Perfluorooctane Sulphonate

Risk Reduction Strategy and Analysis of Advantages and Drawbacks

Stage 4 Final Report

prepared for
Department for Environment,
Food and Rural Affairs

RPA

in association with

BRE Environment

March 2004

Risk Reduction Strategy and Analysis of Advantages and Drawbacks for Perfluorooctane Sulphonate (PFOS)

Stage 4 Final Report – March 2004

prepared for

Department for Environment, Food and Rural Affairs

by

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Executive Summary

1. Background

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[1] are polymers of high molecular weights in which PFOS is only a fraction of the polymer and final product (OECD, 2002).

On 16 May 2000, 3M (a major global producer of PFOS based in the United States) announced that the company would phase-out the use of PFOS voluntarily from 2001 onwards[2]. 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 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 study is being undertaken by Risk & Policy Analysts Limited (RPA) in association with BRE Environment and overseen by the Environment Agency for England and Wales.

The Department for Environment, Food and Rural Affairs (Defra) has also contracted RPA to prepare a Risk Reduction Strategy for PFOS related substances, including an analysis of the advantages and drawbacks of potential risk reduction options. This Risk Reduction Strategy will follow the provisions of the EU Existing Substances Regulation (ESR[3]) according to which, where controls on the marketing and use of the substances in question are proposed, an analysis of the advantages and drawbacks of the substance should be undertaken. It should be noted that the UK RER has informed the development of the RRS (and vice versa).

This Report presents the findings of Stage 4 of the study ('Preparation of the Final Risk Reduction Strategy') and recommends the risk reduction strategy to be taken forward.

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[1] 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 as Annex 2 to this report.

[2] According to the OECD Hazard Assessment and consultation, the production of PFOS by 3M has now ceased.

[3] Council Regulation (EEC) No. 793/93 of 23 March 1993 on the Evaluation and Control of the Risks of Existing Substances, OJ L 84, 5.4.1993, p.1.

2. Usage of PFOS Related Substances

Based on information received thus far, it can be said that 3M's voluntary phase out of PFOS production has led to a significant reduction in the use of PFOS related substances in the UK and the EU more generally. This is due not only to the limited availability of these substances (3M had at the time the greatest capacity of PFOS related substances production in the world), but also to action within the relevant industry sectors to decrease companies' dependence on these substances.

The historical[4] use of PFOS related substances in the following applications has been confirmed either in the UK or the EU[5]:

- fire fighting foams;
- carpets;
- leather/apparel;
- textiles/upholstery;
- paper and packaging;
- coatings and coating additives;
- industrial and household cleaning products; and
- pesticides and insecticides.

Detailed information has been received from the following sectors that currently use PFOS related substances (where these all represent industrial and professional uses):

- use of existing PFOS fire fighting foam stock;
- photographic industry;
- photolithography and semiconductors;
- hydraulic fluids; and
- metal plating.

Information received from consultation with representatives of these sectors suggests that the quantities of PFOS related substances and PFOS based preparations currently being consumed is limited. The table below outlines the estimated current demand for PFOS related substances in the EU.

Table 1: Estimated Current Demand for PFOS Related Substances in the EU

Industry Sector	**Quantity (kg/year)**
Photographic industry	1,500
Photolithography and semiconductors	500
Hydraulic fluids	730
Metal plating	2,500

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[4] Note that there is uncertainty as to whether use in all of these applications has ceased in the UK although the general view is that it has.

[5] No evidence of the historical use of PFOS related substances in the UK and in the EU more generally, was found for the following uses: medical applications, flame retardants, mining/oil surfactants and adhesives.

3. Summary of Recommended Risk Reduction Measures

A range of potential risk reduction measures have been identified that could be applied to reduce or eliminate the risks from emissions of PFOS. These range from voluntary measures through to regulatory mechanisms for controlling emissions and the cessation of use of PFOS related substances. These measures have been assessed according to the following key decision criteria (in accordance with the Technical Guidance Document): (a) effectiveness; (b) practicality; (c) economic impact; and (d) monitorability.

The proposed risk reduction measures for the existing uses of PFOS related substances are summarised in the Table 2 below.

Table 2: Summary of Recommended Risk Reduction Measures for Existing Uses

Existing Uses	**Marketing and Use Restriction (TSD or 76/769/EEC) with classification and labelling suggested)**		**Interim Voluntary Agreement**	**Waste Incineration Directive Requirements**	**Duty of Care provisions under Environmental Protection Act (1990), Waste management Licensing Regulations (1994) and Special Waste Regulations (1996)**
	Cessation	**Conditional Derogation (timescale and emissions control)**			
Metal plating	Yes				
Use of existing PFOS fire fighting foam stock	Yes	5 years	Yes	Yes	Yes
Photographic industry	Yes	5 years with progress reviews	Yes	Yes	Yes
Photolithography and semiconductors	Yes	5 years with progress reviews	Yes	Yes	Yes
Hydraulic fluids used in aviation	Yes	Reviewed	Yes	Yes	Yes

With regard to historical uses, it has been concluded that the only effective means of addressing the risks is through restrictions on the marketing and use of PFOS related substances for such uses.

This can be achieved:

- at National (UK) level through use of the Technical Standards Directive 98/48/EC (TSD) (subject to clearance from EC authorities); and

- at the EU level, through Directive 76/769/EEC concerning restrictions on the marketing and use of certain dangerous substances and preparations.

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GLOSSARY OF ACRONYMS

B	Bioaccumulative, within the meaning of the PBT criteria
BCF	Bioconcentration Factor
bw	body weight
CAS	Chemical Abstract Services
Cr (III)	Trivalent Chromium
Cr (VI)	Hexavalent Chromium
EC50	median Effect Concentration
ECF	Electro Chemical Fluorination
EINECS	European Inventory of Existing Commercial Chemical Substances
EPCI	European Photographic Chemicals Industry
ESD	Emission Scenario Document
ESIA	European Semi-Conductor Industry Association
ESR	Existing Substances Regulation
EU	European Union
FA	Fire Authority
FOSA	Perfluorooctanesulphonamide
IPPC	Integrated Pollution Prevention and Control
Kow	octanol/water partition coefficient
Kd	solids-water partition coefficient
LC50	median Lethal Concentration
LOAEL	Lowest Observed Adverse Effect Level
N-EtFOSE	N-ethylperfluorooctanesulphonamidoethanol
N-MeFOSE	N-methylperfluorooctanesulphonamidoethanol
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
OECD	Organisation for Economic Cooperation and Development
OEL	Occupational Exposure Limits
OSPAR	Oslo and Paris Convention for the Protection of the Marine Environment of the Northeast Atlantic
P	Persistent, within the meaning of the PBT criteria
PBT	Persistent, Bioaccumulative and Toxic
PFAS	Perfluoroalkyl Sulphonate Substances
PFC	Perfluorocarboxylates
PFOA	Perfluorooctane carboxylic acid
PFOS	Perfluorooctane sulphonate
PNEC	Predicted No Effect Concentration
RAR	Risk Assessment Report
RER	Review of Environmental Risks
SEMI	Semiconductors Equipment and Materials International
SIDS	Screening Information Data Set, OECD
SNUR	Significant New Use Rule
T	Toxic, within the meaning of the PBT criteria
TGD	Technical Guidance Document
UK	United Kingdom
US EPA	Environmental Protection Agency, USA
VA	Voluntary Agreement
vP	very Persistent, within the meaning of the PBT criteria

1. INTRODUCTION

1.1 Background to the Study

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[1] are polymers of high molecular weights in which PFOS is only a fraction of the polymer and final product (OECD, 2002).

On 16 May 2000, 3M (the major global producer of PFOS based in the United States) announced that the company would phase-out the use of PFOS voluntarily from 2001 onwards[2]. 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 to produce a hazard assessment. The United Kingdom and the United States assumed the lead in the collection of information from both OECD countries and non-member countries through the Intergovernmental Forum on Chemical Safety (IFCS).

At the 31st Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology (7-10 November 2000), it was agreed that, since this was a matter of sufficient interest to all Member countries, this activity should be undertaken under the Existing Chemicals Programme, overseen by the Task Force. The final draft of the Hazard Assessment was endorsed at the 34th Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology (5-8 November 2002).

The OECD 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. It notes, however, that further information on national and regional exposure would be required to better characterise the risks from PFOS.

In 2003, the Environment Agency for England and Wales, which is responsible for 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. The UK Review of Environmental Risks (RER) of PFOS related substances is being undertaken by Risk & Policy Analysts Limited in association with BRE Environment and overseen by the Environment Agency for England and Wales.

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[1] 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 as Annex 2 to this report.

[2] According to the OECD Hazard Assessment and consultation, the production of PFOS by 3M has now ceased.

The Department for Environment, Food and Rural Affairs (Defra) has also contracted RPA to prepare a Risk Reduction Strategy (RRS) for PFOS related substances, including an analysis of the advantages and drawbacks of potential risk reduction options. This Risk Reduction Strategy will follow the provisions of the EU Existing Substances Regulation (ESR[3]) according to which, where controls on the marketing and use of the substances in question are proposed, an analysis of the advantages and drawbacks of the substance should be undertaken. This includes an analysis of the availability of replacement chemicals. It should be noted that the UK RER has informed the development of the RRS (and vice versa).

1.2 Objectives and Approach

As detailed in the Project Specification, included as Annex 1, the objective of this study is to assess the advantages and drawbacks of different risk reduction options concerning the use of PFOS related substances to:

- enable judgement as to whether the benefits of adopting the restrictions outweigh the consequences to society as a whole of imposing the controls; and
- determine the best risk reduction strategy offering the greatest net benefits.

Guidelines for the development of a Risk Reduction Strategy are set out in a Technical Guidance Document published by the European Commission (CEC, 1998). Based on the TGD and the standard approach taken by Defra to all Risk Reduction Strategies under the ESR Programme, there will be four key stages in this project:

Stage 1: Data gathering and evaluation of all known uses of PFOS related substances. Establishment of the range of potential risk reduction options and current control measures in place.

Stage 2: A systematic qualitative assessment of the advantages and drawbacks for each option identified for the current uses of concern.

Stage 3: Either a semi-quantified or a fully-quantified assessment, examining one or more options for the uses of concern.

Stage 4: Preparation of the final Risk Reduction Strategy, including a presentation of all available cost (and benefit) information for each option considered and any assumptions made in the assessment.

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[3] Council Regulation (EEC) No. 793/93 of 23 March 1993 on the Evaluation and Control of the Risks of Existing Substances, OJ L 84, 5.4.1993, p.1.

This Report presents the findings of **Stage 4** of the study (‘Preparation of the Final Risk Reduction Strategy’) and recommends the risk reduction strategy to be taken forward. The information used in this Report incorporates information received in the period June 2003 - March 2004, and is based upon:

- the OECD Hazard Assessment Report and the 3M Risk Assessment Report;
- the Draft UK Review of Environmental Risks of PFOS related substances;
- a review of relevant literature for all known uses of PFOS related substances;
- information obtained through consultation with the relevant industries/sectors; and
- discussions with the Steering Group comprising of representatives of government, industry and an environmental interest group.

1.3 Structure of this Report

The remaining sections of this Report are organised as follows:

- Section 2 provides background information on all known uses of PFOS related substances (predominantly in the UK), in terms of the applications and markets, including downstream uses;

- Section 3 details the findings of the OECD Hazard Assessment for PFOS, the 3M Risk Assessment Report and the UK RER for environmental endpoints;

- Section 4 discusses the availability and suitability of potential alternatives to PFOS related substances for the identified uses of concern;

- Section 5 describes a range of existing risk reduction measures and how they apply to the various applications of PFOS related substances;

- Section 6 provides an overview of possible further risk reduction measures and outlines how they could apply to the various applications of PFOS related substances;

- Section 7 assesses the possible further risk reduction options against four key criteria (effectiveness, practicality, economic impact and monitorability); and

- Section 8 details the recommended Risk Reduction Strategy.

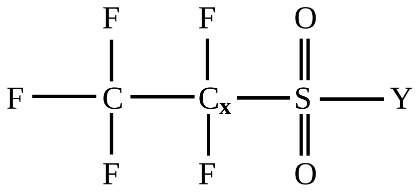
Annex 1 presents the Project Specifications as set out by Defra, while Annex 2 presents the list of PFOS related substances that have been identified as being relevant to this Risk Reduction Strategy. Annex 3 provides historical data on the UK markets for PFOS related substances before 2000 while Annex 4 provides emission estimates for the various use sectors of PFOS from the Draft UK RER. Annex 5 documents the list of consultees that have been contacted for the purposes of this study.

2. USES AND MARKETS FOR PFOS

2.1 Production of PFOS Related Substances

2.1.1 PFOS Chemistry

All of the chemical substances listed in the table provided in Annex 2 have a common chemical structure consisting of a PFOS moiety somewhere in the molecule, as illustrated in Figure 2.1,.



$\mathrm{F{-}CF_2{-}C_xF_2{-}S(=O)_2{-}Y}$

Figure 2.1: Structure of the PFOS Moiety

The number of carbon atoms present in the moiety may vary from 4 to 10 (x = 3 – 9), however, this study is focused on the octyl group of chemicals; therefore, for all chemicals included in the list of Annex 2, ‘x’ is equal to seven.

It has to be noted that the list of substances presented in Annex 2 includes only substances in which the C_8F_{17} group is directly linked to a sulphonyl group (SO_2), since it is assumed that only the presence of the full $C_8F_{17}SO_2$ moiety in the original molecule may allow the potential degradation of that molecule to PFOS in the environment.

There are many examples of different chemical functionality (free acids (Y = OH), metal salts (Y = O^-M^+), sulphonyl halides (Y = X), sulphonamides (Y= NH_2), and other derivatives). The listed chemical substances also include polymers (US EPA, 2000).

It should be noted that all PFOS related substances belong to the larger family of perfluoroalkyl sulphonates (PFAS). All references to *PFAS* substances in this report indicate that it was not possible to identify the exact chemical composition (as shown in Annex 2) of the substance(s) in question, and as such, reference has to be made to the family.

The basic building block of all of the PFOS chemicals is PFOSF (as described in Section 2.1.3 below), which is used as an intermediate in the production of the PFOS chemicals. Perfluorooctane sulphonic acid (PFOSA) results from the chemical or enzymatic hydrolysis of PFOSF. Information submitted by 3M to the US EPA supports the view that PFOSA is an extremely stable substance which resists breakdown by chemical or biological processes. Therefore, PFOSA is the ultimate degradation product from PFOS chemicals and will persist in that form (3M, 2000a; 3M, 1999).

2.1.2 The Simons Electrochemical Fluorination Production Process

PFOS related substances are manufactured by a process known as Simons Electro-Chemical Fluorination (ECF). In this process, organic feedstocks are dispersed in liquid anhydrous hydrogen fluoride, and an electric current is passed through the solution causing the hydrogen atoms on the molecule to be replaced with fluorine. The predominant components of the products created by this process have the same carbon skeletal arrangement as the feedstock used but with all of the hydrogen atoms replaced by fluorine.

