OSPAR Hazardous Substances Committee, PFOS was added to the OSPAR List of Chemicals for Priority Action at OSPAR 2003.

PFOS-related substances are currently used in the following sectors, where these all represent professional and industrial applications: metal plating, production of fire fighting foams, photographic processes, photolithography and semiconductors and hydraulic fluids used in aviation. There have also been confirmed uses in the following consumer applications: carpets, leather/apparel, textiles/upholstery, paper and packaging, coatings and coating additives, industrial and household cleaning products, and pesticides and insecticides. Other identified uses include: uses in medical applications, flame retardants, mining and oil surfactants and adhesives.

On 16 May 2000, 3M (the major global producer of PFOS-related substances in the United States) announced that the company would voluntarily phase-out the manufacture of PFOS from 2001 onwards. At a meeting of the Task Force on Existing Chemicals a few days after this announcement (29-30 May 2000), several OECD countries agreed to informally work together to collect information on the effects of PFOS to the environment and to human health for a hazard assessment to be produced. This Hazard Assessment concluded that the presence and 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.

In response to these findings, the Environment Agency for England and Wales, which is responsible for environmental risk assessment work under the ESR Programme in the UK, commissioned a study to review the environmental risks arising from current uses of PFOS. The Review of Environmental Risks (RER) carried out for the Environment Agency of England and Wales (RPA & BRE, 2004) included an assessment of the persistence, bioaccumulation and toxicity (PBT) characteristics of PFOS, based on the EU criteria for assessing the PBT characteristics of a substance. The UK RER concluded that PFOS met the EU PBT criteria. The RER also identified a risk of secondary poisoning for all ongoing uses and local risks to the terrestrial and aquatic environment for formulation and use of fire fighting foams.

This OSPAR Background Document on PFOS takes account of the UK RER and during discussions within the Hazardous Substances Committee and its associated working groups, further information has come to light which has been incorporated into the relevant chapters.

As a result of the investigation in OSPAR, a number of recommendations for action are presented in chapter 8.

<sup>&</sup>lt;sup>1</sup> The term 'PFOS-related substances' is used in this Background Document to represent any substance that can degrade to PFOS in the environment. These substances include, but are not restricted to the draft list of 96 substances reproduced in Table A1.1 in Annex 1 to this report.

## 1. BASIS AND RATIONALE FOR ACTION

The objective stated in the OSPAR Strategy with regard to Hazardous Substances ('the Strategy'), which was adopted in Sintra in 1998<sup>2</sup> and endorsed by Ministers is:

"to prevent pollution of the maritime area by continuing to reduce discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances".

Setting out the basis for OSPAR's work for achieving this objective, the Strategy also includes a timeframe which states that:

"every endeavour will be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances by the year 2020".

This Background Document addresses this obligation and has the following aims:

- identifying the main sources of PFOS-related substances and its various pathways into the marine environment;
- reviewing the various controls to limit discharges, emissions and losses of PFOS-related substances;
- assessing the extent of the risk posed by PFOS-related substances to the marine environment; and
- assessing what further activities should be undertaken by OSPAR, or other relevant international
  organisations, in order to achieve the various OSPAR commitments.

This Background Document takes into account the "Interim Guidance on how to address Hazardous Substances for Priority Action" agreed by the OSPAR Commission in 1999 (Annex 7 of the Summary Record OSPAR 99/15/1) and follows the basic structure for OSPAR Background Documents outlined in that document.

# **2. I**DENTIFICATION OF ALL SOURCES OF THE SUBSTANCE AND PATHWAYS TO THE MARINE ENVIRONMENT

## 2.1 Properties of perfluorooctane sulphonate

Perfluorooctane sulphonate (hereafter referred to as PFOS) is a fully fluorinated anion, the related compounds of which, are members of the large family of perfluoroalkyl sulphonate substances (PFAS). The majority of PFOS-related substances<sup>3</sup> are polymers of high molecular weights in which PFOS is only a fraction of the polymer and final product (OECD, 2002).

PFOS is not a discrete substance and does not have a CAS number. The parent sulphonic acid and some of its commercially important salts are:

Perfluorooctane sulphonic acid (CAS No. 1763-23-1); Potassium salt (CAS No. 2795-39-3); Diethanolamine salt (CAS No. 70225-39-5); Ammonium salt (CAS No. 29081-56-9); Lithium salt (CAS No. 29457-72-5).

All of the chemical substances listed in the table provided in Annex 1 have a common chemical structure consisting of a PFOS moiety ( $C_8F_{17}SO_2$ ) somewhere in the molecule, as illustrated in Figure 1. The PFOS moiety is very stable, and has been found in biota in many parts of the world.

Amended by the 2003 Ministerial meeting of the OSPAR Commission.

<sup>&</sup>lt;sup>3</sup> The term 'PFOS-related substances' is used in this document to represent any substance that can be degraded to PFOS in the environment. A draft list of 96 substances which could degrade to PFOS has been compiled through literature review and consultation and is reproduced in Table A1.1 in Annex 1.



Figure 1: Structure of the PFOS Moiety

There are many examples of different chemical functionality (free acids (Y = OH), metal salts (Y =  $OM^+$ ), sulphonyl halides (Y = X), sulphonamides (Y = NH<sub>2</sub>), and other derivatives). The listed chemical substances also include polymers (US EPA, 2000).

The basic building block of all of the PFOS-related substances is perfluorooctane sulphonyl fluoride (PFOSF), which is used mainly as an intermediate in the production of the PFOS chemicals. Perfluorooctane sulphonic acid (PFOSA) results from the chemical or enzymatic hydrolysis of PFOSF and is an extremely stable substance which resists breakdown by chemical or biological processes.

## 2.2 Identification of sources of perfluorooctane sulphonate

The main areas of use of PFOS are shown in Table 1 below.

Group	Uses/Applications	End Product	Substances Used (if known)
sı		Apparel/Textile	FOSE alcohols
Itior	Treatment of fabrics (water/oil/soil repellence)	Fabric/upholstery	FOSE silanes FOSE alkoxylates
olica		Carpets	FOSE fatty acid esters
Арр		Automotive interiors	FOSE adipates FOSE urethanes
atment	Treatment of metal and glass	Metal/glass	FOSE polyesters FOSE acrylates FOSE copolymers
face Tre	Leather treatment (water/ oil/solvent repellence)	Leather	As above, including PFOSA amphoterics
Sur	Mist suppressant Corrosion inhibitors	Metal plating baths	PFOSA $K^+$ , Li <sup>+</sup> , DEA and $NH_4^+$ salts
n		Plates and food containers	
ctio ons		Bags and wraps	FOSE acrylates
rote	Water/oil/grease/solvent	Folding cartons	FOSE copolymers
er Pi	repellence	Containers	FOSE phosphate esters
Ape		Carbonless forms	
<u>ш</u>		Masking papers	
	Surfactants	Surfactant in fire fighting foams	
		Surfactant in alkaline cleaners	
		Mine and oil well surfactants	
		Denture cleaners	$NH_4^+$ salts
s	Cleaning agents	Shampoos	
tion		Carpet spot cleaners	
lica		Mould release agents	
l App	Waxes and polishes	Emulsifier in wax and floor polishes	PFOSA $K^+$ , Li <sup>+</sup> , DEA and $NH_4^+$ salts
nica	Coatings	Coating additives	
ce Chen	Photography	Antistatic agents; Surfactants for paper, films, photographic plates;	FOSA carboxylates
rmano	Photolithography	Coatings for semiconductors anti-reflective coatings)	
erfo	De ettelde e Kreen ettelde e	Pesticides active ingredient	FOSA amides
Pe	Pesticides/insecticides	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 fluid agents	
Sources:	Danish EPA, 2002; OECD	, 2002; Consultation	

#### Table 1: **Overview of uses for PFOS (and PFOS-related substances)**

Notes: PFOSA: Perfluorooctanesulphonic acid; FOSA: N-Alkylperfluorooctanesulphonamide; FOSE:

N-Alkylperfluorooctanesulphonamidoethanol; PFOSF: Perfluorooctanesulphonyl fluoride; DEA: Diethanolamine

## 2.3 Pathways to the marine environment

There is limited information on the life-cycle steps that could result in environmental releases of PFOS. Studies 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. Four of the cities (Decatur, Mobile, Columbus, Pensacola) were cities that have manufacturing or industrial use of fluorochemicals; two of the cities (Cleveland, Port St. Lucie) were control cities that do not have significant fluorochemical activities.

Kannan and Giesy (2002) summarised the results of analyses on archived samples from marine mammals, birds, fish, reptiles and amphibians from around the world, 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. 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 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. Very recent studies commissioned by the Norwegian Pollution Control Authority (2004 and 2005) show detectable levels of PFOS in the plasma of polar bears, the livers of northern fulmars and the plasma of glaucous gulls.

Van de Vijver *et al* (2003) measured the concentrations of PFOS in aquatic invertebrates from the Western Scheldt estuary. They found indications of a concentration gradient, with possible sources of PFOS including a fluorochemical manufacturing site and industrial regions drained by a canal entering the estuary.

The first environmental survey of PFOS and related substances in Japan (which followed a Japanese study that showed measurable levels of PFOS in human blood) suggests that PFOS is present in the blood and livers of all fish and surface waters in Japan. The concentrations of PFOS in surface water were similar to those of polyaromatic hydrocarbons (PAHs) and much higher than those of PCBs, dioxins and furans (Taniyasu *et al*, 2002).

A recent screening project for PFOS and PFOA performed by the Nordic Council and the Nordic Council of Ministers examined samples of rainwater, lake water, coastal water, sewage effluent, sewage sludge, landfill effluent, sediments, freshwater fish, marine fish, seal and whale. Most of the samples were collected close to populated areas and possible sources. PFOS and PFOA were found in nearly all samples, but the concentrations are below the reported toxicological threshold levels with a possible exception of marine predating mammals.

Given the wide range of applications and products in which PFOS compounds are used, other sources which could result in emissions to the environment include: leachates from landfills, atmospheric losses during combustion and from certain domestic and commercial uses, and wash-off from various applications such as in fire fighting foam applications. Emissions to the environment may also result from the wear of PFOS treated materials e.g. carpets, textiles and leather (RIKZ, 2002). At installations such as military bases and commercial airports, runoff of fire fighting foams from fire training exercises are understood to be one of the main routes of entry of PFOS to the environment.

## 3. QUANTIFICATION OF SOURCES

## 3.1 Manufacture of perfluorooctane sulphonate

Quantitative historic data on PFOS production exist only for the US (i.e. for 3M's operations). In 1997, 1848 metric tonnes of PFOSF were manufactured or imported into the US with the figure slightly lower at 1820 for the year 2000. For that year, the total global PFOSF production by 3M was estimated as being around 3665 metric tonnes. This figure is now zero as 3M suspended the production of PFOSF-derived chemicals under its voluntary action programme (OECD, 2002).

Production plants are indicated to be located in Germany, Switzerland, Russia and Japan. Production volumes from these facilities have not been provided.

## 3.2 Quantification of uses

This Section summarises the quantities of PFOS-related substances used in various applications in the EU, based on the information received through consultation and literature review undertaken for the UK Risk Reduction Strategy. It should be noted that the information presented does not constitute the definitive state

of the market, rather, it is based on the best available information to date and may not be exhaustive, particularly with regard to the market situation in Contracting Parties outside the EU.

**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, automotive interiors and leather. They were used because they were able to modify the surface properties of these materials to provide repellence and resistance. PFOS-related substances have been used to treat carpet fibres to prevent the adherence of oil, liquid spills, stains and grit to the surface. They have also been used as carpet spot cleaners in which the fluorochemical (usually a low molecular weight fluorochemical substance) provides stain resistance. Treatments were applied to leather and suede to give oil/water/stain repellence. *Data suggests that the suspension of PFOS production by 3M has led to a cessation in the use of PFOS in these applications at present*.

**Metal Plating (Chromium Plating):** PFOS is used in chromium plating processes 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. *It is estimated that the EU market for PFOS-related substances for this application is 10 000 kg per annum*.

**Paper and Packaging:** 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 (1999) and the Environment Agency (2001), 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). Fluorochemicals are applied to paper and paperboard mainly by paper mills which treat paper fibres and, to a much lesser extent, by converters who transform paper and/or paperboard into wraps, bags or cartons for desired end-uses (3M, 1999). *Data suggests that the suspension of PFOS production by 3M has led to a cessation in the use of PFOS in these applications in the EU at present.* 

**Fire Fighting Foams:** information suggests that, in theory, any fluorine based fire fighting foam may contain PFOS-related substances as surfactants (BFPSA, 2003b). However, it is understood that some Aqueous Film Forming foams (AFFF - used for aviation, marine and shallow spill fires) and Alcohol Resistant Aqueous Film Forming Foams (AR-AFFF - multi-purpose foam for hydrocarbon and polar solvent hazards used by Fire Brigades, marine bodies and the petrochemical industry) have been produced using PFOS-related substances. While information suggests that PFOS is no longer used in these foams, because of their long 'shelf life' (15 to 20 years), storage, disposal and emergency use of stored foams may present a continuing source of PFOS. The magnitude of these stocks across Contracting Parties is not known. Consultation in the UK suggests that around 76 tonnes of PFOS-related fire fighting foams are currently held in Fire Authority inventories, with an additional 2370 tonnes held in emergency stores at industrial complexes as part of Mutual Aid Agreements (agreements between industry and civil authorities concerning the provision of fire cover in the event of major incidents). Assuming the UK represents 20% of the EU, this implies a total of 122 tonnes of PFOS-based substances may be maintained as fire fighting stock in the EU. These figures do not include the use of PFOS-based foams in offshore situations, either on installations or as part of the fire fighting systems on ships, which has been indicated as a use area in comments on the draft UK RER.