However, fragmentation and rearrangement of the carbon skeleton can also occur and significant amounts of cleaved, branched and cyclic structures may be formed. The degree of fluorination of the organic feedstock is also dependent upon the specific carbon chain length of the feedstock and parameters of the ECF process such as electrical current and the length of time the process is run.

It is possible to synthesize fully fluorinated or perfluoroorganic molecules where all of the hydrogen atoms of the hydrocarbon feedstock have been replaced by fluorine atoms. Using these perfluororoganic molecules as basic building blocks, unique chemistries can be created by further reactions with functionalised hydrocarbon molecules.

It is of importance that the fragmentation and rearrangement reactions of the carbon skeleton may give, apart from mixtures of isomers, a variable mixture of by-products and impurities (OECD, 2002).

2.1.3 The Production of Sulphonyl Based Fluorochemicals (PFOS)

As noted above, the basic building block for PFOS related substances is perfluorooctanesulphonyl fluoride (PFOSF). The starting feedstock for producing PFOSF is 1-octanesulphonyl fluoride used in the following reaction:

$$C_8H_{17}SO_2F + 34HF \rightarrow C_8F_{17}SO_2F + 17H_2$$

The electrochemical fluorination process yields about 34%-40% straight chain (normal) PFOSF, and a mixture of by-products and waste of variable composition. Some of the non-POSF by-products are recovered and sold for secondary uses (3M, 1999).

PFOSF is reacted with methyl or ethyl amine to produce either N-methyl or N-ethylperfluorooctanesulphonamide (FOSA). FOSA is subsequently reacted with ethylene carbonate to form either N-methyl or N-ethylperfluorooctanesulphonamidoethanol (FOSE). The FOSA and FOSE intermediates are the principal building blocks of 3M's product lines.

Figure 2.2 shows the various chemical intermediates of the ECF process and the major product categories of PFOS related substances, from the wider family of *PFAS* substances.

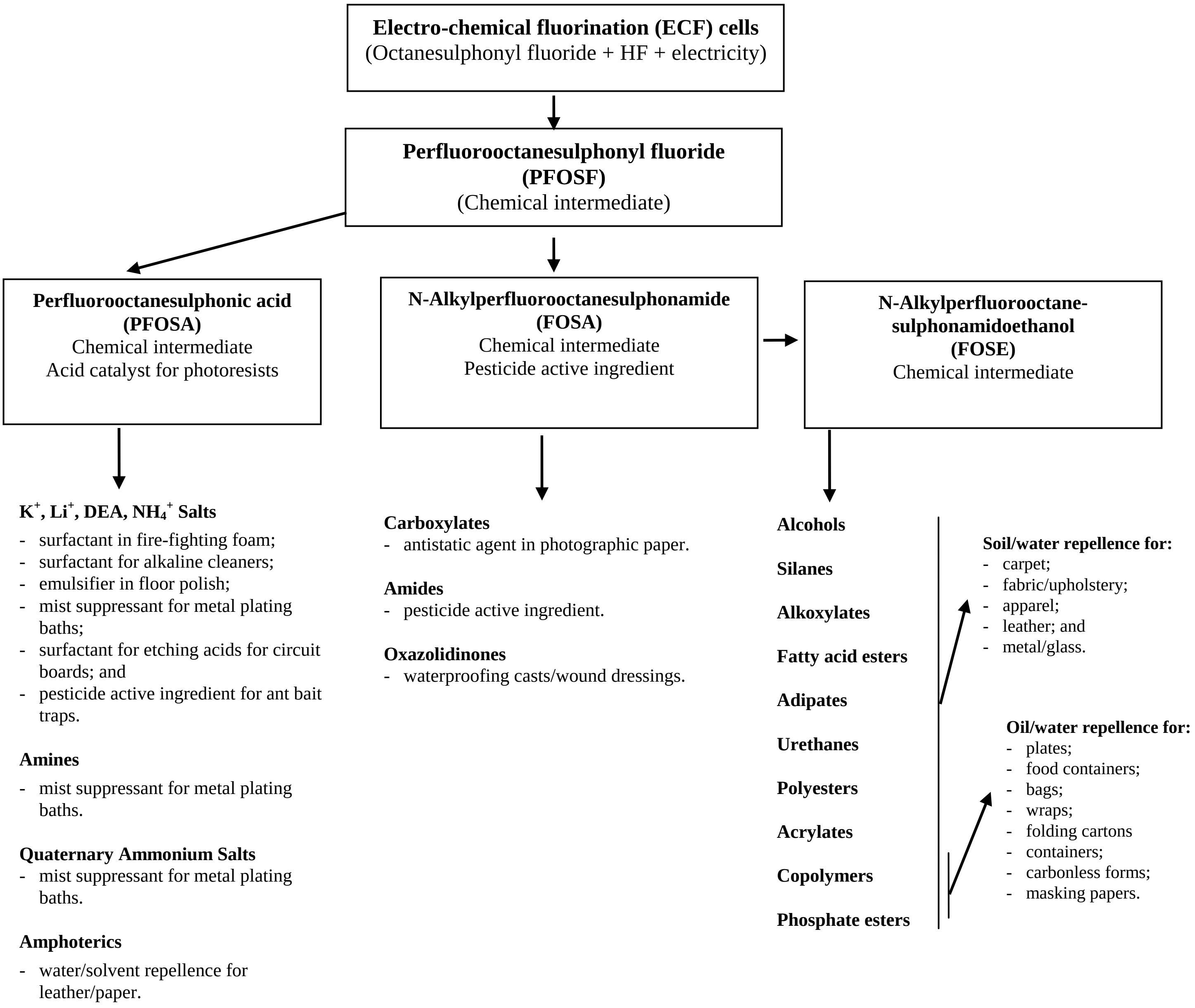


Figure 2.2: Major Product Categories and Applications for Perfluorooctyl-sulphonates (OECD, 2002)

2.1.4 Available Data on Global and UK Production of PFAS and PFOS Related Substances

Historic data on Production

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

Among the European plants, two were located in the UK. Recent reporting, however, indicates that both companies do not manufacture or supply PFOS and/or PFAS[4] substances. One of the UK companies has indicated that it manufactures cyclic perfluorocarbons to be used in cosmetic, medical, refrigeration, and electronics sectors. The other UK company is a specialist supplier of silicones and coatings and has indicated that, although it used to distribute 3M products, it no longer sells products containing PFOS related substances (ENDS, 2002).

In fact, recent research suggests that not all thirteen companies identified by the US EPA and named in the OECD Hazard Assessment were involved in the production of fluorochemicals through the ECF process. It has been suggested that, at the end of the last decade, there were a total of six companies manufacturing *PFAS* by the ECF process, with a total global capacity of 4,650 t/y. Four of the six companies where based outside the EU. One of the EU plants was the 3M plant in Antwerp, Belgium. The other EU based PFOS producer sells products that have been supplied to UK and EU users in the past (and still appear to be) (Environment Agency, 2001). Arguably, the market strength of this company and of other possible manufacturers was very modest compared to that of 3M before the voluntary phase out of 3M's production of PFOS related substances. Available information suggests that 3M's production capacity exceeded the combined capacities of all other PFOS producers by a large margin.

With particular regard to the UK, it is accepted that no production of PFOS related substances has taken place in the UK, at least in volumes allowing commercial marketing of such substances. Manufacturers in the UK are said to have been producing perfluorinated compounds with carboxylate end groups (pers. comm.)[5].

Table 2.1 below provides an overview of companies believed to have been involved in the manufacture and supply of PFOS related substances to the global market in the past decade (Environment Agency, 2001; OECD, 2002).

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[4] It should be borne in mind that all PFOS related substances are in the family of PFAS. All references to *PFAS* substances in this report are thus referring to the larger family of PFOS related substances, and do not in anyway suggest that the entire family of PFAS substances are under review for this RRS.

[5] These chemicals with carboxylate end groups have the same basic molecular shape and properties as PFOS. There are suggestions that the products might breakdown to produce substances with similar persistence and fate properties as PFOS.

Table 2.1: Companies Believed to Have Been Involved in the Manufacture and Supply of PFOS Related Substances to the Global Market in the Past Decade (as Identified in Various Literature)

Company	Location	Env. Agency (2001)[1]	OECD (2002)[2]	RPA (2004)[3]
A	Belgium	*	*	*
B	United Kingdom		*	
C	United Kingdom		*	
D	Italy	*	*	*
E	Italy		*	
F	Germany			*
G	Germany			*
H	Switzerland		*	
I	Russia		*	
J	Russia	*		
K	Japan	*	*	*
L	Japan		*	
M	Japan		*	
N	Japan		*	
O	Japan	*		
P	China	*	*	
Q	India		*	
R	Brazil		*	
S	USA			*
T	USA	*	*	*

[1] All the companies listed in Env. Agency (2001) are involved in the production of *PFAS* substances using the ECF process; the proportion of *PFAS* production made up of PFOS is however unknown.
[2] Only two of the thirteen companies listed in the OECD HAR had been independently corroborated as being involved in the production of PFOS related substances.
[3] RPA (2004) is based on information provided by companies who claim to have purchased PFOS related substances from the listed companies, as well as companies whose involvement in the supply of PFOS related substances has been independently confirmed.

Quantitative historic data on PFOS production exist only for the US (i.e. for 3M's operations). In 1997, 1,848 metric tonnes of PFOSF were manufactured or imported into the US with the figure slightly lower at 1,820 for the year 2000. For that year, the total global PFOSF production by 3M was estimated as being around 3,665 metric tonnes. This figure is now zero as 3M suspended the production of PFOSF-derived chemicals under its voluntary action programme (OECD, 2002).

Table 2.2 below presents an overview of data provided by 3M on their global production volume of PFOS related substances, as used in various applications. It should be noted that the figures represent production volumes for 3M plants only. These tonnages are used in the OECD Hazard Assessment as representing global production based on the assumption that 3M is the sole producer. This, as explained above, is inaccurate but given the low expected relative production capacity of other producers, the approximation is considered acceptable. It should also be noted that existing data on tonnages often represent total solid metric tonnes of fluorochemical containing compound, not PFOS itself. Less than 91 metric tonnes of PFOS and its salts were commercialised as finished products. The bulk of PFOS related chemicals were polymers or functionally derivatised fluoroorganic molecules.

These higher molecular weight products do not typically contain PFOS, although they may contain small amounts of other manufacturing residuals (less than 1%, according to 3M). These manufacturing residuals may degrade to PFOS while the higher molecular weight compounds and polymers tend to be stable with long half-lives (3M, 2003b).

Table 2.2: Global Production of PFOS Related Chemicals in 2000 (based on data from 3M)

Application category	**Production (metric tonnes)**
Surface treatment applications	2,160
Paper protection applications	1,490
Performance chemical applications	891 (of which 151 in fire fighting foams)

Source: OECD (2002)

In the last quarter of 2000, the production of PFOS related substances by 3M was around 1,135 tonnes. The projected phase out of production is presented in Table 2.3.

Table 2.3: Projected Phase Out of PFOS Related Substances by 3M (2000-2003)

Year	**Quarter**	**Projected Production (tonnes)**
2000	4th	1,135
2001	1st	136
	2nd	136
	3rd	136
	4th	136
2002	1st	62
	2nd	62
	3rd	40
	4th	40
2003	1st	0

Source: 3M (2000b)

2.2 Overview of EU Markets for PFOS Related Substances

2.2.1 Use of PFOS Related Substances in the UK

A study by the Environment Agency on *PFAS* suggested that 400 tonnes of *PFAS* (including PFOS) are used in the UK per year, all of which are imported. The main applications of *PFAS* in the UK (Environment Agency, 2001) are shown in Table 2.4 below. It is not known what proportion of these *PFAS* are PFOS related substances.

Table 2.4: Breakdown of PFAS Applications in the UK

Application	**Tonnage**	**Market Size**
Protective treatments for textiles, leather and carpets	195	48.8%
Protective treatments for paper and board	60	15.0%
Speciality surfactants	70	17.5%
Fire fighting foams	65	16.3%
Chemical intermediates	10	2.5%
Total	**400**	**100%**

Source: Environment Agency (2001)

Consultation with suppliers and users of PFOS related substances in the UK suggests that the producers (all of whom are based outside the UK) sell directly to the major UK consumers, when selling in commercially significant quantities (not R&D). Some of these producers have established distributors in the UK who supply the very small quantities of PFOS related substances usually needed by the majority of end-users (e.g. metal platers). These distributors also act as agents or contact points for users who require larger quantities of PFOS related substances (e.g. fire fighting foams).

The above analysis appears to be supported by information on the use (imports) of PFOS related substances in the UK that has recently been made available to the UK Government. This is presented in a total of four tables available as Annex 3 to this report.

The information suggests that, before 2000, the UK market was consuming over 100 tonnes of PFOS related substances per year. Of this, the majority of products were used for the protection of paper and packaging, and the protection of carpets. The smallest uses were as chemical intermediates and as surfactants for baths used in the electrical and electronics industry (see Table A3.1).

The residual organic fluorochemicals (ROF) content[6], ranged between 0% and 7% in the various preparations with an average of 2.4% as a percentage of the PFOS related substances contained (intentionally) in the preparations. The preparations used for paper and packaging protection (from water, oil and grease) contained the largest total amount of ROF, although the maximum ROF content in these products was 1% (the strong overall presence of ROF in paper and packaging products entering the UK market was due to the predominance of these products in the overall UK PFOS market).

A total of 46 CAS Numbers for PFOS related substances have been identified, of which 24 are included in the list of Annex 3. The CAS Numbers are not provided on grounds of confidentiality.

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[6] Most *PFAS* substances (and PFOS related substances) are used in the production of polymers. The ROF content refers to the amount of the unreacted or partially reacted PFOS substance present in the final preparation either intentionally or as impurities, which has the potential to degrade to PFOS.

Table A3.2 provides the number of different products that contain each PFOS related substance, while Tables A3.3 and A3.4 provide an indication of the significance of each PFOS related substance within each application sector (type) and across the overall UK market (prior to 2000). Most sectors have a specific CAS Number which dominates the relevant products, while the overall market has three PFOS related substances which each account for more than 5% of the total market (see Table A3.4).

Note that this analysis is included for indicative purposes only. Since initiation of voluntary action by 3M, the UK market has significantly changed.

With respect to users, only a limited number of industry groups (metal plating, fire fighting foams, semiconductors and photographic) were able to estimate the tonnages of PFOS related substances used within their industry sectors (in the UK and/or the EU). The hydraulic fluids sector has also provided indications of tonnages of relevance to their industry sector globally. In some instances, trade associations (for example, the British Coatings Federation) have not provided historic information due to members' concerns over commercial confidentiality. In other cases, the trade associations appear to have no information on the use of PFOS related substances. This was the case for PFOS based paper protection products where, despite reportedly representing a significant part of the market (at least before 3M's voluntary action), none of the trade associations contacted were able to identify UK applications or possible users.

Other trade associations, such as that representing the fire fighting foams manufacturers, were keen to distinguish between PFOS based products and the products currently used in their industries. This reflects the desire of some manufacturers to differentiate between their telomer based chemistry and the ECF chemistry used by 3M; and others to differentiate between fluorine-free fire fighting foams and foams containing fluorine.