**Cleaning Products:** 3M PFOS-related 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 cleaning services. In the EU, PFOS-related substances have been used in very low concentrations (0,01%) in film making water based floor polish products. *Data suggests that the suspension of PFOS production by 3M has led to a cessation in the use of PFOS in these applications at present.* 

**Coatings:** The full range of uses for *PFAS* in the paint, pigment and finishing industries may include:

- levelling, anti-cratering adjuvants for finishes and paints;
- agents to control differential evaporation of solvents;
- levelling agent for floor waxes;
- adjuvant for waxes to improve oil and water repellence;
- agents to combat pigment flotation problems;
- improvers for automotive finishes, based on water based coatings in which the pigments are rendered non-reactive;
- gloss and anti-static improvers;
- pigment grinding aids to promote wetting, dispersion, colour development; and
- foam generator substances for the application of dyes, inks.

## Data suggests that the suspension of PFOS production by 3M has led to a cessation in the use of PFOS where it has been used for these applications.

**Photographic Industry:** PFOS-related chemicals are used for the following purposes in mixtures used in coatings applied to photographic films, papers, and printing plates (EPCI, 2003):

- surfactants;
- electrostatic charge control agents;
- friction control agents;
- dirt repellent agents; and
- adhesion control agents.

Since 2000, the use of PFOS-related chemicals for imaging purposes has declined significantly on a worldwide basis and it is estimated that the total reduction in tonnage is as high as 83% (EPCI, 2003). It is estimated that the total amount of PFOS used for imaging products in the EU is 1000 kg/y.

**Photolithography:** PFOS-related substances are used as photo acid generators (PAGs) in the semiconductor industry in the production of circuits on semi-conductor wafers. PFOS PAGs are used predominately for 193 nm and for photoresists that are specifically designed for 157 nm wavelength. These PFOS PAGs generate strong acids and are used wherever strong acid catalysis is required. The main benefits from the use of PFOS-related substances as PAGs are:

- they offer improved performance at a 248 nm wavelength;
- they dissolve in the photoresist without phase separation;
- they are non-volatile at room temperature (apart from some of the lowest, e.g., C1-PFOS PAG which volatilise from the photoresist at 115°C and are generally avoided);
- they improve chemical sensitivity at low wavelengths;
- they provide critical functionality in photoresists and concurrent ARCs; and
- in photoresists, they are the only feasible photo acid generator (PAGs) at the shorter wavelengths of 193 and 157 nm.

They may also be used in antireflective coatings (ARC), subdivided into Top (TARC) and Bottom (BARC) coatings and used in combination with DUV photoresists. It is estimated that 471 kg PFOS per year are used at present in the semiconductor industry in the EU. The potential for this level of use to increase with the adoption of the newer shorter wavelength production methods is not known.

**Pesticides and Insecticides:** PFOS-related substances are used for the manufacture of baits and insecticides against beetles and ants. The PFOS substance used was the lithium salt of PFOSA. Information received from 3M indicates that PFOS-related substances are processed by customers into active ingredients in bait stations for leaf cutter ants, pharaoh ants, cornfield ants and a variety of household ants. According to 3M, these products were used mainly in commercial and industrial applications and may find applications in household environments (3M, 1999). *Data suggests that the suspension of PFOS production by 3M has led to a cessation in the use of PFOS where it has been used for these applications.* 

**Medical Applications:** The OECD Hazard Assessment suggests that oxazolidinones of PFOS may be used in waterproofing casts and wound dressings. Other relevant applications include surgical items such as gloves, masks, drapes and undersheets. Consultation with 3M has indicated that this category could also include surgical gowns that had in the past been treated with fluorochemicals related to PFOS. The use of perfluorochemicals was based on their ability to give repellence against alcohol. Infection is generally transmitted in aqueous media such as blood and other body fluids and, therefore, operation sites are liberally doused with alcoholic tinctures of antiseptic. If, however, the non-woven drape used to cover the patient, or the gowns worn by the theatre staff are only water repellent, then the alcohol from the antiseptic will wet the fibres and allow aqueous fluids to follow. The alcohol resistance of the treated fibres prevents this from taking place. Data suggests that the suspension of PFOS production by 3M has led to a cessation in the use of PFOS where it has been used for these applications.

**Hydraulic Fluids Used in Aircraft:** PFOS inhibits erosion (and controls damage) of mechanical parts of hydraulic systems that are used in 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. It is indicated that the total global market for PFOS substances in aircraft hydraulic fluids is around 2,2 tonnes per annum. Industry indicates that PFOS-related substances are used in hydraulic fluids at concentrations less than 500 ppm (Industry, pers. comm.). Assuming the EU comprises a third of the global market, this suggests 0,73 tonnes is used in the EU each year.

**Mining and Oil Surfactants:** PFOS-related substances may also have been used in mining and oil surfactants. These help to increase wetting of the sulphuric acid or cyanide that leaches the ore, as well as enhancing the amount of metal recovery in copper and gold mines. Oil well service firms and oil companies also use these surfactants in a "well stimulation" formulation that is injected into wells to enhance oil or gas recovery. These products contain low molecular weight fluorochemicals/carbons. Perfluorinated compounds have also been reported as being used as film evaporation inhibitors for gasoline, jet fuel, solvents and hydrocarbons, and as cutting oil improvers to improve penetration times. Consultation with European associations involved in offshore oil extraction and the production of chemical preparations used in mining have not found evidence of use in the EU. The British Lubricants Federation indicates that there has been no use of PFOS-related substances in these sectors/applications.

**Flame Retardants:** There have been suggestions that PFOS-related substances were used to provide flame retarding properties in textile applications particularly in the 1980s and early 1990s. Consultation, however, suggests that PFOS-related substances are not and cannot be used as flame retardants; rather they are added into flame retardant formulations to provide other qualities (such as water and stain repellence), and the final mixture is then coated/sprayed onto the textile.

**Adhesives**: Literature suggests that adhesive related applications could include specialty tapes and low adhesion backs for industrial tapes. No evidence to confirm the use of PFOS-related substances as surfactants in adhesives in the EU has been found.

Volumes of confirmed uses of PFOS in the EU are provided in Table 2.

Industry Sector	Application	Quantity (kg/year)				
Metal Plating	Chromium plating Anodising and Acid pickling	<b>10 000</b> 20-30				
Photographic Industry	Paper products Printing plates Film products Total	<50 <100 >850 <b>1000</b>				
Semiconductor Industry	Photoresists Edge bead removers Top antireflective coatings Bottom antireflective coatings Developers (surfactant) Total	46 86 136 8 195 <b>471</b> (assumed 500)				
Aviation Industry	Hydraulic fluids	730				
Storage for Emergency Use (Note not annual usage)						
	EU Total Storage (kg)					
Fire fighting foam storage for	or emergency use	122 000				

Table 2: Estimated current d	lemand for PFOS-related substances in the EU
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## 4. MONITORING DATA ON DISCHARGES, EMISSIONS AND LOSSES

## 4.1 Aquatic inputs to the marine environment

No data are available on loads of PFOS entering the OSPAR convention waters and the Greater North Sea.

## 4.2 Atmospheric inputs

Research has been undertaken on the presence of perfluorochemicals in indoor and outdoor air. Shoeib *et al* (2003) measured the octanol/air partition coefficient ( $K_{oa}$ ) of perfluorochemicals over the range 0° to +20°C.<sup>4</sup> Values of logK<sub>oa</sub> (at 20°C) ranged from approximately 5 for the fluorotelomers to 7,5 to 8 for the fluorosulphonamides. Based on empirical relationships derived for non-polar, hydrophobic chemicals, the fluorosulphonamides should exist mainly in the gas-phase. However, results from indoor air samples (collected using conventional high volume samplers) showed that they are mainly associated with particulate matter, indicating that revised partitioning relationships are necessary for these compounds. Indoor air concentrations were in the range 10 – 10 000 pg/m<sup>3</sup> and were approximately 400 times greater than outdoor values. A second, more extensive survey of fluorosulphonamides compared indoor (n = 80 homes) versus outdoor (n = 10) levels using passive air samplers.

## 4.3 Concentrations in the marine environment (and other waters/sediments)

Hansen *et al* (2002) reported concentrations of PFOS measured from surface water samples taken from the Tennessee River upstream and downstream of the outfall from the fluorochemical manufacturing facility of 3M at Decatur. Upstream of the facility the average concentration of PFOS was  $32 \pm 11 \text{ ng/L}$ ; the downstream concentrations were observed to increase at a point approximately six miles below the outfall; the average PFOS concentration from that point downstream was  $114 \pm 19 \text{ ng/L}$ .

3M (2003) included measured levels from the vicinity of the facility outfall at Decatur for 2001. The mean concentration in water for seven sites (one sample from each) was 61  $\mu$ g/l. The corresponding sediment concentration was 2740  $\mu$ g/kg dwt.

The first environmental survey of PFOS and related substances in Japan (which followed a Japanese study that showed measurable levels of PFOS in human blood) found the highest concentration in surface water in Tokyo Bay at 59 ng/L (mean: 26 ng/L). The concentrations of PFOS in surface water were similar to those of polyaromatic hydrocarbons (PAHs) and much higher than those of PCBs, dioxins and furans (Taniyasu *et al*, 2002).

Saito *et al* (2003) determined the PFOS concentrations in surface water samples from 142 locations in Japan (single samples from each location). The geometric mean concentration for river waters (126 samples) was 2,37 ng/l (geometric standard deviation 4,13), the median was 1,68 ng/l, the range 0,3 - 157 ng/l. For coastal water samples, the geometric mean concentration was 1,52 ng/l (SD 4,14), median 1,21 ng/l and range 0,2 - 25,2 ng/l. The authors comment that the levels are much lower than those reported for the US, with the exception of two rivers where 135 and 157 ng/l were measured.

In 2003 a survey carried out by the Netherlands showed that PFOS can be found in fresh inland waters and in the sea throughout the Netherlands. The highest concentrations were found in suspended matter (a few tens of nanograms per gram) whereas the concentrations in sediment tended to be lower than this. Sediment samples from an area in which fire fighting foams containing perfluorinated compounds had been used proved to contain increased concentrations of PFOS (between 2 and 5 times higher than elsewhere). In Germany an ongoing research study carried out by the Federal Maritime and Hydroraphic Agency (BSH) found PFOS in water in the German North Sea. The highest concentrations of 20 ng/litre were found in the mouth of the river Elbe. Towards the open sea, concentrations dropped to 1,2 ng/litre.

## 4.4 Concentrations in biota

PFOS and related fluorochemicals have also been traced in animals in a number of studies. These studies (a selection of which are outlined in Table 3) have taken place in a variety of locations around the globe and have shown concentrations exceeding 2 ppm in birds and 4 ppm in mink.

<sup>4</sup> 

Octanol has been successfully used to describe the partitioning of hydrophobic, non-polar chemicals to environmental phases such as soil, vegetation and aerosols.

Kannan and Giesy (2002) summarised the results of the analyses on archived samples referred to in the first item in Table 3. The tissues analysed came from marine mammals, birds, fish, reptiles and amphibians from around the world, 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 to 35 ppb wet weight.

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 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. The sulphonamide compound, FOSA, was only detected in ~10-15% of samples.

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 (all except the black guillemot). The highest levels were found in polar bear, with a mean level of 3100 ng/g from seven animals (maximum value >4000 ng/g). Generally, higher levels were found in animals higher up the food chain. The sulphonamide FOSA was also found in most of the samples. It was associated with PFOS to some extent. The concentration of FOSA was higher than that of PFOS in fish, but not in mammals. The pattern may be the result of both exposure and metabolism.

# Table 3: Monitored levels of PFOS in animals (data from selected studies, based on OECD, 2002)

Description	Ref	Highest Reported Concentration	Location of Highest Concentration		
Global monitoring survey of marine mammals (Florida,	OECD.	Bottlenose dolphin: 1520 ng/g wet wt (liver)	Florida		
California, Alaska, northern Baltic Sea, Mediterranean Sea, Arctic, Sable Island (Canada))	2002	Ringed seal: 475 ng/mL (blood)	Northern Baltic Sea		
US Fish & Wildlife Service	А	Bald eagle: 1047 ppb (plasma)	US		
survey of piscivorous fish	χ	Six bird species: 2055 ppb (liver)	US		
Survey of fish-eating water birds	-	Fish: 923 ng/g wet wt. (muscle)	Belgian estuary		
(US, Europe, North Pacific Ocean, Antarctic)	В	Carp: 296 ng/g wet wt. (muscle)	US Great Lakes		
Survey of fish-eating birds (US,		Bald eagle: 2200 ng/mL (plasma)	Midwest US		
Baltic Sea, Mediterranean Sea, Japanese coast, Korean coast)	С	Brandts cormorant: 1780 ng/g wet wt. (liver)	US		
Survey of mink and river otter in	D	Mink: 4800 ng/g wet wt. (liver)	US		
the US		River otter: 994 ng/g wet wt. (liver)	US		
Survey of oysters in the US (Chesapeake Bay & Gulf of Mexico)	E	Oysters: 1225 ng/g dry wt.	US		
Clam and fish samples upstream and downstream of 3M facility in Decatur, Alabama,	F	Fish: 59,1 µg/kg wet wt. (whole body - upstream) Fish: 1332 µg/kg wet wt. (whole body - downstream)	Decatur, US		
US		Clam: 15,6 µg/kg wet wt. (upstream) Fish: 14,1 µg/kg wet wt. downstream)	Decatur, US		
First Environmental Survey of PFOS in Japan	G	Fish: 345 ng/mL (average blood levels)	Lake Biwa, Japan		
Swedish urban and background fish samples	Н	Perch: 3 - 8 ng/g (urban sites in the vicinity of municipal STPs); 20-44 ng/g in Lake Malaren and near Stockholm	Sweden (Lake Malaren)		
Sources: <b>A</b> : 3M (2000c); <b>B</b> : Giesy JP & Kannan K (2001a); <b>C</b> : Giesy JP & Kannan K (2001b); <b>D</b> :					

Giesy JP & Kannan K (2001c); **B**: Giesy JP & Kannan K (2001a); **C**: Giesy JP & Kannan K (2001b); **D**: Giesy JP & Kannan K (2001c); **E**: Giesy JP & Kannan K (2001c); **G**: Taniyasu S et al (2002); **H**: Jarnberg U & Holmstrom K (2003)

A recent conference presentation (personal communication, KEMI, Sweden) reported that the concentration of PFOS in guillemot (*Uria aalge*) eggs collected from the Baltic Sea has increased by more than 30-fold since 1968, with annual average increases of 7-11%.

Van de Vijver *et al* (2003) measured the concentrations of PFOS in aquatic invertebrates from the Western Scheldt estuary, in starfish (*Asterias rubens*), crab (*Carcinus mainas*) and shrimp (*Crangon crangon*). Eight locations were sampled. Mean whole body concentrations were  $16\pm3 - 93\pm34$  ng/g in starfish,  $40\pm13 - 319\pm70$  for shrimp and  $93\pm38 - 292\pm45$  ng/g for crab. There were indications of a concentration gradient, with possible sources of PFOS including a fluorochemical manufacturing site and industrial regions drained by a canal entering the estuary.

Hoff *et al* (2003) sampled fish (bib, *Trisopterus luscus*, and plaice, *Pleuronectes platessa*) from the Western Scheldt and the Belgian North Sea, with four separate locations for each fish. Some of the locations were similar to those in the Van de Vijver *et al* (2003) study above. PFOS was found in the livers of all of the plaice collected (detection limit 10 ng/g wwt); levels up to 7760 ng/g were found at estuarine sites, the values at marine sites were lower. In plaice muscle, PFOS was detected in 20-30% of the marine samples and 75% of the estuarine samples (maximum concentration 87 ng/g). For bib, again all liver samples had

concentration above the detection limit, though the highest concentration were lower than those found in plaice, at ~200 ng/g. In bib muscle, marine sites had 50% of samples above 10 ng/g, while the two innermost estuarine sites had all samples above the detection limit. The maximum concentration measured was 111 ng/g.

The first environmental survey of PFOS and related substances in Japan (which followed a Japanese study that showed measurable levels of PFOS in human blood) suggests that PFOS is present in the blood and livers of all fish and surface waters in Japan (Taniyasu *et al*, 2002).

Very recent studies commissioned by the Norwegian Pollution Control Authority (2004 and 2005) show detectable levels of PFOS in all samples taken of the plasma of polar bears (mean of 97,2 ng/g wet weight), the livers of northern fulmars (mean of 3,4 ng/g wet weight) and the plasma of glaucous gulls (148 ng/g wet weight).

In 2003 a survey carried out by the Netherlands showed that PFOS was detected in fish, to more than 100 nanograms per gram of fish (RIZA-RIKZ 2004).

## 5. ASSESSMENT OF THE EXTENT OF THE PROBLEM

## 5.1 Introduction

In 2003, the Environment Agency for England and Wales, which is responsible for environmental risk assessment work under the ESR Programme in the UK, commissioned a study to review the environmental risks arising from current uses of PFOS-related substances. This risk evaluation was based on the guidance developed by OSPAR and the EC in recent years<sup>5</sup>. The marine part of the risk evaluation involved two steps. Firstly, the preparation of a PBT assessment to ascertain whether the substance is so hazardous that measures should be developed solely on the basis of the information available on sources and pathways to the marine environment. This was followed by a more traditional risk assessment approach where the predicted environmental concentrations were compared with the predicted no effect concentrations to give a PEC/PNEC ratio for various scenarios. The PEC/PNEC ratios give a numerical indication of the degree of risk. The details of the marine risk evaluation are given in **Annex 2** of this document. The marine risk evaluation as presented in this document draws heavily on data and information in the UK RER, which will be published in due course when it has been finalised. It is clear that the marine risk evaluation would be greatly improved with the provision of better quality information.

## 5.2 PBT assessment

The classification of PFOS against the EC Technical Guidance Document (TGD) PBT criteria gave the following results:

*Persistence*: PFOS is not considered to be readily biodegradable in the environment, hence it meets the screening criteria for P or vP.

*Bioaccumulation*: bioconcentration factors of up to 2800 have been measured in laboratory studies, and this meets the B criterion.

*Toxicity*: the criteria for toxicity relate to effects on aquatic organisms, on birds or to the classification of the substance for health-related effects. PFOS does not meet the criterion for toxicity on the basis of aquatic effects. It does meet the criterion for effects on birds through food. Although PFOS has no formal classification, an assessment of the relevant data concludes that it would be classified as "Toxic" and carry the risk phrase R48 (other classifications may also be justified). On this basis, PFOS meets the T criterion.

*Conclusion of the PBT assessment:* PFOS meets the P and vP screening criteria, the B criterion and the T criterion. Hence overall, PFOS is a PBT substance.

With regard to human health, the OECD Hazard Assessment concluded that:

- PFOS is persistent, bioaccumulative and toxic in mammals;
- PFOS has been detected in the serum of occupational and general populations;
- there is a statistically significant association between PFOS exposure and bladder cancer; and

<sup>&</sup>lt;sup>5</sup> This risk assessment (evaluation) methodology has been formally agreed by the EC in April 2003 and has been adopted by the OSPAR Commission in June 2003 as the common EU/OSPAR risk assessment methodology for the marine environment.

• there appears to be an increased risk of episodes for neoplasms of the male reproductive system, the overall category of cancers and benign growths, and neoplasms of the gastrointestinal tract.

With regard to environmental effects, the OECD Hazard Assessment indicates that:

- PFOS is persistent and bioaccumulative;
- PFOS is highly toxic (acute) to honey bees and bioconcentrates in fish; and
- it has been detected in tissues of wild birds and fish, in surface water and sediment, in wastewater treatment plant effluent, sewage sludge and in landfill leachate.

In conclusion, PFOS meets the **PBT** criteria.

It has also been indicated that PFOS may meet the requirements for a Persistent Organic Pollutant (POP). In an exercise aimed at prioritising chemicals likely to fulfil the criteria for POPs set by the Stockholm Convention and the UNECE-LRTAP<sup>6</sup> Convention involving the Swedish National Chemicals Inspectorate (KemI) and the US EPA, PFOS was selected as probably fulfilling the PBT and L criteria (persistence, bioaccumulation, toxicity, and potential for long-range transport) (UNECE, 2002). Sweden has subsequently started an initiative under the Stockholm Convention to include PFOS on the POP list.

#### 5.3 PEC/PNEC ratios for the local marine risk evaluation

The concentrations of PFOS in marine waters and in marine food chains have been calculated as part of the modelling for the UK RER (RPA & BRE, 2004). The values are included in the main evaluation report and are included in Annex 2 of this document. The PNEC for effects on marine aquatic organisms is  $2,5 \mu g/l$ . The PNEC for effects through the food chain is 0,0167 mg/kg in food. The resulting PEC/PNEC ratios are presented in Tables 4 to 6.

Use area	Scenario number								
	1	2	3	4	5	6	7		
Chromium plating	0,002	0,003	0,002	0,002	0,004	0,004	0,002		
Photography -	0,006	0,008	0,006	0,006	0,008	0,008	0,006		
formulation	NA	0,003	NA	NA	NA	NA	NA		
- processing									
Aviation	0,005	0,006	0,005	0,005	0,006	0,006	0,004		
Fire fighting foams -	5,4	5,4	5,4	5,4	5,4	NA	NA		
formulation	1,14	1,14	1,14	1,14	1,14	1,14	NA		
- Use A	2,28	2,28	2,28	2,28	2,28	2,28	NA		
- Use B									
Photolithography	NA	0,053	NA	NA	NA	NA	NA		
Fabrics - application	NA	0,028	NA	NA	NA	NA	NA		
Paper treatment	NA	3,4	NA	NA	NA	NA	NA		
Coatings	NA	0,088	NA	NA	NA	NA	NA		
Regional	0,002	0,003	0,002	0,002	0,004	0,003	0,002		

## Table 4: Risk characterisation ratios for the marine aquatic compartment

NA - local concentration not calculated for this use pattern in the particular scenario

<sup>&</sup>lt;sup>6</sup> UNECE-LRTAP: United Nations Economic Commission for Europe - Long-range Trans-boundary Air Pollution Convention.

Use area	Scenario number							
	1	2	3	4	5	6	7	
Chromium plating	1,3	2,59	1,6	1,51	2,91	2,63	1,24	
Photography - formulation	2,86	4,06	3,17	3,07	4,47	4,2	2,81	
- processing	NA	2,5	NA	NA	NA	NA	NA	
Aviation	2,5	3,53	2,81	2,71	4,11	3,84	2,45	
Fire fighting foams - formulation	1860	1860	1860	1860	1860	NA	NA	
- Use A	2,61	3,8	2,91	2,82	4,21	3,94	NA	
- Use B	3,92	5,11	4,22	4,13	5,52	5,25	NA	
Photolithography	NA	23,2	NA	NA	NA	NA	NA	
Fabrics – application	NA	9,08	NA	NA	NA	NA	NA	
Paper treatment	NA	1170	NA	NA	NA	NA	NA	
Coatings	NA	31,7	NA	NA	NA	NA	NA	
Regional	1,26	2,46	1,56	1,50	2,87	2,57	1,20	

## Table 5: Risk characterisation ratios for fish-eating bird or mammal (marine)

NA - local concentration not calculated for this use pattern in the particular scenario

## Table 6: Risk characterisation ratios for marine top predator

Use area		Scenario number							
		1	2	3	4	5	6	7	
Chromium plat	ing	2,59	5,03	3,2	3,01	5,81	5,27	2,48	
Photography	- formulation	3,22	5,61	3,83	3,64	6,44	5,89	3,11	
	<ul> <li>processing</li> </ul>	NA	4,99	NA	NA	NA	NA	NA	
Aviation		3,08	5,4	3,68	3,5	6,29	5,75	2,97	
Fire fighting foams - formulation		747	749	748	747	750	NA	NA	
	- Use A	3,12	5,51	3,72	3,54	6,33	5,79	NA	
	- Use B	3,64	6,03	4,25	4,06	6,86	6,31	NA	
Photolithograp	hy	NA	13,3	NA	NA	NA	NA	NA	
Fabrics - application		NA	7,61	NA	NA	NA	NA	NA	
Paper treatment		NA	474	NA	NA	NA	NA	NA	
Coatings		NA	16,6	NA	NA	NA	NA	NA	
Regional		2,57	4,91	3,11	2,99	5,75	5,15	2,46	

NA - local concentration not calculated for this use pattern in the particular scenario

## 5.4 Conclusions of the risk evaluation for the marine compartment

The risk evaluation for the marine compartment<sup>7</sup> indicates that the major area of concern is for secondary poisoning. All of the use patterns considered in the evaluation lead to a risk for secondary poisoning in the relevant scenarios, for the freshwater, marine predator and marine top predator endpoints. This is true of the uses releasing only small amounts overall, such as photography and aviation, as well as for the uses with larger emissions. Calculations for each of the uses considered to be continuing, carried out individually and not shown in this evaluation, indicate that four (chromium plating, photography (formulation), aviation and photolithography) could lead to a risk based on the assumptions made in this evaluation (and assuming instant conversion of PFOS-substance to PFOS where relevant).

The only use pattern not leading to a risk is the use in photography (developing). Risks are indicated at the regional level for secondary poisoning through the freshwater and marine food chains for all scenarios considered.

There are a number of areas of uncertainty associated with the risk evaluation. These include the appropriate property values for the PFOS-substances, and in particular the rate of degradation in the environment and the degree to which PFOS is produced through this. The effects of a number of different

<sup>&</sup>lt;sup>7</sup> This risk assessment (evaluation) methodology has been formally agreed by the EC in April 2003 and has been adopted by the OSPAR Commission in June 2003 as the common EU/OSPAR risk assessment methodology for the marine environment.

assumptions about these issues on the evaluation have been examined in the UK RER. For the majority of cases, the identified use areas still indicate a potential risk through food chain exposures. It is also noted that concentrations of PFOS above the PNEC for secondary poisoning have been measured in aquatic biota in some locations.

The PNEC value for this endpoint is derived from a two-year feeding study, and is not likely to be changed by further tests. An alternative interpretation of the mammalian toxicity data proposed during consultation on the draft UK RER would give a higher PNEC of 0,067 mg/kg in food. Using this PNEC, most of the use areas would have a ratio above one for at least one of the scenarios, although there would be no ratios above one for the marine food chains for Scenario 7. The bioconcentration factor for fish comes from valid measurements, and PFOS has been measured in fish. The biomagnification factor used in the calculations, a value of two, is the default value from the Technical Guidance Document, and so could be revised through measurement, but reducing this to a factor of one would not remove the concerns in most cases. The main scope for revising the evaluation would appear to be through better estimates of emissions.

There are also indications of risk for the aquatic compartments for direct effects on organisms. These relate mostly to the fire fighting foams, where releases on use may be sufficient to cause concern. It should be recognised that the assumptions leading to the amounts released are necessarily arbitrary, as real fires may be of very different scales. Although the scenarios were developed for the terrestrial environment, they could be taken as indicative of possible releases in offshore situations (on installations or as fire fighting systems on ships) in the first instance. The calculation for the formulation of the foams also shows a risk, but the exposure estimate is based on defaults and on a site which no longer uses PFOS-related substances.