2.2.2 Use of PFOS Related Substances in Denmark

A study assessing the presence of PFOS related substances in the Danish market (Danish EPA, 2001-2) found that the most widespread uses of PFOS related substances were in:

- impregnation agents for textiles, leather and paper;
- wax and other polishes;
- paint, varnish and reprographic agents;
- cleaning products (general products and speciality products for metal surfaces and/or carpets);
- flame retardants; and
- mould release agents.

The total registered sales of PFOS related substances were estimated at 8-16 t/y, however, many products/materials (for example, textiles, wax and polish products) are not subject to notification in Denmark. The registered sales do not, therefore, provide an accurate picture of the Danish market. The Danish EPA publication estimates that total Danish consumption (registered and non-registered) may be as high as 50 t/y (and as low as 5 t/y).

As part of its study, the Danish EPA tested 21 consumer products for perfluorosulphonates. Thirteen were impregnating agents for shoes and textiles and a further eight products were wax and floor polishes. In three products, PFOS related substances were found; two impregnating agents contained 212 µg/mL perfluorodecanesulphonate and another contained 3.5 µg/mL perfluorooctanesulphonamide. One of the wax and polish products contained 9 µg/mL ethyl perfluorooctanesulphonate (Danish EPA, 2002). The Danish EPA report suggests that the production of PFOS related substances still occurs in the EU.

A note should be made of the fact that studies in both the UK and Denmark have highlighted that there appear to be applications of perfluorinated substances which are unknown to the users. As PFOS related substances are not classified for their environmental and/or human health effects, they do not appear in the documentation accompanying preparations and products. The absence of information on their presence may also be due to the fact that their identities are considered commercially sensitive information. Moreover, there are products in which PFOS related substances are present unintentionally, usually at concentrations of parts per million (ppm). These substances are likely to be found not only as impurities but also as unreacted monomers in polymers.

2.2.3 Use of PFOS Related Substances in the Netherlands

In January 2002, the University of Amsterdam's Institute for Biodiversity and Ecosystem Dynamics (IBED), Department of Environmental and Toxicological Chemistry (MTC) were contracted by the Royal Institute for Coasts and Sea (RIKZ) to carry out a desk study of *PFAS*. This study examined the lifecycle of *PFAS* in the environment, including production, emissions, waste generation and effects (RIKZ, 2002).

For this study, fifteen *PFAS* were selected. These substances are used in commercial products, monomers in polymers, important production intermediates or important degradation products. Table 2.5 below presents the results of this research project with regard to the market for the substances in the Netherlands.

Table 2.5: Markets for *PFAS* in the Netherlands (estimates for 2002)

Application Area	**Consumption of PFAS (t/y)**	**Form of PFAS**
Carpet protection	15	Polymers
Paper and board protection	60 - 105*	Phosphates
Leather protection	10 – 20	Polymers
Textile protection	Not available	Polymers
Fire fighting foams	1.13 - 3.81	Monomers
Specialty surfactants	Not available	Monomers
Polymerisation aids	>1	Monomers

** The study indicates that the use of PFAS on paper takes place outside the Netherlands and subsequently the treated paper and board is imported into the country.*
Source: RIKZ (2002)

2.2.4 Sweden

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.

KemI notes that a couple of tonnes of *PFAS* and PFOS related substances were found to be registered on the Swedish Product Register. The uses of the PFOS related substances in Sweden are indicated to be similar to the uses described later in this report, although of particular interest are uses in metal plating, textile and leather protection, industrial and household cleaning products and photolithography (KemI, 2004).

2.2.5 Overview of Applications for PFOS Related Substances

The sections that follow provide detailed information on the applications and markets for PFOS according to industry sectors. This information includes:

- a description of how PFOS related substances are used in each application type;

- information on the sizes of the downstream markets for products based on PFOS in terms of quantities and value, where available; and

- information on trends in the use of PFOS, where available.

The OECD Hazard Assessment report provides the starting point for information on the production and markets for PFOS. The report has identified the use of PFOS related chemicals in a large variety of applications, including surface treatment of fabric for soil/stain resistance, paper protection applications and performance chemicals. As indicated in the report, the majority of PFOS related chemicals are high molecular weight polymers in which PFOS represents only a small fraction of the total molecular weight.

Table 2.6 outlines the major uses of PFOS related substances as identified in the OECD Hazard Assessment. Additional information has been incorporated from consultation for this study and from the Danish EPA study of 2002.

Table 2.6: Overview of Uses for PFOS (and PFOS Related Substances)

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

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

Notes: PFOSA: Perfluorooctanesulphonic acid; FOSA: N-Alkylperfluorooctanesulphonamide; FOSE: N-Alkylperfluorooctanesulphonamidoethanol; PFOSF: Perfluorooctanesulphonyl fluoride; DEA: Diethanolamine

2.3 Textiles Protection

2.3.1 Use of PFOS Related Substances for Textile Protection

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

When applied to a material's surface, the perfluorocarbon chain tends to be orientated away from the surface, lowering the surface energy of the material, thereby creating a protective barrier. When applied as a finish to certain textiles, such as polyester and polyamide garments, these treatments give water, oil and soil repellence and a soft handle; while in technical textiles, they impart or enhance properties such as resistance to water, mechanical loads and intense heat. Such treatments are used for rainwear, bed linen, upholstery fabric, curtain material etc., and are stable to laundering and dry cleaning.

Other potential uses have included protective clothing such as fast food restaurant work-wear, industrial apparel, helmets and shoes, mechanics' overalls, and clothing and head covers for workers in clean rooms. In the automotive and aeronautical industries, fluorochemical treated non-wovens are used as floor-covering underlays and seat covers in acoustic insulators, as well as in air, gas and liquid filtration systems.

In the production of textiles, *PFAS* substances are also used as wetting agents to improve the coverage and penetration of substrates, achieve finish-on-yarn uniformity, enhance dyeing and as a binder in non-woven fabrics. They are also used as antifoaming agents in textile treatment baths, penetrating agents for finishes on heavy denier fibres, emulsifying agents/lubricants for fibre finishes, flow modifiers for spinning of hot melts and solutions, and as penetration aids for bleaches. Finally, the finishes can be used in furnishings to make wallpaper resistant to paste and glue migration and on lining fabrics used in upholstered furniture.

2.3.2 Types of PFOS Related Substances Used

The *PFAS* that are, in general, used for textile (and carpet) surface treatment applications are the acrylate, adipate and urethane polymers produced from the ECF intermediate, N-ethylperfluorooctanesulphonamide ethanol (FOSE).

There are a large number of products in the textile auxiliaries market that provide soil and water repellence to textiles. Table 2.7 gives a summary of the number of different products and number of companies worldwide that sold such agents for use in textiles in 2002. Note that not all of these products contain PFOS related substances.

Table 2.7: Number of Global Suppliers of Textile Auxiliaries that may contain PFOS (2002)

Type of Products	**Stain repellent finishes/soil release agents**	**Water repellent agents**
Number of marketed products	68	191
Number of companies worldwide	43	48
Number of companies in the EU	39	37
Number of companies in the UK	25	26

Source: WTP (2002)
Note: The number of EU companies includes those which may have branches in the UK only

2.3.3 Current Uses of PFOS Related Substances - Consultation Findings

RPA has received communications from the Confederation of British Wool Textiles (CBWT)[7] and the Textile Finishers' Association (TFA). The information received indicates that individual user companies generally purchase technical chemicals (often termed auxiliaries in the industry) from suppliers. The exact chemical composition of the various preparations used in this way may not be known to the user and indeed may, to a degree, be regarded as commercially sensitive information by the supplier.

Users of these auxiliaries generally rely on the information contained in the supplier's material safety data sheets for information on composition, environmental and human health effects, etc. and, although these sheets provide basic information, they are by no means complete. The CBWT suggests that, should a substance raises concerns with regard to its environmental and/or human health effects, users in the textiles industry would rely on the expertise of the manufacturers/suppliers for information and guidance. This was the case with the 3M stain release preparations based on PFOS and supplied by 3M (CBWT, pers. comm.).

The CBWT, thus, believes that the suppliers of the chemical preparations are in a better position to provide information on the use of PFOS related substances, the relevant applications and any trends in the market.

Detailed consultation with UK companies involved in the textile auxiliaries market supplying soil and water repellence products for downstream users, however, showed that the companies themselves were not more knowledgeable as regards the exact chemical composition of the substances they purchased. While there was a general acknowledgement of the use of perfluorinated chemicals (particularly the acrylate polymers) in these products, none of the companies was able to provide the exact chemical names of the perfluorinated chemicals being used. The majority relied mainly on the information provided in the material safety data sheets (MSDS) for technical data.

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[7] CBWT represents the interests of wool dyers and finishers in the UK and incorporates the TFA, which represents the finishers and coaters of textiles other than wool. CBWT thus represents downstream users of preparations designed to impart technical properties to textiles rather than chemicals manufacturers or suppliers.

Based on the responses obtained from consultation with suppliers, it would appear that only the producers of the PFOS related substances (such as 3M) would be in a position to state categorically if a formulation contains PFOS related substances or other perfluorinated chemicals[8]. Interestingly, one company supplying auxiliaries to the textile market indicated that one such producer of PFOS related substances (supplying this particular company with the 'perfluorinated chemicals') informed them that PFOS related substances may be found in their formulations. The amount or concentration of PFOS which may be found in their formulations was not disclosed however (pers. comm.). It should be noted that textile preparations containing PFOS related substances are no longer used in the UK textile industry. The consultation suggests that the last stocks were probably used up by the end of 2003.

Consultation also shows that a significant proportion of the suppliers of textile auxiliaries in the UK have manufacturing plants in various parts of Europe, where most of the actual production takes place. The UK companies simply purchase the chemicals from their parent companies and pass them on to customers, thereby acting as a distribution outlet. As a result, the end users of the 'perfluorinated chemicals' could vary widely. One textile auxiliaries manufacturer indicated that, in the UK, the supply and use of perfluorinated compounds is restricted to back coating of fabrics, while a branch located in Spain uses much more significant quantities of perfluorinated chemicals in a wider variety of applications. It should be noted that a significant number of the companies contacted indicated that they obtained their perfluorinated chemicals from Japan.

In general, the main end users of textile preparations in the UK are textile finishers, with possible uses including back coating of fabrics, dyeing and finishing and the production of umbrella coatings (pers. comm.). There are also indications that most of the textiles coated with these perfluorinated chemicals are used by consumers at the top end of the market, in the production of high quality curtains and upholstery (representing the largest use).

The European Apparel and Textile Organisation (Euratex) has contacted its members with regard to this study, but has received no information of relevance. Euratex therefore, believes that the use of PFOS related substances is not of relevance to their members. The German Textile Association has also indicated that PFOS related substances are no longer used in textile preparations present in Germany.

2.4 Carpet Protection

2.4.1 Use of PFOS Related Substances for Carpet Protection

In carpets, 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

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[8] It is important to note that, all references to the use of perfluorinated chemicals in textile formulations are not intended to suggest or imply that these formulations definitely contain PFOS related substances.

fluorochemical substance) provides stain resistance. The principle of soil repellence is based on the reduction of the surface energy of the fibre by the fluoroalkyl chains of the PFOS substance. These chains repel both water and oil, so that soil particles cannot enter the carpet (RIKZ, 2002).

These products were also marketed to consumers in pump and aerosol cans for spray application to carpets (3M, 1999), although available information suggests that 95% of all carpet protectors based on perfluorochemicals are for application at point of manufacture in the carpet mill. In the mill, there are three main ways in which these preparations can be applied to the carpet fabric (GUT, 2003):

- foam applications;
- dye-bath applications; and
- spray applications.

The commercial products for carpet protection contain approximately 15% fluoroalkyl acrylic polymers, and are generally used as foam-applied emulsions for the finishing of the carpets (RIKZ, 2002). Any PFOS related substances were not usually present as pure products, but as copolymers in concentrations of 0.001% of the final product (GUT, 2003).

2.4.2 Consultation Findings

Consultation has involved a number of UK and EU carpet associations and carpet manufacturers within the UK. Little or no information has been received thus far from UK carpet makers contacted for this study and it has been suggested that for most carpet manufacturers, stain repellence is a small part of the market. On the other hand, one consultee has suggested that there are still carpet manufacturers in Europe who market their products with a Scotchguard label (formerly based on PFOS related substances and marketed in the past by 3M) and 3M products may still be in use. Consultation with the UK National Carpet Cleaning Association to ascertain the exact situation in the UK did not yield any relevant information.

It has not been possible to estimate the size of the market for anti-soil/anti-stain preparations, as not all carpets are treated with soil and stain repellent preparations. The main field of application is the domestic market, and not all the carpets for the domestic market are treated. It has also been noted that wool has natural resistance to staining and does not require the use of chemicals.

Information received from the GUT[9] indicates that stain and soil repellent products based on fluorinated polymers are used by members of the European Carpet Association. GUT, however, indicates that currently all fluorinated chemicals used in anti-stain/anti-soil preparations are prepared via the telomerisation route. According to GUT, since the withdrawal of 3M from the market, preparations based on the ECF process have not been used in carpet preparations (GUT, 2003).

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[9] Gemeinschaft umweltfreundlicher Teppichboden (GUT) is the section responsible for technical issues in the European Carpet Association.

2.5 Leather Protection

2.5.1 Use of PFOS Related Substances in Leather

Treatments are applied to leather and suede to give oil/water/stain repellence. Tanning treatments react with the leather in the tanning drum and on subsequent drying. On losing water, they release hydrochloric acid and react with the proteins in the leather. This treatment is normally used on hides that require very high levels of oil and water repellence throughout the thickness of the leather (for instance in upholstery grades), but can present problems if further treatments are required as the surface is rendered almost unwettable.

Fluorinated surfactants have also been reported as being used in various leather manufacturing processes to improve the efficiency of the process, reduce processing time and increase the quality of the product. They can also improve the levelling of acrylic brightener emulsions on leather.

The UK market for fluorinated active ingredients in textile, leather and carpet treatment is estimated to be 195 tonnes per annum (49% of the estimated total market). The contributions of the individual segments are not known.

According to the International Leather Guide 2002, there are 20 suppliers of waterproofing and repelling agents in the UK (including 3M) and a total of around 50 in the EU. It is unclear how many of these (if any) supplied PFOS based preparations. A total of 13 UK tanneries have been reported as manufacturing waterproof leather (Polygon Media, 2001). Water repellent consumer sprays for leather products are also available.

2.5.2 Current Use of PFOS Related Substances in Leather - Consultation Findings

Information received to date from consultation with the major UK and EU associations, as well as individual companies, suggests that there is no use of PFOS related substances in leather applications in the UK, or in the EU more generally.

Consultation has also involved the leather technology centres across most of the EU Member States. According to information received from VAL[10] in Austria, leather tanners are not generally aware of the composition of their auxiliaries (technical chemicals used in leather) and have to rely only on the safety data sheets provided by their suppliers. Consultation indicates that only one company in Austria produces auxiliaries for the leather industry - and they have indicated that they do not use PFOS related substances (VAL, 2003).

According to information received from AIICA[11] in Spain, fluorocarbon compounds are used in modern leather applications to provide water and oil repellence. AIICA, however, was not able to say whether PFOS related substances were used in these

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[10] Versuchsanstallty fur lederindustrie (VAL) is the leather technology centre in Austria.

[11] Asociacion de Invetigacion de las Industrias del Curtido y Anexas is the leather technology centre in Spain.

fluorocarbon compounds or not, as information relating to the exact chemical composition of the various preparations is usually held by the chemical suppliers. Since 3M's withdrawal from the market, AIICA believes that PFOS related substances are no longer used for these applications in the leather industry (AIICA, 2003).

TEGEWA, the body representing the producers of leather auxiliaries in Germany, indicated that their members buy substances from producers and formulate them into auxiliaries. According to TEGEWA, 3M was the only supplier of PFOS related substances in Germany. Since production stopped in 2000, and the stocks were sold off in the two years following, the German leather industry has had no interest in PFOS related substances (TEGEWA, 2003).

2.6 Metal Plating

2.6.1 Use of PFOS Related Substances in Metal Plating (Chromium Plating)

Information obtained from consultation indicates that the main uses of PFOS related substances in the UK in metal plating are for chromium plating, and anodising and acid pickling.

PFOS related substances lower the surface tension of the plating solution so that mist containing chromic acid from the plating activity is trapped in solution and is not released to air. The mist is created due to the release of oxygen and (mainly) hydrogen during the plating process. Given this process, application patterns are:

- additives for chromium electroplating that reduce surface tension;
- surfactants with suitable foaming ability to prevent mist formed by gas bubbles evolving at electrodes during electroplating; and
- corrosion inhibitors.

Other uses for fluorinated surfactants are identified in the literature by the Environment Agency (2001):

- agents to prevent haze of plated copper by regulating foam and improving the stability of plating baths while improving brightness and adhesion;
- non-foaming surfactants in nickel plating baths to reduce the surface tension and increase the strength of nickel electroplate by eliminating pinholes, cracks and peeling;
- agents added to a tin plating bath to produce plating of uniform thickness; and
- agents to impart a positive charge to fluoropolymer particles and to aid electroplating of the polymer (e.g. PTFE) onto steel for surface protection.

2.6.2 Importance of PFOS Related Substances in Metal Plating

According to communications with chromium platers, PFOS related substances are stable in hostile environments, such as hot chromic acid, where they form a foam blanket on the surface of the treatment bath, thereby preventing the release of acid mists by acting as a barrier. PFOS is thus vital to their operations, ensuring the health and safety of workers and reducing the risks of health impacts (e.g. lung cancer, chrome ulcers, etc.) associated with chromium plating (Industry, pers. comm.).

Before the introduction of the PFOS based applications to control the emissions of hexavalent chromium, mists were controlled through extraction. Hexavalent chromium is a known carcinogen and has been targeted by the UK COSHH Regulations[12]. Downstream users consider that the use of PFOS related substances has made the control of such mists much more efficient and it helps considerably in meeting UK Health and Safety Occupational Exposure Limits (OELs) for hexavalent Chromium (Cr (VI)) and associated health surveillance.

2.6.3 Production of Formulations for Plating Applications

Consultation suggests that there are four major players in the market producing preparations for UK metal platers. Information has been received from all four, although one did not provide detailed information in the form of a completed questionnaire.

The suppliers usually purchase aqueous solutions of PFOS related substances which they occasionally dilute further and then forward to their customers. Typically, 10% solutions are used although, as shown below in Table 2.8, the products supplied may have higher concentrations. A downstream user has noted that a relevant product is used with a PFOS concentration of 5%, however, this may be due to prior further dilution of the original preparation.

The source of PFOS related substances appears to be companies (if not one single company) in the EU and 3M. One of the companies that has returned a completed questionnaire could not provide detailed information on its supplier.

An overview of the available data from UK suppliers of metal plating additives is provided in Table 2.8. Information received appears to support the view that UK platers are served predominantly by UK suppliers of chemical preparations.

On the basis of available information, the total tonnage of PFOS related substances used in the production of preparations used in metal plating is less than 0.5 t/y. Of this, the majority is used in chromium plating rather than anodising and acid pickling. The latter is expected to be associated with a total of around 20-30 kg/y of PFOS related substances consumed (pers. comm.).

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[12] Control of Substances Hazardous to Health Regulations 1994.

Table 2.8: Overview of Use of PFOS Related Substances in Mist Suppressants by UK Suppliers (used by the chromium plating industry)

Company	Quantities Used (t/y)	PFOS Substances Used (CAS No.)	Concentration of PFOS Substance(s)	Quantities of Suppressants Sold (t/y)	Origin of PFOS	Shelf-life (y)	UK Sales Trend
A		56773-42-3	5 - 7%	0.25		2	
B	0.12	56773-42-3	10%	1.23	EU	2	Stable
C	0.15	56773-42-3	50%	0.3	EU	1	Stable
D					3M		
Totals	**<0.5**						**Stable**

Source: Consultation

2.6.4 Types of PFOS Related Substances Used and Current Trends

As discussed in the OECD Hazard Assessment, PFOS related substances used for mist suppression in metal plating baths are the potassium, lithium, diethanolamine, and ammonium salts of perfluorooctanesulphonic acid (PFOSA) as well as quaternary ammonium salts and amines.

Consultation confirms the above as it has shown that a substituted (quaternary) ammonium salt of PFOSA is used by both suppliers that have provide information to date. This substance is presented as substance 33 in the list of substances in Annex 2.

Two of the suppliers that have provided information thus far suggest that over the last few years their UK sales have been relatively stable. However, there is a general downward trend in the level of operations in the UK metal plating industry. The main reason for such a trend is the shift of operations from the UK to cheaper markets, such as the Far East. Downstream users have indicated that the EU metal plating industry generally faces this problems.

We have been in contact with a company producing and supplying preparations containing PFOS related substances for metal plating applications in Germany. The amount of PFOS related substances sold in the EU is approximately 3 tonnes/year and the supplier of the PFOS related substances is indicated as being based in Germany. The PFOS related substance is the same substance used in the UK (substance 33 in Annex 2) and is present as a pure substance in the preparation. The company believes it represents approximately 30 –35% of the EU market share for PFOS related substances in the EU. It also indicates that no significant changes have been observed in market trends in the last 5 years, neither in volumes sold nor in market size. They also do not envisage any changes to the market (Industry, pers. comm.).

2.6.5 Shelf-life of PFOS Based Preparations

The shelf-life of the product (reported at 1-2 years) is limited, according to industry, not due to degradation of the PFOS related substance but rather due to the shelf-life of the plastic packaging that contains the preparation or due to the effects of temperature extremes (Industry, pers. comm.).

2.6.6 Downstream User Data

It is estimated that there are around 300 platers in the UK, all of which could be using PFOS related substances. Important applications for chromium plating in general include aircraft, medical industries, vehicles and general engineering.

2.7 Paper and Packaging Protection

2.7.1 Possible Applications of PFOS Related Substances in 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).

PFAS in general may find applications as grease, oil and water repellents in:

- liner board (for packaging machine parts, rope, twine, meat);
- folding cartons (for snack foods, fast food, cake mixes, margarine, confectionery and bakery products, and pet foods);
- multiwall bags (snack foods, cake mixes, pet food);
- moulded pulp products for plates and food containers;
- flexible packaging (fast food and confectionery wrappings);
- flexible or lightweight papers primarily for bags, wraps and micro flute containers;
- support cards (confectionery and bakery products); and
- business and specialty papers for carbonless forms and masking papers.

Other experts from within the paper industry have suggested that PFOS related substances should not be expected to be used in corrugated paper in the UK (Industry, pers. comm.)

2.7.2 Types of PFOS Related Substances Used in Paper and Packaging Applications

Paper protection can be achieved using two different classes of chemistries. One class consists of the mono, di and tri phosphate esters of N-ethylperfluorooctanesulphonamidoethanol (FOSE), in rough proportions of 10%, 85% and 5% respectively. The other class is N- methylperfluorooctanesulphonamidoethanol-acrylate copolymer. When applied to paper, the perflurocarbon moiety in these classes of products has the effect of lowering the surface energy of the individual paper fibres. This lowered surface energy greatly contributes to the blocking of low surface energy liquids such as greases and oils (3M, 1999).

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).

A market survey of the Netherlands estimated that 6,000 to 7,000 tonnes of coated paper are sold annually. The products used for this application are generally based on the fluoroalkyl phosphates. It is estimated that for these types of paper 1.0-1.5% (based on the dry weight of the fibre) fluoroalkyl phosphate is needed, corresponding to 60–105 tonnes of fluoroalkyl phosphate used in the Netherlands (RIKZ, 2002).

2.7.3 Use of PFOS Related Substances in the UK Paper Industry

Consultation has involved associations of paper manufacturers and of companies that produce chemical preparations which are used in the production of different grades of paper. The Paper Chemicals Association (PCA), which claims that its members supply almost 80% of the chemicals used in the UK paper industry, has suggested that at present there is limited interest in PFOS related substances and the chemistry of their effects. Further communication with the PCA, however, indicated that two of their member companies have a registered interest in PFOS related substances. Both companies have their main plants outside the UK, but within Europe, and were reported to be in contact with their European Associations (PCA, pers. comm.).

This is in line with information received from consultation with the Paper Federation of Great Britain (PFGB), which represents about eighty paper mills in the UK. The PFGB's understanding is that the use of PFOS related substances in paper mills in the UK stopped as a result of the withdrawal of 3M from the market (i.e. there was no supplier and the market had to move to other producers of relevant formulations) (PFGB, pers. comm.). A major producer of boards for the paper and packaging industry in the UK has also indicated that the sudden nature of 3M's withdrawal from the market resulted in most of the users having to move to alternative formulations by other companies.

Overall information received from industry indicates that there is no longer any interest in PFOS related substances in the UK paper industry. It is believed that the majority of the PFOS related substances that were used have been replaced by non-PFOS based fluorochemical alternatives; while the remainder have either moved to non-fluorochemical alternatives or withdrawn completely from the market. This trend is believed to have occurred throughout Europe, although the extent to which this has occurred remains unclear.

Existing evidence also appears to suggest that, in 2001, *PFAS* substances found limited applications in the paper industry in the UK (and the EU) since these chemicals were considered very costly. It should be noted that the UK is a relatively small player in paper making, with most paper made in the Scandinavian countries or elsewhere. The number of UK companies that could possibly be involved in processes relevant to this study is at the most five (if there are any at all). The situation is similar for the Netherlands, where proofing of paper does not take place at all, as the majority of the coated paper used is imported from Germany and Scandinavia (RIKZ, 2002).

The PCA also suggests that it may be the case that the specifications for the paper (for example, for paper used to wrap fast food meals) are set outside the UK or even outside the EU, and the production of paper may take place outside the UK and then be imported for use in the UK.

2.8 Fire Fighting Foams

2.8.1 Background to Fire Fighting Foams

Water is vital and effective in extinguishing a majority of fires. However, when fighting fires involving flammable liquids (Class B), water tends to sink below the burning fuel due to its higher specific gravity and, thus, has little effect in extinguishing the fire (and in some cases could even result in the flammable liquid spilling out of its contained area). Fire fighting foams were therefore developed for use on flammable liquid fires and have proven to be one of the most important and effective tools for dealing with such fires. Fire fighting foams are produced by a combination of foam concentrate (the form in which it is stored) and water, which is then aspirated with air to form the finished foam. The resulting foam forms a low-density blanket that extinguishes fires from flammable liquids (HM Fire Service Inspectorate, 2000) by:

- excluding air from the surface of the fuel;
- separating the flames and the fuel;
- reducing the release of flammable vapour from the fuel;
- forming a radiant heat barrier, which reduces the feedback of heat from the flames to the fuel and therefore reduces the production of flammable vapour; and
- cooling the fuel surface as the foam solution drains out of the foam blanket, producing steam in the process which dilutes the oxygen around the fire.

Class A foam concentrates are used on fires involving wood, paper and rubber. These rely mainly on organic mixtures of anionic surfactants, ammonium sulphate and or phosphates, clay thickeners and stabilisers with other solvents and colourants. Class A foams are designed primarily to lower the surface tension of the water to allow better penetration of the solution into the mass of burning material. Class B foam concentrates are used on fires involving flammable liquids, oils or grease and usually contain synthetic fluorochemical surfactants together with additives.

2.8.2 Types of Fire Fighting Foams

There are approximately eight different types of fire fighting foams, based on the classifications given in the Fire Service Technical Manual on fire fighting foams (HM Fire Service Inspectorate, 2000) and information received by the British Fire Protection Systems Association (BFPSA, 2003a). These are:

Fluorine containing foam types:

- Fluoroprotein foams (**FP** - widely used for hydrocarbon storage tank protection and marine applications);
- Aqueous Film Forming foams (**AFFF** - used for aviation, marine and shallow spill fires);
- Film Forming Fluoroprotein foams (**FFFP** - used for aviation and shallow spill fires);
- 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); and
- Alcohol Resistant Film Forming Fluoroprotein foams (**AR-FFFP** - multi-purpose foam for hydrocarbon and polar solvent hazards used by Fire Brigades, marine bodies and petrochemical industry).

Fluorine-free foam types:

- Synthetic detergent foams (**SD** - often used for Class A/forestry/high expansion applications);
- Protein foams (**P** - mainly used for training, but some marine use); and
- Fluorine-free foams (**FFF** - used for Class A and Class B applications, as well as in training).

It is understood that some AFFFs and AR-AFFFs have been produced using PFOS related substances and, as such, are of particular relevance to this study. However, this is only a general guide. Information received indicates that, in theory, any fluorine based foam may contain PFOS related substances as surfactants (BFPSA, 2003b). It should, however, be noted that the UK manufacturers of foams use only PFOS-free fluorochemicals in their foams, including the protein based products.

Aqueous Film Forming Foams

AFFFs, which are a combination of fluorocarbon surfactants, synthetic foaming agents, solvents, and other ions were developed during the 1960s for use on flammable liquid fires.

In fires involving flammable liquids, the fluorinated surfactants contained in the foam position themselves on the foam solution-air interface, leading to the formation of a very thin film which spreads over the hydrocarbon liquid fuel, limiting the evaporation of the fuel, excluding oxygen and thereby extinguishing the fire (Dlugogorski, *et al,* 2002).

Alcohol-resistant Aqueous Film Forming Foams

Alcohol resistant (AR) foams were developed to deal with fires involving polar solvents, water miscible liquids such as alcohol and petrol containing up to 20% alcohol. Conventional foams tend to disintegrate on contact with polar solvents or alcohol; thus, AR foams serve as useful fire fighting tools for hydrocarbon and polar solvent hazards. ARs are used mainly by the Fire Brigades and the petrochemical industry.

AR-AFFFs were developed during the 1980s. They are composed of a synthetic detergent based film forming foam, which contains water-soluble polymers. The soluble polysaccharide polymers form a polymeric membrane at the fuel/solvent interface, which prevents the water miscible liquids from mixing with the foam blanket and prevents the foam blanket breaking down by water being drawn out of foam into the fuel or solvent.

The foams produced from AFFFs and AR-AFFFs are relatively fluid and provide fast fire extinction, which results in benefits such as: minimised risks of escalation into other areas, minimised losses to the fire of assets; efficient usage of foam and water resources, minimised environmental impacts and life savings (workers, public, fire-fighters).