Recently, the Scientific Committee on Health and Environmental Risks (SCHER) issued a report (SCHER 47/05) on the risk reduction study prepared by the UK on PFOS. The report makes a number of scientific criticisms in particular the derivation of PECs and the modeling used to determine the secondary poisoning risk. These views are currently being studied by the UK. However, from the OSPAR perspective, the crucial factor for deciding whether risk management is justified is the fact that PFOS has been clearly identified as a PBT substance (Sweden have further proposed that it meets the criteria for a POP laid down under the Stockholm Convention). The OSPAR/EC joint work on marine risk assessment, which has now been incorporated into the EC Technical Guidance Document concluded that for a PBT substance, the assessment requires only the identification of emissions, losses etc, and that risk management is required to achieve cessation of such emissions, discharges and losses. The SCHER Report supports the view that PFOS is a POP.

## 6. ACHIEVING THE DESIRED REDUCTIONS

## 6.1 **OSPAR** targets

The OSPAR Strategy with regard to Hazardous Substances sets out that the OSPAR objective with regard to hazardous substances is "to prevent pollution of the maritime area by continuing to reduce discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances."

The timeframe given in the Strategy states that

"every endeavour will be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances of concern by the year 2020."

As PFOS meets the PBT assessment in the EC Technical Guidance Document, PFOS may pose a risk to the marine environment, and it is therefore imperative from OSPAR's point of view that appropriate actions, commensurate with the estimated risks, and taking account of the uncertainties in their estimation, should be taken to achieve the 2020 cessation target.

## 6.2 OSPAR's role in achieving the desired targets

In order to meet the targets specified in the OSPAR objective and timeframe, it will be necessary to:

- assess the need for reductions and the practicability of such reductions from the various existing sources;
- review existing regulations and controls in all Contracting Parties in the light of the need and practicability of reductions;
- determine which organisation(s) is responsible for and/or best placed for carrying out assessments and/or implementing controls;

- inform the relevant organisation(s) (if OSPAR sees fit) of the OSPAR Ministerial commitments with regard to hazardous substances and the need for action to address OSPAR concerns;
- set up mechanisms for monitoring compliance with measures adopted in the relevant forums; and
- set up mechanisms to monitor inputs to and concentrations in the marine environment and biota
  to monitor reductions, where this should take consideration of the potential long range transport
  issues associated with the substance, historical use and the potential for there to be an increase
  in levels in the short term.

For a number of the sources of PFOS, OSPAR may not be the most appropriate international body to instigate further controls or to assess whether controls and monitoring are practicable or necessary. As such, setting and achieving the desired reduction targets will need to be carried out through close cooperation with other international forums.

## 7. IDENTIFICATION OF POSSIBLE MEASURES

## 7.1 Review of Existing OSPAR, EU and National Activities and Measures

#### 7.1.1 Ongoing Activities in OSPAR

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 move towards the target of cessation of discharges, emissions and losses of hazardous substances that could reach the marine environment by the year 2020 (OSPAR, 1998).

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 together and how to establish fact sheets for produced and marketed substances.

The approach, suggested by the UK and Sweden, is based on prioritising PFOS itself rather than identifying all PFOS precursors on the market and adding them to the OSPAR List of Substances of Possible Concern and to the OSPAR List of Chemicals for Priority Action. This latter alternative would entail considerably more effort and time in order to identify all such PFOS precursors on the market (OSPAR, 2003).

Under the proposed prioritisation, in achieving a cessation in discharges, emissions and losses would require a consideration of all emissions that can give rise to PFOS, including not only all PFOS-related substances currently on the market, but also substances not yet in widespread use, that may act as replacements and which eventually give rise to PFOS<sup>8</sup>.

An associated fact sheet could also be developed for PFOS-related substances on fully reviewed data available in the OECD Hazard Assessment (OSPAR, 2003).

Taking into account the OECD Hazard Assessment of PFOS and the US EPA Hazard Assessment of PFOA, the UK recommended (OSPAR, 2002) the following grouping of perfluorinated substances:

- perfluorooctanyl sulphonamide and sulphonyl compounds and derivates (PFOS type): all PFOS-related substances should be added to the OSPAR List of Substances of Possible Concern and the OSPAR List of Chemicals for Priority Action;
- other perfluoroalkyl sulphonamide and sulphonyl compounds and derivates: perfluoroalkyl sulphonyl based substances should be added to the OSPAR List of Substances of Possible Concern, and discussions with industry initiated to determine whether they should be added to a future priority list;
- perfluorooctanoic acid and salts: this group should not be added to OSPAR List of Substances
  of Possible Concern at this stage, but should be revisited when the full dataset is available from
  the further testing programme;

<sup>8</sup> 

Note that a similar approach is followed for other chemicals such as nonylphenols where measures have been introduced for control of emissions of nonylphenol ethoxylates in order to reduce the levels of nonylphenol (see Directive 2003/53/EC OJ L 178 of 17.7.2003, p. 24-27).

- **other perfluorocarboxylic acids**: this group should not be added to the OSPAR List of Substances of Possible Concern at this stage, but should be revisited when the full dataset is available from the further testing programme on PFOA;
- **perfluoroalkanes**: the substances identified in Table 7 should be added to the OSPAR List of Substances of Possible Concern but should not be prioritised at this stage. Further data/testing should be sought from industry to better characterise their hazardous properties; and
- **perfluoroalkane iodides**: the substances in Table 7 should be added to the OSPAR List of Substances of Possible Concern but should not be prioritised at this stage. Further data/testing should be sought from industry to better characterise their hazardous properties.

The expert group (IGE)<sup>9</sup> identified seventeen substances that potentially met the OSPAR criteria for possible concern based on QSARs predictions. Although a large number of perfluoro substances exist, these seventeen were selected because they had been reported on IUCLID and thus were assumed to be supplied at greater than 10 tonnes/annum. These substances have acted as a starting point for consideration of the appropriate groupings outlined above.

Table 7 shows the list of perfluorinated chemicals which are either medium production volume (mpv) chemicals, on IUCLID and/or on the OSPAR List of Chemicals of Possible Concern as presented by the UK (OSPAR 2003). Note that the substances have been clustered according to chemical structure rather than on the basis of ascending CAS number.

CAS Number	Name of Compound
Perfluorinat	ed Octanyl Sulphonyl Compounds and Derivates (PFOS Type)
1691-99-2	1-Octanesulphonamide, N-ethyl-heptadecafluoro-N-(2-hydroxyethyl)- *
13417-01-1	1-Octanesulphonamide, N-[3-(dimethylamino)propyl]-heptadeca fluoro
25268-77-3	2-Propenoic acid, 2-[[(heptadecafluorooctyl) sulphonyl]methylamino] ethyl ester
67969-69-1	1-Octanesulphonamide,N-ethyl-heptadecafluoro-N-[2-(phosphonooxy)ethyl]- diammonium salt *
2991-51-7	Glycine, N-ethyl-N-[(heptadecafluorooctyl)sulphonyl]-, potassium salt *
2795-39-3	1-Octanesulphonic acid,-heptadecafluoro-, potassium salt
Perfluorinate	ed Alkyl Sulphonyl Compound and Derivates
375-72-4	1-Butanesulphonyl fluoride, -nonafluoro- *
423-50-7	1-Hexanesulphonyl fluoride, -tridecafluoro- *
Perfluorooc	tanoic Acids and Salts
335-67-1	Octanoic acid, pentadecafluoro-
3825-26-1	Octanoic acid, pentadecafluoro-, ammonium salt *
Perfluorinate	ed Acids and Salts
6130-43-4	Heptanoic acid, tridecafluoro-, ammonium salt
16517-11-6	Perfluorooctadecanoic acid
67905-19-5	Perfluorohexadecanoic acid
335-95-5	Perfluorooctanoic acid sodium salt
375-95-1	Perfluorononan-1-oic acid
3658-57-9	Octanoic acid, 7-(chlorodifluoromethyl)-2,2,3,3,4,4,5,5,6,6,7,8,8,8-tetradecafluoro-, ammonium salt

# Table 7: List of perfluorinated chemicals which are either MPV chemicals, on IUCLID and/or on the OSPAR list of chemicals of possible concern

<sup>&</sup>lt;sup>9</sup> The former Working Group on Priority Substances (SPS) convened an intersessional correspondence group called Informal Group of DYNAMEC (Dynamic Selection and Prioritisation Mechanism for Hazardous Substances) Experts (IGE).

3658-62-6	Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,8,8,8-tetradecafluoro-7-(trifluoromethyl)-, ammonium salt				
3658-63-7	Decanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,10,10,10-octadecafluoro-9- (trifluoromethyl)-, ammonium salt				
3825-26-1	Perfluorooctanoic acid ammonium salt				
15899-31-7	Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,8,8,8-tetradecafluoro-7-(trifluoromethyl)-				
16486-94-5	Decanoic acid, octadecafluoro-9-(trifluoromethyl)-				
307-55-1	Perfluorododecanoic acid				
16486-96-7	Dodecanoic acid, docosafluoro-11-(trifluoromethyl)-				
376-06-7	Perfluorotetradecanoic acid				
Perfluorinate	d Alkanes				
678-26-2	Pentane, dodecafluoro-				
355-42-0	Hexane, tetradecafluoro- *				
335-57-9	Heptane, hexadecafluoro- **				
307-34-6	Octane, octadecafluoro-				
335-36-4	Furan, 2,2,3,3,4,4,5-heptafluorotetrahydro-5-(nonafluorobutyl)-				
Perfluorinate	d Alkanes with Single lodide Group				
355-43-1	Hexane, -tridecafluoro-6-iodo- **				
507-63-1	Octane,-heptadecafluoro-8-iodo-				
Source: OSPAR (2003) * Substances listed on the draft List of Substances of Possible Concern ** Substances flagged for inclusion in the OSPAR List of Priority Chemicals 2002					

In the light of the discussions mentioned above, perfluorooctanyl sulphonic acid and its salts (PFOS) was added to the OSPAR List of Chemicals for Priority Action at OSPAR 2003.

## 7.1.2 Ongoing activities within the EU

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

Most PFOS-related substances are not present in Annex I of the Dangerous Substances Directive 67/548/EEC (Danish EPA, 2001-2). A search of Annex I of the Directive for the 96 PFOS compounds listed in Annex 1 of this report has confirmed that none of them are included.

Some EU legislation which generally applies to the release of substances to the environment is, in theory, relevant to the release of PFOS to the environment from some sources (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)).

The UK RER on PFOS has been put forward in the EC Existing Substances framework, and comments have been received from interested Member States. It is likely that when the UK notifies the EC of its intended controls, this will initiate a process to put in place marketing and use controls for PFOS in 2005.

#### 7.1.3 National Initiatives within some Contracting Parties

A number of OSPAR Contracting Parties have undertaken studies examining use of PFOS and/or the wide group of PFAS substances. These Contracting Parties include Denmark, the Netherlands, Sweden and the UK.

While PFOS and related substances are not prioritised under the EU Existing Substances Regulations (ESR), the UK has completed the development of a risk reduction strategy following the processes and guidance of ESR. This has concluded that new regulation would be required to provide adequate controls. At present, the UK is considering and consulting on restrictions on the marketing and use of PFOS-related substances. It is currently proposed that there would be immediate restrictions on:

- all known historical applications (including carpets; leather/apparel; textiles/upholstery; paper and packaging; coatings and coating additives; industrial and household cleaning products; and pesticides and insecticides); and
- use in semiconductor developer applications (where above 0,1% by critical mass).

In addition, delayed cessation in use is proposed for the following applications with conditional derogations applying:

- use of PFOS-related substances in Chromium Plating Applications;
- Remaining PFOS-related Stocks of Fire Fighting Foams;
- Aviation, Photographic, Photolithography and Semiconductor (except Developer) Applications.

Information received from the National Chemicals Inspectorate (KemI) indicates that they are in contact with trade associations and industry representatives as regards the current uses of PFOS-related substances, the possible alternatives to PFOS-related substances in these applications and the consequences of phasing out the use of the PFOS-related substances in these applications.

## 7.2 Alternatives

One of the guiding principles of the OSPAR Hazardous Substances Strategy is the principle of substitution.

The issue of substitution with less hazardous alternatives has been a significant consideration in the UK assessment, particularly as regards fire fighting foams where PFOS has already been substituted with telomer fluorine surfactant-based foams but where there exist fluorine free alternatives.

The alternatives available for the metal plating sector are:

- A move away from the use of Chromium V1 to Chromium 111 (decorative plating only);
- The use of local exhaust ventilation;
- Increased freeboard<sup>10</sup>;
- The use of other surfactants.

As regards fire fighting foams, the UK study found that 95% of the substitute foams currently available in the UK are based on telomer technology with an environmental endpoint of perfluorocarboxylates and telomer sulphonates. The study concluded that, whilst this would represent an existing and technically feasible substitution, it may provide only an uncertain reduction in environmental risks compared to PFOS-related foams. As such, convincing evidence will need to be provided of their low potential for long-term effects before a realistic assessment of any reduced risk can be made. In addition, further data in relation to both acute and chronic toxicity are required for the fluorine-free foams that are gradually becoming more available.

In the photographic sector, 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. The industry however notes that some of the alternatives that have successfully replaced uses of PFOS-related substances are telomer products that are currently under review in the US. There are currently no alternatives to PFOS-related substances in the following (although work is ongoing to identify substitutes):

- 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 agents for mixtures used in coatings applied to films, papers, and printing plates; and
- adhesion control agents for mixtures used in coatings.

For semiconductor applications, the only substitutes for PFOS-related substances that are currently available for the on-going applications are for developer applications (although no details of the identity of these was provided to the UK study. There are currently no known substitutes for two applications within photolithography:

- anti-reflective coatings (ARCs top and bottom); and
- photoresists (although alternative processes are in the early stages of development which may mean that PFOS-related substances are not required).

As regards safety critical applications in aviation hydraulic fluids, there are no current alternatives to the PFOS-related substances currently being used in hydraulic fluids for aircraft systems. There is also no known alternative chemistry which will provide adequate protection to the relevant aircraft systems.

<sup>&</sup>lt;sup>10</sup> Freeboard is the distance between the surface of the solution and the top of the bath.

## 8. CHOICE FOR ACTIONS

## 8.1 Introduction

A number of studies have identified risks associated with the continuing use of PFOS. These include work done by individual national OSPAR Contracting Parties, such as the UK, and also assessments of hazard and risk undertaken by outside bodies, such as OECD and the US Environmental Protection Agency (EPA). The work done in the UK to develop a risk-reduction strategy on the basis of risk assessment has explicitly identified risks and potential actions.

From these studies a number of actions appear justified and necessary.

## 8.2 Action in the EC

**Consideration of measures to reduce risks at EU level**. The UK has presented its proposals for possible unilateral action to the European Commission under the Technical Standards Directive (98/34/EC). The European Commission has informed the UK that it has suspended the proposed initiative, since the EC intends to take action on PFOS at Community level.

- OSPAR Contracting Parties should take steps to establish contact with representatives of industries using PFOS-related substances as a means of establishing status and use and options for reduction within their own territories; and
- OSPAR Contracting Parties that are also EU Member States should support the concept of EUlevel controls and prepare dossiers on use and the practicability of reduction.

To support these processes and ensure that the information in this Background Document and the conclusions reached by OSPAR are generally taken into account in the approach of the European Community:

• OSPAR should communicate this Background Document to the European Commission.

OSPAR Contracting Parties which are not parties to the EC or the EEA should pursue parallel national controls.

## 8.3 Action within OSPAR

In view of the clearly established process for establishing marketing and use controls in the EC referred to above, a key activity for OSPAR is to support this process and to encourage any activities to reduce the risks associated with PFOS, including the substitution of PFOS with safer substitutes which pose less risk. In this context, Contracting Parties should encourage efforts to develop and test existing and future substitutes for PFOS in current uses.

In recognition of the uncertainties present in any assessment of risks:

relevant industries should be invited to work with Contracting Parties to improve estimates of
emissions where appropriate and, if necessary, the estimation of PNEC values to ensure the most
effective risk reduction measures are adopted.

OSPAR should review current and future proposals made by individual Contracting Parties and international bodies (such as the EU) to check that the needs identified by this OSPAR Background Document will be met, and to identify any additional action that may be required on the part of these Parties.

OSPAR should also consider whether a monitoring programme should be set up to track the progress towards the cessation of discharges, emissions and losses of PFOS.

## 8.4 Action in other forums

To ensure that the information in this Background Document can be considered in the context of other international agreements which deal with hazardous substances, and with which Contracting Parties are associated.

 OSPAR should send copies of this Background Document to the appropriate bodies dealing with those agreements and invite Contracting Parties who are parties both to OSPAR and those other agreements to promote action to take account of this Background Document by those other international bodies in a consistent manner.

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## ANNEX 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- <i>N</i> -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-

Ref No.	CAS Number	PFOS-related substance
23	25268-77-3	2-Propenoic acid, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester
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]omegahydroxy-
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- <i>N</i> -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]- <i>N</i> -(2- hydroxyethyl)- <i>N</i> , <i>N</i> -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-

Ref No.	CAS Number	PFOS-related substance
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
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- 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, <i>N</i> -ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- <i>N</i> -(2-hydroxyethyl)-, reaction products with <i>N</i> -ethyl-1,1,2,2,3,3,4,4,4,4,4,4,4,4,4,4,4,4,4,4,4,4
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)omegamethoxypoly(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[(pentadecafluoro-hexyl)sulphonyl]amino]ethyl       2-methyl-2-propenoate,       2-[ethyl[(tridecafluoro-hexyl)sulphonyl]amino]ethyl       2-methyl-2-propenoate,       2-[ethyl[(tridecafluoro-hexyl)sulphonyl]amino]ethyl
54	68891-96-3	Chromium, diaquatetrachloro[.mu[N-ethyl-N- [(heptadecafluorooctyl)sulphonyl] glycinatokappa.O:.kappa.O']]muhydroxybis(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]omegamethoxy-

Ref No.	CAS Number	PFOS-related substance					
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, <i>N</i> -(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					
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, C4-8-alkane, perfluoro, N-(hydroxyethyl)-N-methyl, reaction products with epichlorohydrin, adipates (esters)					
63	92265-81-1	Ethanaminium, <i>N</i> , <i>N</i> , <i>N</i> -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 <sub>7-8</sub> -alkane, perfluoro, <i>N</i> -methyl- <i>N</i> -[2-[(1-oxo-2-propenyl)oxy]ethyl], polymers with 2-ethoxyethyl acrylate, glycidyl methacrylate and <i>N</i> , <i>N</i> , <i>N</i> -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 <sub>4-8</sub> -alkyl)sulphonyl]amino]ethyl methacrylate					
68	129813-71-4	Sulphonamides, C <sub>4-8</sub> -alkane, perfluoro, N-methyl-N-(oxiranylmethyl)					
69	148240-78-2	Fatty acids, C18-unsatd., trimers, 2-[[heptadecafluorooctyl)sulphonyl]methylamino]ethyl esters					
70	148684-79-1	Sulphonamides, C <sub>4-8</sub> -alkane, perfluoro, N-(hydroxyethyl)-N-methyl, reaction products with 1,6-diisocyanatohexane homopolymer and ethylene glycol					
71	160901-25-7	Sulphonamides, C <sub>4-8</sub> -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 <sub>4-8</sub> -alkane, perfluoro, <i>N</i> -ethyl- <i>N</i> -(hydroxyethyl)-, polymers with 1,1'-methylenebis[4-isocyanatobenzene] and polymethylenepolyphenylene isocyanate, 2-ethylhexyl esters, Me Et ketone oxime-blocked					

Table A1.1: Draft List of Compounds Poter	ntially Degrading to PFOS in the Environment
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Ref No.	CAS Number	PFOS-related substance
74	182700-90-9	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- <i>N</i> -methyl-, reaction products with benzene-chlorine-sulphur chloride (S <sub>2</sub> Cl <sub>2</sub> ) 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, <i>N</i> -ethyl- <i>N</i> -(2- hydroxyethyl)-1-C <sub>4</sub> -C <sub>8</sub> perfluoroalkanesulphonamide
77	192662-29-6	Sulphonamides, C <sub>4-8</sub> -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, C4-8-alkane, perfluoro, N-(hydroxyethyl)-N-methyl, reaction products with 12-hydroxystearic acid and 2,4-TDI, ammonium salts
81	306974-19-6	Sulphonamides, C <sub>4-8</sub> -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 <sub>6-8</sub> -alkane, perfluoro, compounds with polyethylene-polypropylene glycol bis(2-aminopropyl) ether
84	306974-63-0	Fatty acids, C <sub>18</sub> -unsatd.,dimers, 2-[methyl[(perfluoro-C <sub>4-8</sub> -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 <i>N</i> , <i>N</i> ,2-tris(6-isocyanatohexyl)imidodicarbonic diamide, reaction products with <i>N</i> -ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- <i>N</i> -(2-hydroxyethyl)-1-octanesulphonamide and <i>N</i> -ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro- <i>N</i> -(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 <i>N</i> -ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- <i>N</i> -(2-hydroxyethyl)-1-octanesulphonamide and <i>N</i> -ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro- <i>N</i> -(2-hydroxyethyl)-1-heptanesulphonamide, compounds with morpholine
87	306975-62-2	2-Propenoic acid, 2-methyl-, dodecyl ester, polymers with 2- [methyl[(perfluoro-C <sub>4-8</sub> -alkyl)sulphonyl]amino]ethyl acrylate and vinylidene chloride
88	306975-84-8	Poly(oxy-1,2-ethanediyl), .alphahydroomegahydroxy-, polymer with 1,6-diisocyanatohexane, N-(hydroxyethyl)-N-methyl perfluoro C <sub>4-8</sub> -alkane sulphonamides-blocked
89	306975-85-9	2-Propenoic acid, 2-methyl-, dodecyl ester, polymers with <i>N</i> -(hydroxymethyl)-2-propenamide, 2-[methyl[(perfluoro-C <sub>4-8</sub> -alkyl)sulphonyl]amino]ethyl methacrylate, stearyl methacrylate and vinylidene chloride

Ref No.	CAS Number	PFOS-related substance
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 <sub>4-8</sub> -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, <i>N</i> -ethyl- <i>N</i> -(hydroxyethyl)perfluoro-C <sub>4-8</sub> -alkanesulphonamides-blocked
92	306977-58-2	2-Propenoic acid, 2-methyl-, 3-(trimethoxysilyl)propyl ester, polymers with acrylic acid, 2-[methyl[(perfluoro-C <sub>4-8</sub> -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-C4-8-alkyl)sulphonyl]amino]ethyl acrylate and vinylidene chloride
94	306978-65-4	Hexane, 1,6-diisocyanato-, homopolymer, N-(hydroxyethyl)-N-methyl perfluoro-C4-8-alkane sulphonamides- and stearyl alcblocked
95	306979-40-8	Poly(oxy-1,2-ethanediyl), .alpha[2-(methylamino)ethyl]omega[(1,1,3,3-tetramethylbutyl)phenoxy]-, N-[(perfluoro-C <sub>4-8</sub> -alkyl)sulphonyl]
96	306980-27-8	Sulphonamides, C4-8-alkane, perfluoro, N,N-[1,6-hexanediylbis[(2-oxo-3,5-oxazolidinediyl)methylene]]bis[N-methyl-
Sourc	ce: RPA & BRE (	2004)

## ANNEX 2: MARINE RISK EVALUATION

## 1. Introduction

This Annex considers the risks to the marine environment from the production, use and disposal of PFOS. The methodology used is based on the marine risk assessment chapter of the Technical Guidance Document<sup>11</sup> for EU Regulation 793/93. The annex is based on the full marine assessment in the draft UK Risk Evaluation Report, and further details can be found in that document.

As part of the work in developing the Risk Reduction Strategy, a list of substances containing the PFOS moiety was produced (Annex 1 in this Background Document). These substances are considered to have the potential to lead to releases of PFOS to the environment. These include salts of PFOS, simple derivatives and polymeric materials. In attempting to assess the emissions of PFOS-related substances to the environment, it is neither practical nor realistic to attempt to assess the release and fate of each individual substance. Rather, these substances have been grouped in a way that takes account of the apparent relative ease with which PFOS could be produced. This has been done on a fairly subjective basis, as there is little information on the breakdown of these substances in the environment. In grouping these substances, the general type and description of the PFOS-related substances used in each sector have been used to select the relevant group for the substances. A three way division has been employed on the above basis.

The first group includes substances which are effectively PFOS itself, in the form of salts of perfluorooctane sulphonic acid - salts with potassium, lithium, sodium, ammonium (including quaternary ammonium) and diethanolamine. The use of products containing these substances can lead to the direct emission of PFOS to the environment. The properties of PFOS salts have been used as far as possible in estimating emissions and behaviour in the environment. Measured property values have been used as far as possible, rather than the usual estimates from QSAR approaches - in particular, measurements of sorption coefficients and bioaccumulation. For the purpose of estimating releases and environmental behaviour, these substances will be called PFOS-salts (salts rather than acids as the species will be fully ionised in water in the environment).

In the second group are individual substances which are made from perfluorooctane sulphonyl fluoride (PFOSF) in a parallel route to the production of PFOS. These are the FOSA and FOSE-type substances, together with their relatively simple derivatives. These are considered to be potential sources of PFOS in the environment through degradation. There is some evidence for this with the substance N-EtFOSE, but little or none for any other substance. The 3M report (3M, 2003) comments that no production of PFOS was seen through hydrolysis or aqueous photolysis of a number of compounds; formation of PFOS was only seen through biodegradation, largely in studies on N-EtFOSE. Thus assumptions about the extent to which this happens, and the rate, have been made in the model calculations in Section 2. It is not possible to treat each substance of this group individually, so a generic set of properties has been used to estimate emissions and behaviour. There is also little information on the properties of these substances. Most of the information available relates to N-EtFOSE, and this will be used as the basis for these calculations. For the purpose of estimating releases, these substances will be called PFOS-substances.

The third group are polymeric materials, higher molecular weight polymers derived largely from the FOSEtype substances. These have also been suggested as potential sources of PFOS in the environment. RIKZ (2002) assumed that all of the PFOS contained in these substances was released. 3M in contrast considered that the polymers were non-degradable. No specific evidence on this has been located. The properties of these polymers may vary over a considerable range, and generic values will be needed. It has been assumed that they have low vapour pressures, low solubilities and a higher affinity for solid phases in the environment. Assumptions have been made about the extent to which they will break down to PFOS in the environment in the model calculations in Section 2. These substances may contain residual PFOSsubstances, and releases of these are also considered. This group of substances will be called PFOSpolymers.

<sup>&</sup>lt;sup>11</sup> Available from ECB web-site – http://ecb.jrc.it/existing-chemicals

## 2. Marine exposure assessment

## 2.1 **Properties**

The calculations for the exposure assessment have been carried out using the EUSES 2 program, which implements the methods of the Technical Guidance Document. The program performs calculations for the freshwater and terrestrial environments as well as the marine. Only one set of values for physico-chemical properties can be used in the program at one time. As the set of property values for the 'on land' environment is more complete than for the marine environment, the former have been used in the calculations. It is recognised that the properties of PFOS may differ in the marine environment; for example, the solubility in salt water has been measured and found to be reduced from that in freshwater.