2.8.3 Current Use of PFOS in Fire Fighting Foams in the UK and EU

Consultation with fire fighting foam manufacturers, foam users and relevant associations indicates that any PFOS containing foams currently used in the UK are the AFFF and AR-AFFF manufactured by 3M before its withdrawal from the market. These were manufactured in the 3M plant in Belgium or formulated in Norway and sold under the 3M brand name and, as such, should be easily identifiable. A number of Fire Brigades and sections of the chemical industry have been identified in the UK as having stocks of such PFOS based foams.

Other possible sources of PFOS based foams in the UK have been suggested, although these are believed to be for smaller users and would have been bought as low priced competitive products without extensive independent approval. It is thus unlikely that bodies such as the UK Fire Service or the Armed Forces would have invested in these products. The Ministry of Defence has confirmed that PFOS based foams are no longer used in any of their applications. There were, however, previous uses of PFOS based foams in the Navy.

In the EEA (European Economic Area), there is a reported total of ten companies manufacturing fire fighting foams based in (BFPSA, 2003b):

- Germany (four);
- France (two);
- Italy (two);
- Spain (one); and
- Norway (one).

Note that one of the above companies is a sister company of one of the three major companies active in the UK, although it has been indicated that the two plants specialise in the production of different types of foams. In line with the main UK foam manufacturers, most other European manufacturers produce foams which are based on selected blends of PFOS-free fluorocarbon surfactants, hydrocarbon surfactants and other ingredients (BFPSA, 2003a).

The BFPSA has suggested that there were, until the recent past, four European companies (in Germany, Italy and Norway) that are believed to have bought at least some of their fluorosurfactants from 3M, so some of their products may also contain PFOS. It is understood that these companies also have alternative PFOS-free formulations (BFPSA, 2003a).

One of the four companies has been reported as having previously provided PFOS based foams to the UK market. Consultation with this company indicates that this particular plant acted before 1999 as a mixing plant for 3M, with production of PFOS based foams ceasing in December 2002 based on the 3M decision. Table 2.9 below shows the amount of PFOS based fluorosurfactants used in fire fighting foams by this company.

Table 2.9: Amount of PFOS based Fluorosurfactant used in Fire Fighting Foams

Year	Tonnes
2000	35
2001	40
2002	40

Source: Industry, pers. comm.

There is therefore reason to believe that fire fighting foams containing PFOS may have been purchased or supplied in the UK until December 2002, when production of PFOS based foams by this company are reported to have ceased. The company also retains significant amounts of PFOS based foams which could be supplied into the UK market on special demand. According to this company, these foams are only shipped on special order to combat certain types of fires that have proven difficult to extinguish with the available foams. It should be noted that this company currently produces only PFOS-free foams (Industry, pers. comm.).

The remaining two companies are represented by two UK based suppliers of foams. These foams may contain PFOS related substances, although it has not been possible to corroborate this with the companies themselves, as communication with them has failed to yield any information. It has been suggested that the companies are now using PFOS-free foams.

Companies from the US, Japan and Israel have also been indicated (in the literature and during consultation) as possible sources of PFOS based fire fighting foams.

Estimated quantities of fire fighting foams and their use in the UK are provided in Table 2.10 below. The estimates are based on questionnaire responses from Fire Authorities (FA) concerning both their own stocks (and rate of use) as well as those held at major accident industrial/civil installations as part of the industry/FA mutual agreement packages for the provision of fire cover in the event of major incidents. The response rate for all Fire Authorities in England and the UK to the questionnaires was approximately 50% and 42% respectively[13].

Table 2.10: Estimates of Quantities and Use of Fire Fighting Foams in the UK		
	All Foam Concentrates (Litres)	**PFOS based Foam Concentrates (Litres)**
Estimated current quantities in Fire Authority (FA) Inventories	986,347	76,187
Estimated current emergency stores at industrial complexes as part of Mutual Aid agreements	2,959,041	2,367,223
Quantity used by FAs (2002)	147,778	377
Total	**3,945,388**	**2,443,419**

The assumptions underlying the above figures are as follows:

- approximately 76 tonnes of PFOS based foams are currently held in Fire Authority (FA) inventories; these are held in 11 of the 59 FAs (thus making up an average of 38% of the total stock held by these 11 FAs);

- use rates of fire fighting foams by FAs are estimated as being an average of 15% per year (based on the questionnaire responses) and, as such, all foams are generally used before they reach the end of serviceable life (taken as a 15 year average);

- estimates of non FA mutual aid foam stock are based on an average of three times the FA quantities being held at major incident installations. This is based on information provided by FAs and substantiated on the basis of the calculations used by FAs to work out how much fire fighting foam is required to be held in the case of a major incident. The number of hazardous installations (HI) in the UK and the number of fire incidents in previous years have also been factored into the calculations based on the HSE HI Directorate data on dangerous occurrences and major incidents involving fire;

- as the stocks are maintained *in situ* in the event of an incident and given the low frequency of major incidents, it is assumed that, in the main, stocks are unlikely to be used and more likely to reach the end of their (15 year average) serviceable life when they are then replaced. This is based on information received from relevant industry contacts and substantiated by the number of fire incidents in UK HI sites in previous years[14]; and

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[13] It should be noted that an alternative set of estimates of the existing stocks of PFOS based foams was provided by the BFPSA based on an alternative approach. These estimates were not adopted as they were not corroborated by the data provided by the Fire Authorities or the Ministry of Defence.

[14] Fires resulting in a stoppage of work for more than 24 hours in a plant/premises accounted for 185 incidents in the 1,100 UK COMAH sites from 1991 - 2002, thus the calculated frequency of a fire in a COMAH site in one year is 0.015. Fire Authorities have indicated that the use of fire fighting foams in any significant quantity (e.g.>1000 litres) would result in such a stoppage (>24 hours) and must be reported to the HSE as a dangerous occurrence.

- it is assumed that 80% of the fire fighting foam stock on HI sites is made up of PFOS based foams, while 20% are non-PFOS based foams.

It should be noted that no detailed estimates have been derived for PFOS based foams used by the Ministry of Defence (MoD) Navy. The MoD, however, indicates that there are no stocks of PFOS based foams and any PFOS based foams held by the Navy at present are out at sea. These foams will be disposed of appropriately at the end of their useful life.

2.8.4 Lifecycle and Uses of PFOS Based Fire Fighting Foams

While the great bulk of PFOS based fire fighting foams are sold to fire fighters, they are also known to be used by other categories such as: chemical and petroleum plants, pharmaceuticals, vessels, off-shore drilling platforms and environmental remediation companies. This has implications for its lifecycle and dispersal in the environment.

Since the lifespan of most fire-fighting foams is between 10-20 years shelf-life, BFPSA suggests that PFOS containing foam products could be around until at least 2015 (as a conservative estimate) in the absence of any risk reduction measures. This is based on a belief that many users of PFOS based foams still have significant stocks remaining (BFPSA, 2003a).

With regard to the potential use of PFOS based foams in households, other buildings and vehicles, it is unlikely that considerable amounts may be found in such environments as a significant number of foam fire extinguishers are supplied by three UK manufacturers who do not use PFOS related substances. The same may not be true in the EU where foam extinguishers are potentially filled with 3M based products and are used in laboratories, schools, universities, hospitals, garages, mechanics workshops and elsewhere (BFPSA, 2003b).

Table 2.11 presents an overview of the possible sources of releases of fire fighting foam, as described by BFSPA.

Table 2.11: Possible Sources of Releases of Fire Fighting Foam

Cause	**Possible forms of foam released**	
	Solution	**Concentrate**
Fire	V	
Inadvertent system release	V	
Commissioning	V	
Testing	V	V
Spillage	V	V
Disposal	V	V

Source: BFPSA (2003a)

Apart from the use of fire fighting foams in emergency situations for fighting flammable liquid fires, it is understood that the use of foams in training exercises results in large-scale and repeated discharges of fire fighting foams in designated areas. It has been indicated that the most common means of disposal for old foam is to use it for training and then allow it to pass through waste water treatment facilities. Some users will dispose of old foams to landfill or incineration (BFPSA, 2003b). This suggests the potential for PFOS based fire fighting foams used in training exercises to have a pronounced effect on the environment.

2.8.5 UK Market for Fire Fighting Foams

The UK market for fluorinated active ingredients in fire-fighting foams is estimated to be around 65 tonnes per year (approximately 16.25% of the total fluorochemicals market of 400 tonnes per year). Table 2.12 shows the tonnages for fire fighting foams containing PFOS related substances in the UK (BPFSA, 2003). The estimates show a gradual reduction in the presence of PFOS since the announcement of the voluntary cessation of production by 3M. These data should be considered in the light of the long lifetime of fire fighting foams which means that PFOS based products bought in 2002 may be available for use (with any associated emissions this infers) in the years to come.

Table 2.12: Tonnes of PFOS containing material within fire fighting foams in the UK market (estimates)

Year	Tonnes
1998	16.25
1999	16.25
2000	16.25
2001	13
2002	9.75
Total (1998-2002)	***71.5***

Source: BPFSA (2003a)

2.9 Industrial and Household Cleaning Products (Surfactants)

2.9.1 Use of Flurorochemicals in Cleaning Products

Table 2.13 presents an overview of the different products that may contain perfluorinated surfactants.

With regard to the use of PFOS related substances in these products, 3M indicates that PFOSF derived chemistries used as performance chemicals are relatively low molecular weight (<500 daltons) surface active materials and monomers. Their ability to act as surfactants in these applications can be explained if their properties are considered in comparison with other surfactants.

<table>
<tr><th colspan="2">Table 2.13: Personal & Household Care and Industrial Cleaning Applications of Fluorosurfactants</th></tr>
<tr><td>Household products
• dishwashing liquids (rinse-aid);
• liquid polishing compositions;
• floor polish (levelling agent);
• alkaline oven cleaners (additive);
• disinfectants (synergistic improver);
• detergent formulations (synergistic wetting agent);
• protective coatings on metals (tarnish resistance, grease resistance - additive); and
• gloss and antistatic improver for surface coatings.</td><td>Industrial use products
• cleaning compositions (wetting agent);
• alkaline cleaners (additive);
• glass cleaners (additive);
• automobile waxes (wetting agent);
• waxes (adjuvant to improve repellence);
• lubricant/corrosion inhibitor for antifreeze
• car washes (rinse-aid);
• dry cleaning compositions and solvent cleaners (for water displacement and foaming);
• agent for improving soil suspension and decreasing re-deposition in dry cleaning;
• pipe cleaning products (foaming agent);
• anti-mist film foamer for glass and plastics; and
• in foams (for dust suppression).</td></tr>
<tr><td colspan="2">Cosmetic and personal care products
• hair shampoo and shaving foam ingredient;
• denture cleaners ingredient;
• cosmetic powders ingredient (oil and water repellent); and
• lotions or creams for skin or hair</td></tr>
<tr><td colspan="2"><i>Source: Literature Review & Consultation</i>
<i>Note that the above products do not include preparations described under different categories in this report (e.g. carpet spot cleaners or upholstery care products)</i></td></tr>
</table>

3M PFOS based products were sold in the past to a variety of formulators to improve the wetting of water based products marketed as alkaline cleaners, floor polishes (to improve wetting and levelling), denture cleansers and shampoos. Several of these products (alkaline cleaners, floor polishes, shampoos) were marketed to consumers; some products were also sold to janitorial and commercial cleaning services. A number of the alkaline cleaners were spray-applied (3M, 1999).

It should be noted that the survey by the Danish EPA (2002), described earlier in Section 2.2.2, showed that PFOS related substances were found in waxes and polishes available to consumers in 2002.

2.9.2 Types of PFOS Related Substances Used in Cleaning and Personal/Household Care Products

As described above, the active ingredients of these products tend to be low molecular weight fluorochemicals. Literature review suggests that common salts of PFOS have been used in the past for these purposes. There have been suggestions that sales of fluorochemical surfactants in the UK are small compared to those of the hydrocarbon types.

2.9.3 Consultation Findings

Consultation has involved both the European Association representing the manufacturers of cleaning products (AISE) and a wide range of UK producers of cleaning products.

With regard to the UK cleaning products industry, the responses received to-date (from consultation with the major UK and EU associations, as well as individual companies), do not indicate the use of PFOS related substances in the aforementioned products.

Information has been received from the Swedish Association of Industrial and Institutional Hygiene Products (IIH). IIH has issued a position paper on the use of PFOS related substances by its member companies. The paper indicated that:

- PFOS related substances have been used in very low concentrations (0.01%) in film making water based floor polish products; the substances have outstanding wetting qualities;

- PFOS is accepted in low quantities in Swan-labelled[15] floor polish;

- companies in this industry sector were working with the aim of finding acceptable alternatives to PFOS in the above mentioned products with possible alternatives being other surfactants. Problems identified include that suitable alternatives would have to be used at significantly higher concentrations and the results may be of poorer quality compared to PFOS based products (Industry, pers. comm.).

Based on information provided in product registers, the Swedish National Chemicals Inspectorate (KemI) has indicated that PFOS related substances are still being used in Sweden. Approximately 66 kg of PFOS related substances were used as surfactants in cleaning products for both industrial and household use in Sweden, in 2002 (KemI, 2004). KemI is working with trade associations and other stakeholders to collect information on the uses of PFOS related substances, their human health and environmental effects and the presence of PFOS in the Swedish environment.

2.10 Coatings and Coating Additives

2.10.1 Use of *PFAS* Related Substances in Coatings

The full range of uses for *PFAS* in the paint, pigment and finishing industries could 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;

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[15] The Nordic Swan is an eco-labelling scheme. The criteria document for eco-labelling of film forming floor products indicates that fluorinated surfactants are usually added at a quantity corresponding to 0.01% of the product (KemI, 2003). Information from industry suggests that the reason for their acceptance in the eco-labelling scheme is that they are difficult to replace.

- improvers for automotive finishes, based on water based coatings in which the pigments are rendered non-reactive;
- gloss and antistatic improvers;
- pigment grinding aids to promote wetting, dispersion, colour development; and
- foam generator substances for the application of dyes, inks.

One major UK coatings manufacturer indicated that PFOS related substances were previously used as additives in coating preparations used in automotive refinishing, aerospace and general industrial applications. These additives were useful in achieving not only product differentiation, but also in meeting customer specifications and legislative requirements (Industry, pers. comm.). Another coatings manufacturer also suggested that that PFOS related substances were coated onto fluorinated polyesters used in the automotive industry, particularly in the 1980s and early 1990s. These coatings were said to result in weather and scratch resistant textiles (Industry, pers. comm.).

3M indicates that prior to the voluntary phase out of PFOS production, the company would sell fluorochemical polymer coatings and coating additives which were used undiluted or diluted with water or butyl acetate to impart soil or water repellence to surfaces (including printed circuit boards and photographic film). These polymers contained fluorocarbon residuals at a concentration of 4% or less. Other applications were aqueous coatings used to protect tile, marble and concrete. It is unclear which of these products were actually based on PFOS related substances (3M, 1999).