PFOS has unusual sorption and uptake properties. The values used in the calculations are based as far as possible on measurements on PFOS itself (as PFOS-salts), and are not estimated from the octanol-water partition coefficient (log Kow) as would usually be the case. The choice of property values is described in the Risk Evaluation Report. The chosen values are included in Table A2.1. Property values are also required for PFOS-substances and PFOS-polymers, and these are also included in the table. A more limited set of specific values was required for the calculations for the substances and polymers; other properties such as sorption coefficients were estimated from the log Kow in the usual way.

## 2.2 Emissions

The emissions of PFOS-salt, PFOS-substance and PFOS-polymer, as appropriate for each use area, were estimated in the Risk Evaluation Report. The resulting emissions are in Table A2.2.

Property	PFOS-salt	PFOS-substance	PFOS-polymer	
Molecular weight	538	571,25	10,000	
Vapour pressure	3,31x10 <sup>-₄</sup> Pa	0,5 Pa	10 <sup>-6</sup> Pa	
Water solubility	519 mg/l	0,15 mg/l	10 <sup>-6</sup> mg/l	
Henry's law constant	3,19x10 <sup>-4</sup> Pa m <sup>3</sup> mole <sup>-1</sup>		10 <sup>-4</sup> Pa m <sup>3</sup> mole <sup>-1</sup>	
Octanol-water	not used	4,4	6	
partition coefficient				
(log)				
K <sub>sed-water</sub>	5,16			
K <sub>susp-water</sub>	3,08			
K <sub>soil-water</sub>	40,6	estimated from log	estimated from log Kow value	
BCF fish	2,796	Kow value		
BCF worm	60,5			
BMF <sub>1</sub> , BMF <sub>2</sub>	2			
Biodegradation	Not biodegradable	0,0014 h <sup>-1</sup>	30 year half life	
Photodegradation in	114 d half life	16 hr half life	EUSES defaults	
air				
Other abiotic	EUSES defaults	EUSES defaults	EUSES defaults	
processes				

## Table A2.1:Property values used in EUSES calculations

Use area	Compartment	Local	Regional	Continental
PEOS colto		(per day)	(per year)	(per year)
Chromium Diating	ain	0.00 mm		
Chromium Plating	air	0,33 mg	4000 1.0	0000 1
	waste water	180 mg	1000 kg	9000 kg
Photographic	air	0,11 g	0,034 kg	0,051 kg
	waste water	2,27 g	0,68 kg	1,02 kg
Aviation	waste water	1,5 g	0,44 kg	3,94 kg
	soil	3,4 g	1,02 kg	9,2 kg
Fire fighting foams -	air	0,13 kg		
formulation	waste water	1,07 kg		
Fire fighting foams -	surface water	0,57 kg	28,5 kg	257 kg
use	soil	0,57 kg	28,5 kg	257 kg
(alternative local)	waste water	1,14 kg		
PFOS-substances				
Photolithography	waste water	27 g	25 kg	226 kg
Photographic	waste water	8,8 mg	0,75 kg	6,75 kg
Fabrics – treatment	waste water	13,5 g	3,4 kg	30 kg
Fabrics – service life	water		114 kg	1018 kg
	soil		66,5 kg	599 kg
Paper treatment	waste water	1,8 kg	800 kg	7,2 tonnes
Coatings	waste water	0,15 kg	45 kg	405 kg
PFOS-polymers				_
Fabrics – treatment	waste water	1,35 kg	336 kg	3024 kg
Fabrics – service life	water		11,35 tonnes	101,8 tonnes
	soil		6,65 tonnes	59,9 tonnes

## Table A2.2: Emissions of PFOS-salts, PFOS-substances and PFOS-polymers to the environment

Notes: Waste water - all releases treated in wwtp.

Surface water - release direct to surface water and not treated.

Water - releases split 80:20 wwtp:direct to surface water.

The PFOS-salt emissions are considered as emissions of PFOS itself, and are entered directly. For the PFOS-substances, the approach depends on the assumptions made about the breakdown of the substances to PFOS. The first assumption is that the PFOS-substances effectively break down immediately to PFOS on release (or are converted to PFOS before release). In this case the emissions of PFOS-substance are converted to PFOS-salt emissions. It is assumed that the degradation proceeds to PFOS with no by-products, so that the yield is 100%. The relative molecular weights for the chosen representative substances mean the yield is 0,94 kg for 1 kg of PFOS-substance. The resulting emissions are added to those of PFOS-salt directly.

Where the degradation of the PFOS-substances is assumed to take a longer time, the emissions of PFOSsubstance are modelled using the properties for PFOS-substance above to allow for the effect of movement of air and water in the model. From the concentrations predicted and the appropriate degradation half lives the rate of degradation of PFOS-substance in each environmental compartment at steady state can be calculated. As above, degradation is assumed to proceed to PFOS with no by-products, so that 1 kg/day degradation of PFOS-substance is assumed to give 0,94 kg/day PFOS. Hence the rates of degradation of PFOS-substance are converted to rates of production of PFOS in each compartment, and these are added to the direct releases of PFOS-salt. The results presented in the tables are for the combined releases as appropriate to the particular scenario. This is done for both half lives chosen.

It is recognised that the assumption of 100% production of PFOS from the PFOS-substances is a worst case assumption (although Cahill and Mackay (2002) quote an estimated yield of 92% from N-EtFOSE).

The approach for PFOS-polymer is similar to that for the substances. From the information on polymer composition provided for the Risk Reduction Strategy consultation, the PFOS moiety makes up on average about 30% of the polymer by weight, so a yield of 30% by weight has been used.

## 2.3 Scenarios

The baseline scenario is considered to be the situation in 2000. This includes all of the uses for which emission estimates are included in Table A2.2, including the service life of treated fabrics. In order to consider the possible contributions of PFOS-substances and PFOS-polymers, calculations have been carried out with and without these included. Hence there are five scenarios using the baseline emissions:

- 1 PFOS-salt releases only.
- 2 PFOS-salt plus PFOS-substances, assuming instant degradation to PFOS.
- 3 PFOS-salt plus PFOS-substances, assuming a 20 day half life for degradation to PFOS.
- 4 PFOS-salt plus PFOS-substances, assuming a 1 year half life for degradation to PFOS.
- 5 PFOS-salt, PFOS-substances with 20 day half life, PFOS-polymer with 30 year half life degradation to PFOS.

There are no data for the breakdown of PFOS-polymers, and so the fifth scenario is considered to be much more speculative than the others. A 30 year half life is assumed, with complete release of the PFOS moiety from the polymer on this time scale. It should be noted that all of these scenarios reflect the situation in the past as far as emissions are concerned.

Two further scenarios have been used to try to consider the 'current' situation and a possible future. For the 'current' scenario (Scenario 6), continuing use in chromium plating, photolithography, photography and aviation has been assumed, with use of stocks of fire fighting foam and continuing release from fabrics in use. These last two uses will only continue for a number of years, whereas the calculations assume a continuous use to steady state, and so will overestimate.

The future scenario (Scenario 7) is that where the use of stocks of PFOS foams has been completed and the fabrics have reached the end of their service lives.

Local concentrations have been calculated for all releases of PFOS-salt substances where there is a local source. Local concentrations have also been calculated for releases of the PFOS-substances where instant conversion to PFOS has been assumed (in Scenario 2). For other scenarios, the breakdown of the PFOS-substances (or PFOS-polymer) occurs after dispersion in the environment and so local scenarios are not appropriate. Note that for local emissions to the marine environment, the Technical Guidance Document approach assumes that the releases do not pass through a waste water treatment plant before discharge. The contributions of each use area to the total regional emissions for each scenario are shown at the end of this annex.

## 2.4 Predicted environmental concentrations

The environmental concentrations related to the marine environment from the EUSES calculations are shown in Tables A2.3 to A2.6.

Use area	Scenario number								
	1	2	3	4	5	6	7		
Chromium plating	4,76x10 <sup>-6</sup>	8,33x10 <sup>-6</sup>	5,67x10 <sup>-6</sup>	5,39x10 <sup>-6</sup>	9,56x10 <sup>-6</sup>	8,75x10 <sup>-6</sup>	4,6x10 <sup>-6</sup>		
Photography - formulation	1,52x10 <sup>-5</sup>	1,88x10⁻⁵	1,61x10⁻⁵	1,58x10 <sup>-5</sup>	2,0x10⁻⁵	1,92x10 <sup>-5</sup>	1,51x10⁻⁵		
- processing	NA	7,47x10 <sup>-6</sup>	NA	NA	NA	NA	NA		
Aviation	1,14x10⁻⁵	1,49x10⁻⁵	1,23x10⁻⁵	1,2x10⁻⁵	1,62x10⁻⁵	1,53x10⁻⁵	1,12x10⁻⁵		
Fire fighting foams -	0,0135	0,0135	0,0135	0,135	0,135	NA	NA		
formulation	2,85x10 <sup>-3</sup>	2,86x10 <sup>-3</sup>	2,85x10 <sup>-3</sup>	2,85x10 <sup>-3</sup>	2,86x10 <sup>-3</sup>	2,86x10 <sup>-3</sup>	NA		
- Use A	5,7x10 <sup>-3</sup>	5,71x10 <sup>-3</sup>	5,7x10⁻³	5,7x10 <sup>-3</sup>	5,71x10 <sup>-3</sup>	5,71x10 <sup>-3</sup>	NA		
- Use B									
Photolithography	NA	1,32x10 <sup>-4</sup>	NA	NA	NA	NA	NA		
Fabrics - application	NA	7,09x10⁻⁵	NA	NA	NA	NA	NA		
Paper treatment	NA	8,51x10 <sup>-3</sup>	NA	NA	NA	NA	NA		
Coatings	NA	2,19x10 <sup>-₄</sup>	NA	NA	NA	NA	NA		
Regional	3,86x10⁻ <sup>6</sup>	7,43x10⁻ <sup>6</sup>	4,77x10 <sup>-6</sup>	4,51x10 <sup>-6</sup>	8,68x10⁻ <sup>6</sup>	7,87x10 <sup>-6</sup>	3,71x10 <sup>-6</sup>		

## Table A2.3: Predicted environmental concentrations in marine water

NA - local concentration not calculated for this use pattern in the particular scenario.

Use area	Scenario number							
	1	2	3	4	5	6	7	
Chromium plating	1,27x10⁻⁵	2,23x10⁻⁵	1,52x10 <sup>-5</sup>	1,44x10⁻⁵	2,56x10⁻⁵	2,34x10⁻⁵	1,23x10⁻⁵	
Photography - formulation	4,07x10 <sup>-5</sup>	5,03x10 <sup>-5</sup>	4,31x10 <sup>-5</sup>	4,24x10 <sup>-5</sup>	5,35x10 <sup>-5</sup>	5,14x10 <sup>-5</sup>	4,03x10 <sup>-5</sup>	
- processing	NA	2,0x10⁻⁵	NA	NA	NA	NA	NA	
Aviation	3,04x10 <sup>-5</sup>	4,0x10⁻⁵	3,28x10⁻⁵	3,21x10⁻⁵	4,32x10 <sup>-5</sup>	1,5x10⁻⁵	3,0x10 <sup>-5</sup>	
Fire fighting foams -	0,036	0,036	0,036	0,036	0,036	NA	NA	
formulation	7,6410 <sup>-3</sup>	7,65x10 <sup>-3</sup>	7,64x10 <sup>-3</sup>	7,64x10 <sup>-3</sup>	7,65x10 <sup>-3</sup>	7,65x10 <sup>-3</sup>	NA	
- Use A	0,015	0,015	0,015	0,015	0,015	0,015	NA	
- Use B								
Photolithography	NA	1,32x10 <sup>-4</sup>	NA	NA	NA	NA	NA	
Fabrics - application	NA	7,09x10 <sup>-5</sup>	NA	NA	NA	NA	NA	
Paper treatment	NA	8,51x10 <sup>-3</sup>	NA	NA	NA	NA	NA	
Coatings	NA	2,19x10 <sup>-4</sup>	NA	NA	NA	NA	NA	
Regional	1,72x10 <sup>-5</sup>	3,3x10⁻⁵	2,12x10 <sup>-5</sup>	2,0x10 <sup>-5</sup>	3,85x10⁻⁵	3,49x10 <sup>-5</sup>	1,65x10 <sup>-5</sup>	

## Table A2.4: Predicted environmental concentrations in marine sediments

NA - local concentration not calculated for this use pattern in the particular scenario.

## Table A2.5: Predicted concentrations in marine fish (mg/kg wwt)

Use area		Scenario number							
		1	2	3	4	5	6	7	
Chromium plating		0,0216	0,0432	0,0267	0,0251	0,0484	0,0439	0,0207	
Photography - formulat	on	0,0477	0,0676	0,0528	0,0512	0,0745	0,07	0,0468	
- processi	ng	NA	0,0416	NA	NA	NA	NA	NA	
Aviation		0,0417	0,0588	0,0468	0,0452	0,0685	0,064	0,0408	
Fire fighting foams	-	31	31	31	31	31	NA	NA	
formulation		0,0434	0,0634	0,0485	0,047	0,0702	0,0657	NA	
- use A	<b>`</b>	0,0653	0,0852	0,0703	0,0688	0,0921	0,0875	NA	
- use E	6								
Photolithography		NA	0,386	NA	NA	NA	NA	NA	
Fabrics - application		NA	0,151	NA	NA	NA	NA	NA	
Paper treatment		NA	19,6	NA	NA	NA	NA	NA	
Coatings		NA	0,528	NA	NA	NA	NA	NA	
Regional		0,021	0,041	0,026	0,025	0,048	0,043	0,020	

## Table A2.6: Predicted concentrations in marine predators (mg/kg wwt)

Use area	Scenario number							
	1	2	3	4	5	6	7	
Chromium plating	0,0432	0,0838	0,0533	0,0502	0,0968	0,0878	0,0414	
Photography - formulation	0,0536	0,0935	0,0638	0,0607	0,107	0,0982	0,0518	
- processing	NA	0,0831	NA	NA	NA	NA	NA	
Aviation	0,0513	0,090	0,0614	0,0583	0,105	0,0958	0,0495	
Fire fighting foams -	12,5	12,5	12,5	12,5	12,5	NA	NA	
formulation	0,0519	0,0918	0,0621	0,059	0,106	0,0965	NA	
- use A	0,0607	0,101	0,0708	0,0677	0,114	0,105	NA	
- use B								
Photolithography	NA	0,221	NA	NA	NA	NA	NA	
Fabrics - application	NA	0,127	NA	NA	NA	NA	NA	
Paper treatment	NA	7,9	NA	NA	NA	NA	NA	
Coatings	NA	0,277	NA	NA	NA	NA	NA	
Regional	0,043	0,082	0,052	0,050	0,096	0,086	0,041	

## 3. Effects

## 3.1 Water

Results from tests on freshwater and saltwater species are available. The lowest results from tests considered valid in the Risk Evaluation Report are presented in Table A2.7.

	Fish	Fathead minnow ( <i>Pimephales promelas</i> ) (96-h): $LC_{50} = 4,7 \text{ mg/L}$ Rainbow trout ( <i>Oncorhynchus mykiss</i> - saltwater) (96-h): $LC_{50}=13,7 \text{ mg/l}$
	Invertebrates	Daphnia magna (48-h): $EC_{50}$ = 27 mg/L Mysid shrimp ( <i>Mysidopsis bahia</i> - saltwater) (96-h): $LC_{50}$ = 3,6 mg/L
Acute	Algae	Selenastrum capricornutum (96-h): $EC_{50}$ =126 mg/l Skeletonema costatum (saltwater) (96-h): $EC_{50}$ > 3,2 mg/L
Ε	Fish	Fathead minnow ( <i>Pimephales promelas</i> ) (42-day): NOEC <sub>survival</sub> = 0,3 mg/L
	Invertebrates	Daphnia magna (28-day): NOEC <sub>reproduction</sub> = 7 mg/L Mysid shrimp ( <i>Mysidopsis bahia</i> - saltwater) (35-day): NOEC <sub>reproduction</sub> = 0,25 mg/L
Long-tei	Algae	Selenastrum capricornutum (96-h): NOEC=44 mg/l, Skeletonema costatum (saltwater) (96-h): NOEC>3,2 mg/l Duckweed (Lemna gibba) (7-day): NOEC = 15,1 mg/L

 Table A2.7:
 Summary of aquatic toxicity data

Acute toxicity data are available for fish, invertebrates and algae in freshwater and in seawater. The values for freshwater and saltwater fish are similar, those from invertebrates are more varied with the salt water value lower. The algal values cannot be compared as the lower, marine, value is a limit value with no effect at the highest concentration achievable in the test medium.

Results from long term tests with species in three taxonomic groups (fish, invertebrates, algae) are available for the freshwater environment. There are also long term results with a salt water invertebrate and a salt water algae (again a limit value). The results of a number of microcosm tests (not included here) are similar to the lowest NOEC values obtained in single species tests.

The lowest NOEC from the whole data set is 0,25 mg/l, for Mysid shrimp. This will be used for the PNEC derivation. The next lowest value is 0,3 mg/l, for fathead minnow (and for part of a microcosm test) so a PNEC based on freshwater data alone would be similar. As three taxonomic groups are represented a factor of 10 is used, giving a PNEC for freshwater of 25  $\mu$ g/l.

For the marine environment, there are three taxonomic groups represented. Although there are saltwater species for two of these, there are no additional marine taxonomic groups in the data set. The TGD indicates a factor of 100 in this situation, giving a PNEC of 2,5  $\mu$ g/l.

There are some intermittent release scenarios. For these, the PNEC is based on the acute data. The lowest acute value is 3,6 mg/l, again for Mysid shrimp (the saltwater algal value is lower, at 3,2 mg/l, but this is a limit value and no effects were seen at this level). A factor of 100 is used, giving a PNEC of 36  $\mu$ g/l. This is used for both freshwater and marine intermittent releases.

## 3.2 Sediment

No test results on sediment-dwelling organisms have been located.

## 3.3 Secondary poisoning

Mammalian toxicity data were reviewed for the OECD assessment (OECD, 2002). Results from acute, subchronic and chronic exposures to rats, sub-chronic exposures to monkeys, and a two-generation study on rats are available. Details of these studies are not included here, they can be found in the OECD assessment.

In a two year carcinogenicity assay using rats, effects on the liver were monitored. From this study the NOAEL for PFOS was considered to be 0,5 ppm in food in male rats and 2 ppm in food in female rats. The corresponding LOAELs were 2 ppm for males and 5 ppm for females. These values are taken from the main text of the OECD assessment. In the summary of the OECD assessment the LOAEL for male rats is said to be 0,5 ppm, with no NOAEL established. The main text indicates that the effects seen on male rats at 0,5 ppm were considered to be due to old age and were not treatment related. For comparison, a level in

food of 0,5 ppm is equivalent to a dose of 0,025 mg/kg bw/day using the conversion factors in the Technical Guidance document. The range of doses estimated from the study was 0,015 to 0,057 mg/kg bw/day, so this fits into the observed range. The value required for the risk evaluation is the concentration in food.

Doses of 4,5 mg/kg bw/day were lethal to Rhesus monkeys over a seven week exposure.

In the two generation study on rats, the NOAEL for reductions in pup weights in the second generation was 0,1 mg/kg bw/day, with a LOAEL of 0,4 mg/kg bw/day.

Dietary reproduction studies over 21 weeks have been conducted on two bird species, mallard and northern bobwhite quail. In both species, the NOAEC for the majority of endpoints was 10 ppm in food. Some effects on testes and sperm in males (both species), and on offspring survival (in quail) were noted at this concentration, which was the lowest tested.

The lowest no effect level is 0,5 ppm, for liver effects in male rats. This is from a chronic study, so an assessment factor of 30 is appropriate. This gives a PNEC of 0,0167 mg/kg in food.

In comments from the consultation on the draft risk evaluation report, it was suggested that the above may be an over-conservative choice of endpoint for the assessment of secondary poisoning. Alternatives proposed were the 2 ppm LOAEC from the same study, or the NOEAL of 0,1 mg/kg bw/day from the reproduction study. The 2 ppm level from the carcinogenicity study gives a PNEC of 0,067 mg/kg using the same assessment factor of 30 as above. For the NOEAL of 0,1 mg/kg bw/day, the conversion factor from dose to concentration in food is 20 from the Technical Guidance Document, so that the NOEC from this study is 2 mg/kg. With an assessment factor of 30 for a chronic study this also gives a PNEC of 0,067 mg/kg. This value will also be considered in the risk evaluation.

The chronic studies on birds show an NOAEC of 10 ppm for most of the endpoints, but a LOAEC for effects on males and on survival of offspring. A PNEC derived from this figure would be 0,33 mg/kg using an assessment factor of 30. Although the no effect level is not fully defined, this result suggests that the PNECs derived from the mammalian data can be considered to cover the risk to birds as well.

## 4. Marine risk evaluation

#### 4.1 **PBT** assessment

The PBT assessment included here relates to PFOS itself, and uses data from tests on PFOS salts. It does not apply directly to PFOS-substances. However, the potential for the substances to degrade to PFOS in the environment makes this assessment relevant to the general consideration of the group of substances.

#### 4.1.1 Persistence

PFOS (as the potassium salt) has been tested for biodegradability in a series of tests commissioned by 3M and reported in the risk assessment of PFOS (3M, 2003). The following tests were conducted:

- activated sludge;
- acclimated activated sludge (including added soil and sediment materials) in both aerobic and closed vial exposures;
- aerobic soil and sediment cultures;
- anaerobic sludge from sludge digester; and
- pure microbial cultures.

None of these studies showed any evidence for the biodegradation of PFOS. 3M also reported the results of standard studies on hydrolysis (at 50°C and a range of pHs) and photolysis. Neither study showed any evidence for degradation of PFOS. The OECD hazard assessment (OECD, 2002) includes the results of a MITI-I study (ready biodegradability) which showed no evidence for ultimate or primary degradation (removal of the parent compound). The conclusion is that PFOS meets the screening criteria for P (Persistent) or vP<sup>12</sup> (very Persistent) criteria.

<sup>&</sup>lt;sup>12</sup> Classification as a vP is on the basis that no degradation has been observed in any study to date, which makes it likely that the substance would meet this criterion.

#### 4.1.2 Bioaccumulation

There are a limited number of studies available on bioaccumulation of PFOS. A flow-through study on bluegill sunfish (*Lepomis macrochirus*) is cited in both 3M and the OECD assessment. The bioconcentration factors for edible tissues, non-edible tissues and whole fish were calculated from the rates of uptake and depuration because steady state had not been reached after 56 days of exposure.<sup>13</sup> The values obtained were 1 124 (edible), 4 103 (non-edible) and 2 796 (whole fish). The exposure concentration was 0,086 mg/l.

A flow-through study on carp (*Cyprinus carpio*) resulted in lower values of 720 at 20  $\mu$ g/l exposure and 200-1 500 at 2  $\mu$ g/l exposure. Higher values of 6 300 – 125 000 have been reported (for bioaccumulation factors) for in situ measurements at the scene of a spill of fire fighting foam, but these were considered to be due to the uptake of derivatives which were then metabolised to PFOS, hence the values were over-estimated.

In summary, BCF values up to 2 800 have been measured in laboratory studies, and this meets the B or 'Bioacumulative' criterion.

The occurrence in a range of biota supports this; PFOS has been found in a wide range of higher organisms in Europe, including seals, dolphins, whales, cormorants, eagles, swordfish, tuna and salmon. The Global Biophase Monitoring Programme found PFOS in livers, blood and other tissues of animals, especially in fisheating animals.

#### 4.1.3 Toxicity

According to the assessment criteria laid out in the EU TGD, the toxicity criterion is based on either aquatic toxicity or on classification.

The lowest aquatic NOEC value is 0,25 mg/l, which is above the criterion level of 0,01 mg/l for the T criterion. On this basis, PFOS does not meet the T criterion. The NOAEC from chronic bird studies is 10 ppm for most endpoints, which is below the criterion value of <30 mg/kg in food. The level of 10 ppm was also considered a LOAEC for some effects in the same studies. Hence PFOS meets the T criterion on this basis.

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, lithium). The mammalian toxicity data included in the OECD and 3M assessments has thus been used to consider what classification would be appropriate for PFOS.

Various toxicity studies have been conducted (as highlighted in earlier sections) to determine the toxicity of PFOS-related substances, with the tests conducted in:

- a 90-day repeat dose toxicity study on rats showing that all rats died when fed on diets containing 300ppm PFOS and above (equivalent to 18 mg/kg bw/day and above). Some deaths (5 out of 10 animals) were also noted in rats fed diets containing 100 ppm PFOS (6 mg/kg bw/day)<sup>14</sup>. 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. The effects seen in rats receiving 6,0 mg/kg/day suggest that PFOS fulfils the criteria for classification as Toxic, with the risk phrase R48, and hence meets the PBT criteria for T;
- a two year carcinogenicity study showing significant increases in hepatocellular adenomas observed in both male and female rats at 1 mg/kg bw/day. In view of the lack of effects in a number of genotoxicity test systems, the 3M report concluded that the carcinogenic effect was due to a threshold mediated non-genotoxic mechanism. This test could result in a Category 3 classification for carcinogenicity or could even provide insufficient evidence to warrant classification as a carcinogen, and thus may not fulfill the PBT criteria for T;
- a two generation rat study with PFOS showing significant reductions in the viability of pups in the F1 generation at exposure levels of 1,6 and 3,2 mg/kg bw/day. A subsequent study determined a NOAEL for pup mortality and growth of 1,2 mg/kg bw/day. No effects on mortality were observed

<sup>&</sup>lt;sup>13</sup> The robust summary in the OECD hazard assessment has different values to those used in the main OECD text (which are those cited here). The 3M (2003) report explains that the original study used an inappropriate method to estimate the kinetic BCF values, and that those were revised in a later amended study report. This is assumed to explain the different values in the OECD robust summary, as the BCF values in the main report and the 3M report agree.

<sup>&</sup>lt;sup>14</sup> The criteria for the classification of a substance as 'Toxic' with a risk phrase R48 are based on observations of serious damage to health at concentrations ≤5,0 mg/kg bw/day in a 90-day study, while the classification of a substance as 'Harmful' with a risk phrase R48 is based on observations of serious damage to health at concentrations of the order of ≤50 mg/kg bw/day in a 90-day study.

over the whole study at 0,4 mg/kg bw/day. This may not fulfill the criteria for classification as "Toxic for Reproduction", and hence not meet the T criterion for PBT. The view of Sweden in their comments on the draft RER is that the data fulfill the criteria for reproductive toxicity as category 3, and possibly also for category 2. Comments from the Norwegian Institute of Public Health also support classification as a reproductive toxicant category 3;

- developmental and reproductive toxicity studies on rabbits showing effects on the development of the foetus at doses of 5 and 10 mg/kg bw/day. These are largely maturational delays and reduced foetal body weight. A NOAEL of 1 mg/kg bw/day has been determined for most of these effects in rats. Signs of maternal toxicity are also observed at similar levels, and in some cases the NOAEL for maternal effects is lower than that for developmental effects. The 3M RAR concluded that there was no indication of specific teratogenic effects. These may not meet the requirements for classification as "Toxic for Reproduction" and hence not meet the T criterion for PBT; and
- tests on rhesus monkeys showing that all animals died at 10 mg/kg bw/day, the lowest dose tested, with a follow up study showing deaths at 4,5 mg/kg bw/day. There were no deaths at 1,5 mg/kg bw/day, but there were signs of gastrointestinal toxicity. The results of this test show that PFOS fulfils the criteria for classification as Toxic, with the risk phrase R48, and hence meets the T criterion for PBT.