2.10.2 Consultation Overview

Communication with the British Coatings Federation (BCF) suggests that the use of PFOS related substances as additives in coatings manufacture is very limited, if indeed it still exists in the UK. BCF has advised that fairly recently a survey among members showed that PFOS related substances found very limited use in the UK. Information collected to date by BCF for the purposes of this Risk Reduction Strategy appears to support this view. Two companies indicated that in the past they have used PFOS related substances; they have since discontinued use.

One of them has used a substance (substance with reference number 15 in the table of Annex 2) as a wetting agent for a floor coating preparation. The fluorosurfactant has now been replaced "satisfactorily" by a polyether-modified polydimethyl siloxane. The second company indicated that the replacement of the PFOS related substance has provided a number of performance benefits and, therefore, the company is not at present prepared to disclose any information that could be of value to a competitor (BCF, 2003).

The assertion that PFOS related substances find limited use in the coatings sector is confirmed by completed questionnaires received by a number of coatings manufacturers (some of them having branches across the EU). One major UK coatings manufacturer with production plants elsewhere in the EU indicates that, in the year 2002, they purchased a total of 0.5 tonnes of PFOS containing additives with the source being 3M. The concentration of these additives in coatings was 0.1-1%, which suggests that a total of 50-500 tonnes of paint across the EU contained PFOS related substances. The producer cannot provide data on the percentage of these tonnages which are relevant to the UK market.

In 2003, the same company has purchased no PFOS containing additives, as they have withdrawn the products requiring PFOS from their range (Industry pers. comm.). Some of the reasons proffered by the company for this withdrawal include the following:

- the additives were used in an old technology which has now been replaced by new products;
- the major market for these products is now outside Europe (Asia and US); and
- the high reformulation costs which would arise in the event of substitution would far outweigh raw material costs.

Recent trends in the UK or EU more generally are towards the use of more specialist additives to achieve performance specifications, especially in waterborne coatings.

2.10.3 Shelf-life of PFOS Based Coatings

The shelf-life of coatings containing PFOS related substances has been defined by the manufacturer who purchased 0.5 tonnes of PFOS containing additives in 2002 as being between six months and two years. The manufacturer advised that the shelf-life is restricted by the general physical properties of the paint and their changes (viscosity drift, settlement, etc.) rather than any degradation of the chemical constituents (Industry, pers. comm.).

2.10.4 Use of *PFAS* in Inks

The literature review suggests that fluorochemicals are also used in inks. A suitable fluorochemical surfactant lowers the surface tension of the ink to a very low level and the interfacial tension between the ink and the solid is also significantly reduced, causing it to wet and spread a film on this hard-to-wet surface.

Many printing ink formulations contain fluorosurfactants to enhance ink flow and levelling to improve cylinder life, and to eliminate snowflaking or non-uniform printing. However, there is at present no specific information on whether PFOS related substances have actually been found in the previous or current applications of inks in the UK.

2.11 Photographic Industry

2.11.1 PFOS Related Applications in the Photographic Industry

As the European Photographic Chemicals Industry Sector Group of CEFIC advises, PFOS based chemicals were not used for imaging purposes prior to 3M's development of this class of chemicals. However, with the development of materials that were more sensitive to light (i.e. faster film speeds, more sensitive diagnostic X-ray products), the control of static became more difficult and required the use of perfluorinated coating aids.

PFOS based 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.

EPCI suggests that PFOS based chemicals are important because they are able to:

- **control dynamic and static surface tension and static charge**: the ability to control surface tension in imaging materials (films, papers, and printing plates) is a critical aspect of the use of PFOS based substances as coating aids. In order to function, imaging materials must be coated with multiple thin (up to eighteen) layers of light sensitive materials at high speed to prevent drying as they are laid down. The overall thickness of an imaging film with eighteen imaging layers on a 3 mil film base is of the order of 0.11 mm. The fact that PFOS based coatings can control static charge at low concentrations is particularly important for imaging materials that have a high sensitivity to light (i.e., high speed), as these products are unusually sensitive to light produced by static discharge during the transport of imaging materials;

- **minimise manufacturing waste**: PFOS materials play a key role in minimising manufacturing waste by contributing to the technology for creating coatings of high complexity in a highly consistent manner (see also point below on the elimination of unwanted photographic effects);

- **ensure operational and employee safety**: the film (or paper) is moving rapidly across metal surfaces and the developed static charge may be discharged either on a metal surface or on a worker; PFOS related substances help in preventing such occurrences; and

- **enhance transport characteristics**: they improve camera, projector, and printer transport by eliminating unwanted photographic effects; excessive friction during the transport of imaging materials and contamination of imaging materials by dirt or clogging of magnetic strip readers with debris can lead to significant waste of imaging materials during manufacturing and use.

Imaging materials that are more sensitive to light (i.e. high-speed films) have a greater requirement for the properties provided by PFOS based materials and are consequently more difficult to reformulate. EPCI (2003) suggests that PFOS based chemical agents are also important because:

- **they control splicing tape adhesion properties**: control of adhesion of various tapes to imaging materials is important because tape is the primary way in which imaging materials are attached to spools and to each other during processing. The strength of the bond between the tape and the imaging materials must be controlled so that imaging devices (e.g. cameras, photoprocessors) and imaging materials are not damaged during transport (i.e. the adhesive bond between the tape and the imaging material must be broken by a force that will not damage devices or materials being transported);

- **they lack photoactivity and, thus, do not interfere with the imaging process**: for example, fogging or speed effects in the coatings are avoided;
- **they promote uniformity of photoprocessing results**: any irregularity in coating thickness makes imaging materials useless and increases manufacturing waste significantly; and
- **they are compatible with photo-retouching materials**: the PFOS based surfactant reduces the surface tension and allows a uniform blending of the retouching solution with the existing emulsion so that it is not possible to distinguish the areas of a photograph that have been retouched by the expert.

According to the EPCI, PFOS based coating aids have a combination of surface-active properties that are unique and not found with any other type of coating aid. Only small quantities of PFOS materials are required to function as coating aids in imaging media. This property is important because the required addition of non-photoactive materials to coatings in significant quantities diminishes the ability of the imaging material to form the sharpest images. In short, thinner coatings make clearer, sharper images (EPCI, 2003).

2.11.2 PFOS Related Substances Used in the Photographic Industry

Six different PFOS based chemicals have been reported as being used by the photographic industry in Europe. These are shown in Table 2.14.

Materials 1-6 are significant dilutions of the fluorochemical solids with organic solvents or water. The PFOS equivalents in these products are actually less than the percentages listed above because there are shorter chain perfluorochemicals in each of the products that have not been accounted for by EPCI in the calculations used to identify PFOS content. EPCI has suggested that up to three different companies have provided *PFAS* to the photographic industry (including 3M before the voluntary phase out of PFOS production).

Work is currently being undertaken to develop methods of production that do not rely on PFOS related substances (EPCI, 2003).

Table 2.14: PFOS Related Substances Used by the Photographic Industry in Europe

No.	Annex 2 Ref No.	CAS Number	Type of preparation	Residual Fluorochemicals	PFOS Moiety %	Applications
1	7	1652-63-7	Emulsion (mixture with other fluorochemicals)	V	67%	Used in the manufacture of photographic film, paper, and plates
2	33	56773-42-3	Emulsion	-	77%	Used in the manufacture of photographic film
3	U	(confidential)	Polymeric - mixture of fluorochemicals	V	7%	Used in the manufacture of photographic film, paper, and plates
4	U	(confidential)	Polymeric - mixture of fluorochemicals	V	5%	Used in the manufacture of photographic film, paper, and plates
5	N/A	Unknown	Polymeric - proprietary information (to be submitted)			
6	N/A	Unknown	Polymeric - proprietary information (to be submitted)			

* It should be noted that Items 1 and 2 are supplied in solution but are used in preparations as emulsions.
Source: EPCI (2003)

2.11.3 Quantities of PFOS Related substances Used in the Photographic Industry

Historic Perspectives and Current Trends in Europe

The current trend in imaging has been towards the development of digital products that are processed dry. The trend towards dry processing has increased demands for static control and tended to increase the use of PFOS related substances. Thus, until the mid-1990s, the historic use of PFOS materials was one-half to one-third of the level used in 2000 when 3M announced its voluntary PFOS phase-out.

Since 2000, the use of PFOS related chemicals for imaging purposes has declined significantly on a world-wide basis and it is estimated that the total reduction in tonnage is as high as 83% (EPCI, 2003). Some uses have been discontinued totally by the industry, including use as:

- a defoamer in the production of processing chemicals for films, papers, and printing plates;
- a (photo-acid generator) PAG in photolithographic processing solutions in the manufacture of printing plates (see also Section 2.12);
- a surfactant in photolithographic processing solutions in the manufacture of printing plates; and
- a surfactant in photographic processing solutions in the processing of films and papers.

The imaging industry has decreased its use of PFOS related substances across other uses as well. As a result, the demand for PFOS related chemicals is now expected to be 1,500 kg/y in the EU. Of this amount, less than 50 kg/y are used for paper products and less than 150 kg/y are used for printing plates, with the remainder being used for various types of film products.

When the use volumes are viewed in terms of PFOS equivalents, actual PFOS use is significantly lower (5-77% of the stated use level depending on which PFOS chemical is used for a particular imaging product type (i.e., film, paper, printing plate), see Table 2.14 above). In terms of PFOS equivalents, the total amount of PFOS used for imaging products is about one-third less or 1,000 kg/y based on the highest PFOS containing chemical.

For films, paper and plates, the concentration of PFOS related substances in coatings is in the range of 0.1-0.8 µg/cm^2. The actual concentration (in ppb or ppt) in the product will depend on the mass of the base material attached to the coating.

Due to the decline (8% in 2003 and 6% in 2004) in film sales reported by imaging companies (as a result of digital substitution), PFOS use is not expected to grow as there are likely to be further reductions in film production over the next few years (EPCI, 2003).

Use of PFOS Related Chemicals in the United Kingdom

Use of PFOS related chemicals for imaging purposes in the UK is estimated to be 270 kg/y. This includes PFOS related substances that are incorporated into articles domestically, as well as PFOS related material present in imported articles (such as film, paper or plates). Note that imaging devices themselves (cameras, printers, scanners, etc.) do not contain any PFOS related substances (EPCI, 2003). Table 2.15 below shows the estimated source and fate of PFOS related substances used in the EU and UK.

Table 2.15: Source and Fate of PFOS Related Substances Used in the EU and UK Photographic Sector (for Uses in Film, Paper and Printing Plate)

	EU (kg/yr)	**UK (kg/yr)**	**Percentage of Total Volume**
PFOS Volume	1,000	270	
PFOS Used in Production	850	230	85% (r/m)
PFOS Imported	150	40	15% (f/a)
PFOS Exported	250	68	25% (f/a)
PFOS in Products	600	162	60% (f/a)

**r/m =As raw material; f/a = As finished article*
Source: EPCI (2004)

2.11.4 Shelf-life of Finished Products

The shelf-life of products is dependent on several factors including temperature and humidity. Under proper conditions, products may last from several years to several decades.

2.12 Photolithography and Semiconductors

2.12.1 Description of Semiconductor Manufacturing Process

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

- implant;
- deposition;
- etch; and
- photolithography.

Photolithography is the most important step towards the successful implementation of each of the other steps and, indeed, the overall process. It shapes and isolates the junctions and transistors; it defines the metallic interconnects; it delineates the electrical paths that form the transistors; and joins them together. Photolithography reportedly represents 150 of the total of 500 steps mentioned above (ESIA, 2003).

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

Miniaturisation refers to the ability to reduce objects, as well as the gap between objects. The ability to effect this separation is proportional to the wavelength of light that is used to pattern the separation. This relationship between separation, i.e. *optical resolution*, and wavelength is well established. To improve resolution, the semiconductor industry has shortened the wavelength that it uses in photolithography four times since 1980, from 436 nm through 365 nm and 248 nm to 193 nm. The latter wavelength is just entering use. A fifth wavelength, 157 nm, is expected to be introduced in 2004-5. This shortening of wavelength, however, comes at a price; the composition of the photoresist must be adjusted to appropriately respond to whichever wavelength is used for the exposure. The role of the photoresist is to record the exposure pattern, known as the aerial image, produced by the photolithography equipment (ESIA, 2003).

The introduction of imaging at 248 nm changed the way in which the acidity of an exposed, positive photoresist[16] is altered. The shorter wavelength uses a mechanism called *chemical amplification* (to make the process more efficient).

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

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[16] Positive photoresists exhibit an increase in their acidity in the exposed area and become more soluble in a developer that is a dilute aqueous base (ESIA, 2003).

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

2.12.2 The Role of PFOS Related Substances in Photolithography

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 semiconductors industry believes that no PAG other than PFOS based ones have been shown to cause effective, efficient transformation in 193 and 157 nm based photoresists (ESIA, 2003).

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.

2.12.3 Other Applications of PFOS Related Substances in the Semiconductor Industry

Antireflective Coatings

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

PFOS Related Substances Used as Surfactants

PFOS related substances may also be used as surfactants in developers, etch mixtures and commercial photoresists (ESIA, 2003). For the latter, suppliers to the semiconductors industry use a surfactant at 100 - 300 ppm as an integral part of several lines of current commercial photoresists. A fluorocarbon surfactant is much preferred to available alternatives because the known alternatives all contain silicon. Etching and ashing photoresists convert the silicon to silicon dioxide, which is a difficult residue to remove and interferes with product quality. PFOS surfactants are used in what are known as ancillary products such as edge bead removers (EBRs), resist edge bead removers (RERs) and strippers.

2.12.4 Levels of Use of PFOS Related Substances and Existing Trends

Table 2.16 presents the indicative levels of concentration of PFOS related substances in the semiconductor related applications mentioned above, as well as the relevant quantities consumed in the EU. ESIA has emphasised that PFOS related substances do not remain on the final product (ESIA, 2003).

Table 2.16: Typical Concentrations and EU Consumption of PFOS Related Substances in Preparations Used in Semiconductor Applications

Application	PFOS Concentration	EU Consumption (kg/y)
Photoresists	0.02 - 0.1%	46
EBR	Not available	86
TARCs	ca. 0.1%	136
BARCs		8
Developers (surfactant)	ca. 0.01%	195

Source: ESIA (2003); SEMI (2003)

With regard to etchants (which are not used in photolithography), information from suppliers of these chemicals suggest that a total of 31kg of PFOS in etchant mixtures was supplied to the European Market in 2002 (ESIA, 2003).

With regard to photoresists and ARCs, ESIA advises that purchasing trends are dependent upon technology requirements and demands of the marketplace. Demands are unclear with respect to PFOS materials, however, with the advent of advanced lithography, the demand for PFOS based chemicals may decrease. It should be noted that the volume of chemicals used generally relates to the semiconductor device production levels. There has been little to no growth of the industry over the past three years, although it is expected that the industry (or production cycle) will return to growth in the future.

Developer consumption is proportional to the production volume. ESIA suggests that the trend amongst manufacturers and suppliers in Europe is to voluntarily phase out PFOS based developers (ESIA, 2003).