PFOS has been shown to cause death in both rats and monkeys at doses of 6,0 and 4,5 mg/kg/day respectively in repeat-dose 90-day toxicity studies, although significant signs of toxicity were not seen in groups of rats or monkeys receiving lower doses of PFOS. Despite this apparent steep dose-response relationship in its toxicity, the severity of the effects seen at doses around 5,0 mg/kg/day warrant classification as "Toxic" and assigned the Risk Phrase R48.

It is therefore concluded that PFOS should be classified as 'Toxic' and carry the Risk Phrase R48. There is also support for classification as toxic for reproduction, category 3. It therefore meets the T or 'Toxicity' criterion.

## 4.1.4 PBT conclusion

PFOS meets the vP, B and T criteria and hence is considered as a PBT substance. It should be noted that this conclusion does not apply directly to PFOS-substances, but the potential for the substances to be degraded to PFOS means that it is of relevance in the consideration of the substances.

## 4.2 Marine risk evaluation

As PFOS meets the PBT criteria, there is strictly no requirement for a risk evaluation. However the relevant results are generated as part of the modelling and so are included here.

## 4.2.1 Marine water

The concentrations of PFOS in marine waters have been calculated as part of the modelling described in Section 3. The values were presented in Table A2.3.

The risk characterisation ratios for the marine aquatic compartment are presented in Table A2.8. The PNEC is  $2,5 \mu g/l$ . For sediment, the exposure and effect concentrations can only be derived from the aquatic values by equilibrium partitioning, and so the ratios are the same as those for the aquatic compartment.

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	0,002	0,003	0,002	0,002	0,004	0,004	0,002
Photography - formulation	0,006	0,008	0,006	0,006	0,008	0,008	0,006
- processing	NA	0,003	NA	NA	NA	NA	NA
Aviation	0,005	0,006	0,005	0,005	0,006	0,006	0,004
Fire fighting foams -	5,4	5,4	5,4	5,4	5,4	NA	NA
formulation	1,14	1,14	1,14	1,14	1,14	1,14	NA
- Use A	2,28	2,28	2,28	2,28	2,28	2,28	NA
- Use B							
Photolithography	NA	0,053	NA	NA	NA	NA	NA
Fabrics - application	NA	0,028	NA	NA	NA	NA	NA
Paper treatment	NA	3,4	NA	NA	NA	NA	NA
Coatings	NA	0,088	NA	NA	NA	NA	NA
Regional	0,002	0,003	0,002	0,002	0,004	0,003	0,002

Table A2.8:	Risk characterisation ratios for the marine aquatic compartment
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NA - local concentration not calculated for this use pattern in the particular scenario.

The main area indicating a potential risk relates to fire-fighting foams. The calculation of emissions from the formulation of fire fighting foams uses a large site and default emission factors, and so could be refined. (The actual site in fact no longer uses PFOS-based chemicals in the production of foams.)

The distinction between the two use patterns for foams is not relevant to the marine assessment, as it relates to the proportion of the releases which is treated in a waste water treatment plant, and the marine assessment assumes no treatment. As such, the calculations for Use A and Use B are effectively for two different amounts being released during a fire-fighting event. The assumptions leading to the amounts released are necessarily arbitrary, as real fires may be of very different scales. Although the scenarios were developed for the terrestrial environment, they could be taken as indicative of possible releases in offshore situations (on installations or as fire-fighting systems on ships) in the first instance. These calculations indicate the possibility of effects on the local environment in the event of releases on this scale.

One other use pattern gives a ratio above one – this is for paper treatment, and assumes the complete conversion of PFOS-substance to PFOS before release. As such it is likely that the PFOS concentration is over-estimated. Against this, there are no data on the toxicity of the PFOS-substances themselves.

The ratios for the regional aquatic environment are all well below one, the highest being 0,004. Hence the risk ratios for the use patterns are governed by the local emissions. The regional concentration in water does not vary greatly between the scenarios, a factor of three covering all of the results. The variation in degradation rate for the PFOS substances between the scenarios has little effect on the water concentration, and so it may not be necessary to have precise information about this rate. The yield of PFOS from the breakdown of the substances (and polymers) may have more influence on the concentrations.

The measured levels in surface water are below the PNEC value.

The PNEC for the aquatic compartment is derived from three long-term NOEC values, and so is not likely to be increased by further testing. The calculations of emissions, and hence the exposure estimates, could be revised.

## 4.2.2 Secondary poisoning in the marine environment

There are two calculations for secondary poisoning in the marine environment, to include two levels of predators. These are a fish-eating bird or mammal, similar to that in the freshwater environment, and a top predator. The concentrations in the food organisms for these endpoints were presented in Tables A2.5 and A2.6. The risk characterisation ratios for these two are presented in Tables A2.9 and A2.10.

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	1,3	2,59	1,6	1,51	2,91	2,63	1,24
Photography - formulation	2,86	4,06	3,17	3,07	4,47	4,2	2,81
- processing	NA	2,5	NA	NA	NA	NA	NA
Aviation	2,5	3,53	2,81	2,71	4,11	3,84	2,45
Fire fighting foams - formulation	1860	1860	1860	1860	1860	NA	NA
- Use A	2,61	3,8	2,91	2,82	4,21	3,94	NA
- Use B	3,92	5,11	4,22	4,13	5,52	5,25	NA
Photolithography	NA	23,2	NA	NA	NA	NA	NA
Fabrics - application	NA	9,08	NA	NA	NA	NA	NA
Paper treatment	NA	1170	NA	NA	NA	NA	NA
Coatings	NA	31,7	NA	NA	NA	NA	NA
Regional	1,26	2,46	1,56	1,50	2,87	2,57	1,20

## Table A2.9: Risk characterisation ratios for fish-eating bird or mammal (marine)

NA - local concentration not calculated for this use pattern in the particular scenario.

#### Table A2.10: Risk characterisation ratios for marine top predator

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	2,59	5,03	3,2	3,01	5,81	5,27	2,48
Photography - formulation	3,22	5,61	3,83	3,64	6,44	5,89	3,11
- processing	NA	4,99	NA	NA	NA	NA	NA
Aviation	3,08	5,4	3,68	3,5	6,29	5,75	2,97
Fire fighting foams -	747	749	748	747	750	NA	NA
formulation	3,12	5,51	3,72	3,54	6,33	5,79	NA
- Use A - Use B	3,64	6,03	4,25	4,06	6,86	6,31	NA
Photolithography	NA	13,3	NA	NA	NA	NA	NA
Fabrics - application	NA	7,61	NA	NA	NA	NA	NA
Paper treatment	NA	474	NA	NA	NA	NA	NA
Coatings	NA	16,6	NA	NA	NA	NA	NA
Regional	2,57	4,91	3,11	2,99	5,75	5,15	2,46

NA - local concentration not calculated for this use pattern in the particular scenario.

For the marine food chains all of the use areas indicate a risk for all of the scenarios for which they are relevant. Consumption of prey exposed only to the regional background concentrations is also indicated as a risk for all scenarios. As noted above the regional water concentrations are only affected a little by the different release patterns in the scenarios. However, in most cases the specific uses also make a significant contribution to the exposure through this route, similar to or greater than that from the regional concentration. The exceptions to this are chromium plating and the processing life stage for photography.

None of the emission estimates are based on specific information about the releases of PFOS from the specific industry area. Hence they could all be refined. Considering only the possible continuing uses (those included in Scenario 7), for chrome plating the local calculation is based on a scenario for the industry, but the overall emissions assume complete release of the amount used each year in the absence of information on its fate. Assumptions have been made on the nature of the substances released in the production of film and its developing. Data on the releases from photolithography come from the industry, but there may be more specific treatment of waste waters than assumed here. The aviation emissions are based on an emission scenario for hydraulic fluids, but do not relate specifically to the aviation industry.

The PNEC value is based on the results of a 2-year study with rats, so it is unlikely that the PNEC would be changed significantly in the light of further tests. An alternative PNEC of 0,067 mg/kg was also derived in the RER. Using this alternative PNEC, most of the use areas would have a ratio above one for at least one of the scenarios, although there would be no ratios above one for the marine food chains for Scenario 7.

A comparison of the PNEC value with measured concentrations for freshwater fish shows that the highest measured concentrations reported exceed the PNEC of 0,0167 mg/kg. A number of values also exceed the alternative PNEC value of 0,067 mg/kg. It should be noted that this comparison is based on the highest

values. In some cases these relate to specific tissues rather than whole body levels. Also, from the global archive sample analysis, PFOS was only detected in 38% of the samples. Nevertheless, measurements such as those in the Scheldt Estuary may indicate the presence of PFOS in aquatic biota at levels expected to have effects.

## 5 References

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## **ANNEX 3: MONITORING STRATEGY FOR PFOS**

As part of the Joint Assessment and Monitoring Programme (reference number 2003-22), OSPAR 2005 adopted a revised Agreement on Monitoring Strategies for OSPAR Chemicals for Priority Action (reference number 2004-14) to implement the following monitoring for tracking progress towards the objectives of the OSPAR Hazardous Substances Strategy (reference number 2003-21) with regard to PFOS. The monitoring strategy for PFOS will be updated as and when necessary, and redirected in the light of subsequent experience.

There is limited information on the life-cycle steps that could result in environmental releases of PFOS. However, studies 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. Emissions to the environment may also result from the wear of PFOS treated materials e.g. carpets, textiles, paper and leather. Its use in fire fighting foams from fire training exercises is understood to be an important route of entry of PFOS to the environment.

The Background Document shows that PFOS reaches the marine environment. It has been detected in marine mammals, birds, fish, reptiles and amphibians from around the world, including the Arctic and Antarctic Oceans. It has also been detected in marine sediments and in the water column in some estuaries and coastal waters. A lot of monitoring information is becoming available as more countries investigate its presence in their waters, sediment and biota.

Some sections of industry have already proposed voluntary restrictions of PFOS in some applications. Several countries (e.g. the UK and Sweden) have proposed national controls on certain uses of PFOS, and the EC have been notified accordingly. In December 2005 the EU Commission adopted a proposal for a Council and Parliament Directive relating to restrictions on the marketing and use of perfluorooctane sulfonates (amendment of Council Directive 76/769/EEC) which will ban the use of PFOS with some limited exemptions.

The monitoring strategy for PFOS needs to take account of several factors. Firstly, PFOS has been detected in the marine environment, and as it is persistent, it is likely to be detected for many years to come, even if the main uses have been restricted. Secondly, PFOS has been proposed as a POP under the Stockholm Convention and if adopted, there would be mandatory monitoring requirements for Contracting Parties in the coming years. Thirdly, if marketing and use restrictions are adopted by the EC, it should be possible to check whether it is being phased out through the monitoring of sales and uses as is being done in the monitoring strategies for other OSPAR Priority Hazardous Substances.

In view of the dynamic situation regarding the controls on PFOS, it may well be prudent for OSPAR not to set up any specific environmental monitoring programmes until the results of the various international efforts become clearer, but to collect, review and evaluate information and data on marine levels in order to decide at a later stage whether any specific OSPAR programmes should be taken forward.

The main components of the monitoring strategy for PFOS should be as follows:

- a. keeping a watching brief on the implementation of any measures on PFOS, particularly in the EC framework, which would enable sales and use of the chemical to be tracked;
- b. gather information collected by Contracting Parties on environmental concentrations of PFOS in marine sediments and biota in order to see how a baseline might be formulated for any future OSPAR monitoring programmes should these be deemed to be necessary;
- c. to keep a watching brief on monitoring requirements in other international forums such as the Stockholm Convention to see how these might assist OSPAR in its own monitoring strategy for PFOS.

PFOS MONITORING STR	RATEGY	
Implementation of actions and measures	•	Examination of progress in a) the implementation of regulations on marketing and/or use or emission and/or discharge which are being developed in the EC, and b) the Stockholm Convention.

PFOS MONITORING STI	RATEGY
Concentrations in sediments	<ul> <li>Contracting Parties will be encouraged to extend their monitoring programmes to cover PFOS and to report results on a voluntary basis to the lead country and through the data-handling mechanism operated by ICES for the CEMP</li> <li>Before 2007 the lead country will collate information on concentrations of PFOS in the marine environment in order to assess whether this is a gap in knowledge which OSPAR should fill prior to the 2009 QSR</li> <li>The need for EACs and BRCs will be considered</li> </ul>
Concentrations in biota	<ul> <li>Contracting Parties will be encouraged to extend their monitoring programmes to cover PFOS and to report results on a voluntary basis to the lead country and through the data-handling mechanism operated by ICES for the CEMP</li> <li>Before 2007 the lead country will collate information on concentration of these substances in order to assess whether this is a gap in knowledge which OSPAR should fill prior to the 2010 QSR</li> </ul>
Biological effects	<ul> <li>Before 2007 the lead country will collate information provided by Contracting Parties on concentrations of PFOS and their effects in order to assess whether this is a gap in knowledge which OSPAR should fill prior to the 2009 QSR</li> </ul>
Sales and use information	<ul> <li>include sales and use information on PFOS in the data collection systems proposed by the OSPAR Secretariat.</li> </ul>