2.12.5 Shelf-life of PFOS Based Chemicals Used in the Semiconductors Industry

The maximum shelf-life of PFOS based chemicals used for the aforementioned applications is typically six months for products used on photoresists and ARCs and only one month for developer surfactants. It should be noted that the shelf life of the photoresist mixture is limited by the other chemical substances inside it and not by the PFOS chemical. ESIA claims that these applications require immediate use by the semiconductor manufacturers and there is limited scope for stocking up or storing such products for longer periods of time.

Chemical degradation is not known to be a factor in defining the shelf-life of commercial products. Suppliers to the semiconductor industry (represented by SEMI) are able, in essence, to retain their stocks for an indefinite period of time. It has been suggested that formulators in this sector (as well as in other sectors) are likely to have acquired significant quantities of PFOS related substances upon the announcement by 3M of its voluntary cessation of production.

2.12.6 Disclosure of Identities of PFOS Related Substances Used in the Semiconductors Industry

The suppliers of chemicals used by the manufacturers of semiconductors are represented by SEMI. SEMI has been reluctant to disclose details of specific chemicals used in their preparations, indicating that identifying substances would be difficult and ultimately does not affect the potential release of PFOS related substances to the environment (the results of the calculation of estimated releases of PFOS related substances during photolithographic processes are not expected to vary significantly if different chemicals are assumed to be used in these processes).

The suppliers actually use only a limited number of chemicals from the list provided in Annex 2. However, disclosure of identities of chemicals is complicated for two main reasons (SEMI, 2003):

- the CAS Numbers may be regarded as confidential business information by some suppliers (noting that occasionally the PFOS related substances are used in such low concentrations that their reference in Safety Data Sheets is not required); and
- individual companies often need some flexibility in the selection of process materials to allow them to be innovative and successful.

Evidently, SEMI's positions appears to be that if the identities of substances currently used in practice by its members are disclosed, any derogation granted for the use of these substances[17] would effectively constitute a ban on other substances which, while they are not marketed, are actually used in laboratories for research and development.

2.13 Pesticides and Insecticides

2.13.1 Information Through Consultation

Information received to date from consultation with the major UK and EU associations, as well as individual companies, shows no use of PFOS related substances in pesticide and insecticide applications in the UK; while in the EU, only one Italian company has indicated that it used these PFOS related substances for the manufacture of baits and insecticides against beetles and ants.

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[17] SEMI believes that PFOS related substances used by their members should be derogated given the criticality of the relevant applications.

The PFOS substance used was the lithium salt of PFOSA (substance 13 in Annex 2). PFOS usage for this application in Italy (and by only one company) is indicated to be around 0.5 tonnes/year, in concentrations less than 1%. It was not possible to receive further information on this application, as this was considered highly confidential and sensitive for competition reasons (Federchimica, 2003).

This use confirms information received from 3M, which indicated 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).

We have been in contact with the UK Pesticides Safety Directorate (PSD) which is responsible for authorisations for active ingredients found in pesticide formulations. Early information received suggested that a few products might contain PFOS related substances. Information received subsequently and confirmed through direct consultation with the relevant companies indicates that these companies are not involved in the use of PFOS related substances in pesticide formulations. It should be noted that the relevant EU association (ECPI) has also indicated that its members are not involved in the use of PFOS related substances in the manufacture of pesticides.

2.14 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.

Consultation suggests that these types of application may not be relevant for the UK. The NHS Purchasing and Supply Agency has been in contact with the main suppliers of such products. The four major suppliers of these products to the NHS have responded that they do not use PFOS related substances in their products (PASA, 2003).

2.15 Hydraulic Fluids for the Aviation Industry

2.15.1 Background to Use of Hydraulic fluids in the Aviation Industry

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

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

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

2.15.2 Importance of PFOS Related Substances in Hydraulic Fluids Used in Aircraft

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

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

In the case of pumps, erosion can result in a decrease in the efficiency of operation and damage, which necessitate a premature overhaul of mechanical parts (with both cost and time implications). This is in addition to increased risks to the environment resulting from the premature draining of the contaminated fluids from the system, filter clogging and filter replacement[18].

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

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

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

2.15.3 PFOS Related Substances Used in the UK Aviation Industry

The specific PFOS related chemicals used in hydraulic fluids are the potassium perfluoro-ethylcyclohexyl-sulfonates, not the perfluorooctane-sulfonates (PFOS related substances). These perfluoro-ethylcyclohexyl-sulfonates are not on the Draft List of Substances in Annex 2 of this report, but are considered in this report because:

- 3M has included these ethyl-cyclohexyl derivatives in the products they have discontinued;

- other global regulatory agencies have included the ethyl-cyclohexyl derivatives in their risk management activities (e.g. US EPA and Environment Canada); and

- the only known substitute should the ethyl-cyclohexyl derivatives become unavailable is the potassium perfluorooctane sulfonate, which is on the draft list.

With regard to the use of these additives in the UK aviation industry, there are indications that these materials were purchased from 3M and then blended into the lubricant manufacturers' aviation hydraulic fluids. These fluids are then marketed in the UK and the rest of the world. It should be noted that the majority of these fluids are manufactured outside the UK and Europe more generally, finished hydraulic fluids imported for use in the UK (and EU).

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.).

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[18] Contact between the metals in mechanical parts in contact with the functional fluid could result in a change in the physical and chemical properties of the hydraulic fluids, thereby necessitating fluid replacement.

With the withdrawal of 3M from the market, it has been suggested that the manufacturers of hydraulic fluids used in the aviation industry are looking for manufacturers who would be willing to produce the PFOS substances needed when existing stocks are exhausted.

2.15.4 Derogation

The US EPA, in producing its SNUR, granted derogation to the aviation industry for the use of PFOS related substances in the production of anti-erosion additives used in aircraft.

According to information received from one of the major producers of hydraulic fluids, there are no alternatives to PFOS substances currently being used in aircraft. Furthermore, the chemistry of the PFOS based fluids is specified as necessary by the manufacturers of commercial aircraft. Information received from this company indicates that there have been attempts over the last 30 years to find acceptable alternatives to PFOS, and efforts have been accelerated since 3M announced its withdrawal from the market. There are currently no promising leads for a substitute for the PFOS related substances now in use, and there are no assurances that an acceptable alternative will be identified (Industry, pers. comm.).

2.16 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. Previous work on *PFAS* in the UK also suggests that fluorine may be used in only very specialist greases, such as those used in satellites.

Communications with UK and European Associations involved in offshore oil extraction and the production of chemical preparations used in mining have not produced results. The British Lubricants Federation also indicates that to the best of their knowledge, there has been no use of PFOS related substances in these sectors/applications.

2.17 Flame Retardants

There have been suggestions that PFOS related substances were used to provide flame retardance 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. Information from industry sources also suggests that the use of PFOS related substances in flame retardant formulations is a (false) technique for achieving the 'soak' requirements for textiles which are flame retarded.[19]

It has been suggested that users of the above (false) technique may be using products of the telomerisation process to achieve their objective. It should also be noted that the users of this process are a significant minority amongst flame retarders.

The potential use of PFOS related substances as flame retardants (in aeroplanes) has also been suggested by the Danish EPA (2001-2). Consultation suggests that this may be related to the use of PFOS related substances in hydraulic fluids, which provide fire resistance as well as anti-erosion properties to aircraft. It should be noted that the phosphate ester moiety (not the PFOS molecule) is responsible for any fire resistance properties of hydraulic fluids.

Consultation with 3M also suggests that PFOSF-derived substances manufactured by 3M in the past have never been used for flame retardants. As no further evidence is available, we assume that this use is of no relevance to the use of PFOS related substances in the UK and the EU.

2.18 Adhesives

The literature review suggests that adhesives related applications could include:

- specialty tapes; and
- low adhesion backs for industrial tapes.

Consultation with the British Adhesives and Sealants Association suggests that PFOS related substances are not used by the UK adhesives industry (BASA, 2003). No further evidence to confirm the use of PFOS related substances as surfactants in adhesives in the UK has been provided to date.

2.19 Current Demand for PFOS Related Substances in the UK

This Section sets out the current demand for PFOS related substances in the UK, based on the information received through consultation and literature review. It should be noted that this does not constitute the definitive state of the market, rather, it reflects the Consultants' assessment of the market, based on the best available information to date.

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[19] Flame retarded textiles are required to pass certain tests indicating that the flame retardant cannot be washed off during the life of the product. Flame retarded curtains; for instance, would not be expected to lose their flame retardant properties after washing. It is thus suggested that the water repellent attributes of PFOS would enable an ineffective (and significantly cheaper) flame retardant pass the standard tests for flame retardance, as the flame retardant would not be washed off due to the PFOS present.

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

- fire fighting foams;
- carpets;
- leather/apparel;
- textiles/upholstery;
- paper and packaging;
- coatings and coating additives;
- industrial and household cleaning products; and
- pesticides and insecticides.

While there is no evidence of current demand in the UK for these uses, it may be suggested that the availability of PFOS related substances in the future could result in resumed use, due to the varying technical and economic advantages provided by the PFOS related substances, as discussed earlier. A possible exception may be the use of PFOS related substances in coatings and coating additives. It should be noted that the EU uses of PFOS related substances (industrial/household cleaning products and pesticides/insecticides) must currently be considered 'continuing uses'.

The following sectors have also been identified as representing 'continuing uses' of PFOS related substances, although information received from consultation with representatives of these sectors suggests that the quantities of PFOS related substances and PFOS based preparations currently being consumed in the UK is limited:

- photographic sector;
- photolithography and semi-conductors;
- hydraulic fluids; and
- metal plating.

Table 2.17 below outlines the estimated current demand for PFOS related substances in these applications in the EU.

Table 2.17: Estimated Current Demand for PFOS Related Substances in the EU

Industry Sector	**Quantity (kg/year)**
Photographic industry	1,500
Photolithography and semi-conductors	500
Hydraulic fluids	730
Metal plating	2,500

Information received suggests that there has been no historical use and, as such, no current demand or use of PFOS related substances in the UK and the EU more generally, for the following applications:

- medical applications;
- flame retardants;
- mining and oil surfactants; and
- adhesives.

2.20 Current Producers and Suppliers of PFOS Related Substances of Relevance to the UK

Table 2.18 presents an overview of the current state of affairs with regard to producers and suppliers relevant to the UK market for PFOS related substances. It should be noted that the information included in this table is based on the best available information and may not be exhaustive, particularly with regard to the market situation outside the EU.

Table 2.18: Producers and Suppliers Relevant to the UK Market for PFOS Related Substances

Company	Location	Producer or Supplier	Links to Other Companies	CAS Numbers Produced/Supplied (if known)	Quantities Supplied to UK market	Notes
A	UK	Supplier	Supplies products of company D	307-35-7	< 1kg/y	Serves laboratories and research and development divisions
B	UK	Supplier	Acts as an agent for company E	-	N/A	Appears to act as an intermediary rather than a supplier
C	UK	Producer/Supplier	Produces around 25% of its products; supplies products of company F	307-35-7 2795-39-3 4151-50-2	<100 g/y	Three PFOS related substances appear in its catalogue; 2002-2003 sales of less than 100 g are for only one product; also supplies non-PFOS PFCs
D	USA	Producer	Supplies products to company A	307-35-7 4151-50-2	N/A	Also produces other PFCs; the company essentially serves laboratories and research and development divisions
E	Italy	Producer	Supplies products to company B	307-35-7 1691-99-2 2795-39-3 4151-50-2 29457-72-5 30381-98-7	N/A	Active in the following sectors: ∉ pharmaceuticals; ∉ agrochemicals (insecticides); and ∉ performance chemicals (AFFFs, Cr plating). Pharmaceuticals and agrochemicals account for more than 75% of production. The company has emphasised that they are active only in the production of intermediates. Greatest market for products is Europe (this including Italy accounts for more than 50% of total sales)
F	Germany	Producer	Appears to supply products to company C	-	N/A	Small company that produces PFOS related substances; these are used by the semiconductor industry (the relevant data have been incorporated in the submission by SEMI)
G	Germany	Producer	Supplies chemicals to several UK companies	56773-42-3	>100 kg/y	Supplies PFOS related substance(s) to at least one UK formulator of mist suppressants; product information suggests possible downstream uses: ∉ chromium electroplating; ∉ wetting and flow control agent for coating photographic paper and film; ∉ antistatic agent for photographic paper and film; ∉ wetting agent for glass etching and opacification baths; and ∉ wetting agent for acid baths for metal surface treatment, e.g. anodising baths and chromatising baths

Table 2.18: Producers and Suppliers Relevant to the UK Market for PFOS Related Substances

Company	Location	Producer or Supplier	Links to Other Companies	CAS Numbers Produced/Supplied (if known)	Quantities Supplied to UK market	Notes
H	Japan	Producer	Supplies chemicals to several UK companies	-	N/A	Appears to be active in the textiles auxiliaries sector and photographic sector.

Source: Literature review (including publicly available information) and consultation
Notes: PFCs = Perfluorocarbons; N/A = Not Available.

3. OECD HAZARD ASSESSMENT AND UK REVIEW OF ENVIRONMENTAL RISKS

3.1 Overview

This section provides an overview of the tests, results and conclusions for environmental and human health endpoints of the:

- OECD Hazard Assessment Report (2002)[20];
- 3M Risk Assessment Report (2003);
- Draft UK Review of Environmental Risks (2004) of PFOS; and
- other research published after the completion and publication of the Hazard Assessment (where applicable).

The aim is to describe the nature of the environmental and health effects of PFOS that are of importance in relation to the Risk Reduction Strategy. The discussion considers:

- the human health effects of concern;
- the PBT characteristics of PFOS; and
- the exposure pathways of PFOS and environmental monitoring data.

A discussion of the environmental emissions for the various use sectors of PFOS related substances which are of relevance to the Risk Reduction Strategy is included as Annex 4.

3.2 Human Health Effects of Concern

3.2.1 PFOS Levels in Blood Serum and Liver – Occupational Exposure

PFOS has been measured and detected in human blood samples of workers involved in the manufacture of perfluorochemicals and the processing of these into products such as those used in fire protection and surface treatment. The highest documented concentration of PFOS was in the blood of a worker in Alabama, US in 1995 (12.83 ppm)[21]. Table 3.1 provides an overview of documented levels of PFOS in the blood serum of workers exposed to fluorochemicals as presented in the OECD Hazard Assessment.

Initial cross-sectional studies conducted on employees at the 3M plants in Alabama (US) and Antwerp (Belgium) in 1995 and 1997 did not show any consistent association between PFOS levels in workers and various biochemical parameters, although age was

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[20] It should be noted that the OECD Hazard Assessment identifies the need for further information to be gathered on a national and regional scale for a more accurate risk characterisation.

[21] It should be noted that since then, the PFOS levels in blood from workers at the same plant have decreased.

found to be significantly associated with higher PFOS levels. Further studies in 2000 showed that mean values for triglycerides, alkaline phosphatase, total bilirubin and ALT (alanine aminotransferase) were significantly higher for employees with the highest PFOS serum levels (1.69 - 10.06 ppm). Longitudinal analysis of these data, however, indicated that there were no significant associations over time between PFOS levels and cholesterol, triglycerides and other lipid and hepatic parameters (OECD, 2002).

Table 3.1: Mean Levels of PFOS in Blood Serum in Workers

Plant Location	Year	Number of Persons Examined	Mean Levels (ppm)	Range (ppm)
Decatur, Alabama, US	1995	90	2.44	0.25-12.83
	1997	84	1.96	0.10-9.93
	1998	126	1.51	0.09-10.6
	2000	263	1.32	0.06-10.06
	All years above		Geometric mean: 0.91	33.3-36.5*
Antwerp, Belgium	1995	93	1.93	0.10-9.93
	1997	65	1.48	0.1-4.8
	2000	258	0.80	0.04-6.24
Sagamihara, Japan	1999	32	0.135	0.048-0.63

Source: OECD (2002)
** 95% confidence interval of the geometric mean*

In a study carried out by Burris *et al.* (1999), PFOS serum levels were measured in workers from a Japanese processing plant. Samples were taken from workers who were regularly involved in processing perfluorinated chemicals into fire protection products and surface treatment products, and from management employees who were not exposed to the same extent. The mean PFOS levels measured from the production employees was 0.135 ppm, whereas the mean of the management employees was 0.04 ppm.

3.2.2 PFOS Levels in Blood Serum and Liver – General Population Exposure

In the general population, PFOS has been detected in human blood samples, with mean levels of 30-53 ppb having been reported for serum available from blood banks and commercial sources. In individual serum samples obtained from adults and children in various regions of the US, the mean levels of PFOS were approximately 43 ppb.

PFOS levels in the general public have also been measured in Europe; samples of serum were taken from blood banks in Belgium, the Netherlands and Germany. Of these sample groups, the highest PFOS levels were observed in serum from the Netherlands (a mean value of 53 ppb) and the lowest in serum from Belgium (a mean value of 17 ppb) (OECD, 2002).

Table 3.2 provides an overview of documented levels of PFOS in the blood serum of the general population as presented in the OECD Hazard Assessment.

Table 3.2: Mean Levels of PFOS in Blood Serum of the General Population

Plant Location	Year	Number of Persons Examined	Mean Levels (ppb)	Range (ppb)
US children (ages 2-12)	1995	599	Geometric mean: 37.5	6.7-515
St Paul, Minnesota (corporate staff or managers)	1998	31	47	28-96
Intergen, US (commercial source - donors)	1998	500	44	43-44
Sigma, US (commercial source - donors)	1998	200	33	26-45
US blood banks (donors)	1998	340-680	29.7	9-56
Sagamihara, Japan (plant management)	1999	32	40.3	31.9-56.6
Tokyo, Japan (plant management)	1999	30	52.3	33-96.7
Seattle, US (ages 65-96)	1999	238	Geometric mean: 31	34-175
Other commercial sources, US (lots)	1999	35	5	85
European blood banks, Belgium (pooled samples)	1999	6	17	4.9-22.2
European blood banks, Netherlands (pooled samples)	1999	5	53	39-61
European blood banks, Germany (pooled samples)	1999	6	37	32-45.6
US blood banks (American Red Cross, ages 20-69)	2000	645	Geometric mean: 34.9	4.3-1,656

Source: OECD (2002)

A comparison of the data in Tables 3.1 and 3.2 indicates that the levels of PFOS in the blood serum of workers is significantly higher than the levels in the blood serum of the general population. It should also be noted that, although the levels of PFOS had decreased over the period 1995-2000 for the two 3M plants in Alabama and in Belgium, they were still significantly higher than the levels indicated in other studies among the general population.

3.2.3 Persistence and Bioaccumulation

PFOS has been found to be persistent and its bioaccumulative potential indicates cause for concern. According to animal studies, PFOS is well absorbed following ingestion and is distributed mainly in the serum and the liver. No further metabolism is expected.

In a test analysing the liver and serum from rats for PFOS related substances, the results indicate that all rats (including controls) had detectable levels of PFOS in their serum and livers. The PFOS concentrations also increased with dose and were higher in the liver than in the serum, with males having greatly increased PFOS concentrations in serum and liver when compared with females. In another test, a single oral dose of PFOS-^{14}C (4.2 mg/kg) was administered to rats, and approximately 86% of the radioactivity recovered was found in the carcass after 24 to 48 hours.

Elimination of PFOS from the body is slow and occurs via the urine and faeces. Urinary excretion is the primary route of elimination for PFOS in the rat. The elimination half-life of PFOS varies among species. Available data are presented in Table 3.3 below which indicates that PFOS has a significantly higher half-life in humans than in rats or monkeys.

Table 3.3: Elimination Half-lives of PFOS in Mammals

Species	**Half-life**
Adult rat	7.5 days
Cynomolgus monkey	200 days
Workers (3M plant, 9 retired workers)	Mean value: 8.67 years (range: 2.29-21.3 years)

Source: OECD (2002)

3.2.4 Toxicity

There have been various studies to determine the acute toxicity of PFOS.

PFOS has shown moderate acute toxicity by the oral route; a rat LD_{50} of 251 mg/kg and a 1-hr LC_{50} of 5.2 mg/L in rats has been reported. PFOS was also found to be mildly irritating to the eyes, but non-irritating to the skin of rabbits. The available data on acute toxicity are summarised in Table 3.4.

Table 3.4: Acute Toxicity of PFOS to Mammals

Study Type	**Value**
Rat (dust in air administration)	LC_{50} = 5.2 mg/L
Rat (oral)	LD_{50} = 251 mg/kg
Rat (oral)	LD_{50} = 50-1,500 mg/kg (all of the rats administered 1,500 mg/kg died before the 14-day)

Source: OECD (2002)

In 90-day rat studies, observed signs of toxicity include: increases in liver enzymes, hepatic vacuolisation and hepatocellular hypertrophy, gastrointestinal effects, haematological abnormalities, weight loss, convulsions, and death. These effects were reported at doses of 2 mg/kg/day and above.

In a two year carcinogenicity assay using rats, pathological effects on the liver were monitored. From this study the no-observed-adverse-effect level (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 low observed-adverse-effect levels (LOAEL) were 2 ppm for males and 5 ppm for females[22].

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[22] These values are taken from the main text of the OECD assessment. In the summary of the OECD Hazard 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 in male rats at 0.5 ppm were considered to be due to old age, and not treatment-related.

Repeat dose studies have also been conducted in monkeys. Adverse signs of toxicity observed in *Rhesus* monkey studies include: anorexia, emesis, diarrhoea, hypoactivity, prostration, convulsions, atrophy of the salivary glands and the pancreas, marked decreases in serum cholesterol, and lipid depletion in the adrenals. The dose range for these effects was reported between *1.5* - 300 mg/kg/day. No monkeys survived beyond three weeks into treatment at 10 mg/kg/day or beyond seven weeks into treatment at doses as low as *4.5* mg/kg/day. In a 6-month study of *Cynomolgus* monkeys, low food consumption, excessive salivation, laboured breathing, hypoactivity, ataxia, hepatic vacuolisation and hepatocellular hypertrophy, significant reductions in serum cholesterol levels, and death were observed at *0.75* mg/kg/day. No effects were observed at doses of 0.15 or 0.03 mg/kg/day.

Conclusions concerning the developmental toxicity of PFOS were made via observations of prenatal development toxicity in rats and rabbits. At dose rates of *5* mg/kg/day, reductions in foetal body weight and skeletal variations were among the effects observed. Signs of maternal toxicity were also observed such as anorexia, alopecia and hunched posture. A NOAEL of 0.1 mg/kg/day and a LOAEL of 1.0 mg/kg/day for maternal toxicity were indicated.

Developmental effects were also reported in pre-natal developmental toxicity studies in the rat and rabbit, although at slightly higher dose levels. Signs of developmental toxicity in the offspring were evident at doses of 5 mg/kg/day and above in rats administered PFOS during gestation. Significant decreases in foetal body weight and significant increases in external and visceral anomalies, delayed ossification and skeletal variations were observed. A NOAEL of 1 mg/kg/day and a LOAEL of 5 mg/kg/day for developmental toxicity were indicated. In rabbits, a NOAEL of 1.0 mg/kg/day and a LOAEL of 2.5 mg/kg/day for developmental toxicity were indicated with significant reductions in foetal body weight but significant increases in delayed ossification in the offspring of pregnant females as a main effect.

Postnatal deaths and other developmental effects were reported at low doses in offspring in a two-generation reproductive toxicity study in rats. At the two highest doses of 1.6 and 3.2 mg/kg/day, pup survival in the first generation was significantly decreased. A cross-fostering study indicates that reduced pup survival is mainly a result of in *utero* exposure to PFOS and that post-natal exposure via milk in conjunction with *in utero* exposure may also contribute to reduced pup survival.

3.2.5 Carcinogenicity

PFOS has been shown to be non-genotoxic in a variety of assay systems,

The results of a study into the carcinogenicity of PFOS related substances in rats showed that PFOS is both hepatotoxic and carcinogenic. A significant increase in cancerous growths associated with the liver, thyroid and mammary glands was observed at the highest dose of 20 ppm.

In a mortality study which spanned 37 years, there was a statistically significant association between PFOS levels in workers and bladder cancer. Workers that died of bladder cancer had been employed by the 3M plant in Decatur, Alabama, for at least 20 years and had also been involved in high exposure jobs for at least 5 years. Statistical analysis of the mortality data indicated that workers who were employed in high exposure jobs were approximately 13 times more likely to die of bladder cancer than the general population of Alabama. Given the magnitude of the risk estimate (approximately 13-fold), it was considered that these effects would not be due to chance, as many years of follow up without another death from bladder cancer would have to occur before there would no longer be an appreciable risk.

It is unclear, considering the paucity of data, whether fluorochemicals are responsible for the excess of bladder cancer deaths or whether other carcinogens may be present in the plant. At a facility where fluorochemicals were manufactured, five bladder cancer deaths were reported, with four of these deaths occurring in employees who did not work primarily in the chemicals division. The study, however, reports that these employees worked mostly in maintenance jobs or at the incinerator and wastewater treatment plant and could have been exposed to many chemicals in addition to fluorochemicals. The OECD Hazard Assessment indicates the need for further work on this issue in order to gain a better understanding of the mortality experience of workers exposed to fluorochemicals.

In order to screen for morbidity outcomes, an ‘episode of care’ analysis was undertaken for employees who had worked at the plant between 1993 and 1998. Increased incidences of other conditions such as cancers and non-malignant growths (that have been investigated through the years) were not found to be of significance and no mortality risks were reported for most of the cancer types. However, 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 was indicated. Risk ratios were, however, found to be highest in the employees with the highest and longest exposures to fluorochemicals (OECD, 2002).

In conclusion, cancer of the bladder is considered a potentially significant but yet uncertain end-point in the analysis of risks from PFOS related substances.

3.3 PBT Assessment of PFOS

3.3.1 Overview

The Sections below outline the OECD conclusions on the environmental behaviour of PFOS, followed by the findings of the Draft UK Review of Environmental Risks (RER) based on the EU criteria for assessing the PBT characteristics of a substance. The UK assessment of the PBT characteristics of PFOS is based on the tests and results reported in the 3M Risk Assessment Report (2003) and the OECD Hazard Assessment Report (2002).

3.3.2 Persistence Properties of PFOS Related Substances

OECD Conclusions

PFOS is persistent in the environment. It does not hydrolyse, photolyse or biodegrade under environmental conditions.

In screening studies to assess the photolytic degradation of PFOS, EtFOSE alcohol, MeFOSE alcohol, EtFOSA, MeFOSA, a surfactant and a foam product, all appeared to undergo indirect photolysis to FOSA, PFOA, a hydride and olefins; PFOS was not detected. In tests to assess the potential degradation pathways for perfluorochemicals based on thermodynamic modelling of the incineration process, it was found that the carbon-sulphur bond in the PFOS molecule is a fairly weak bond. Further tests are being carried out to determine whether PFOS may enter the atmosphere as a result of incomplete combustion of waste. Overall, PFOS is not expected to volatilise, based on an assigned air/water partition coefficient of $<2 \times 10^{-6}$ Pa.m^3/mol., from experimental data generated by 3M (OECD, 2002).

In a test into the biodegradability of PFOS related substances, no significant degradation of PFOS was observed over 28 days, either as net oxygen demand from degradation of a test substance (ultimate degradation), loss of total organic carbon (TOC), or loss of parent compound identity (primary degradation). Average percentage biodegradation after 28 days was observed to be 0% by oxygen demand; 6% by removal of total organic carbon; and 3% by liquid chromatography-mass spectrometry.

Conclusions of the UK RER based on EU Assessment Criteria

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 HAR 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 P (Persistent) and vP[23] (very Persistent) criteria.

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[23] 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.

Significance of the Persistence of PFOS in the Environment

The persistence (and bioaccumulation potential of PFOS) is of importance given the environmental fate of PFOS related substances. Perfluorooctane sulphonic acid will result from the chemical or metabolic hydrolysis of PFOSF-derived fluorocarbons. Under appropriate conditions, the perfluorooctane sulphonate anion can form salts with monovalent metallic cations. As suggested above, on the basis of available information, PFOS or its salts cannot be broken down further chemically under normally occurring environmental conditions. Therefore, PFOS is likely to be the ultimate degradation product from PFOSF derived fluorochemicals and will generally persist in that form.

The secondary reactions producing all of PFOSF derivatives are single or sequential batch processes that do not necessarily produce pure products. There may be varying amounts of fluorochemical residuals (unreacted or partially reacted starting materials or intermediates) that are carried forward to the final product. Examples of such residuals include PFOS, n-methyl and n-ethyl FOSA and N-MeFOSE and N-EtFOSE alcohols.

Typically, where present, these residuals can be found at a concentration of 1-2% or less in final products and, in the aggregate, represent roughly 1-2% of total fluorocarbon production volume (nevertheless, available information suggests that this percentage may be significantly higher and may exceed 5%). Fluorocarbon residuals in PFOS products have the potential to degrade or metabolise to PFOS. Therefore, their presence in commercial products is of importance to this Risk Reduction Strategy.

In addition, during product use or disposal, the non-fluorochemical moieties added to the sulphonyl fluoride group of PFOSF can also be removed through a variety of degradation processes (chemical, environmental and metabolic). In such instances, the fluorochemical species which is ultimately produced as a result of such degradation will generally be PFOS as well (3M, 1999).

Environment Canada and the Toxic Substances Control Act (TSCA) Interagency Testing Committee of the US EPA collaborated with scientists at the University “Prof. As. Zlatarov’” in Bulgaria to evaluate the fate of perfluorinated chemicals in the environment.

For this purpose, a set of principal transformations was developed and implemented in the simulator of microbial degradation using the CATABOL software engine. The simulator was used to generate metabolic pathways for about 500 individual perfluorinated chemicals. It was found that, although the rate of biodegradation can reach 60%, persistent metabolites could be formed in significant quantities. During the microbial degradation a trend was observed according to which perfluorinated chemicals are transformed to more bioaccumulative and more toxic products. Of the studied industrial compounds about 17% were predicted to biodegrade to PFOA or PFOS (Mekenyan *et al*, 2003).

3.3.3 Bioaccumulative Properties of PFOS

OECD Conclusions

PFOS bioaccumulation has been observed in the tissues of some fish species such as bluegill sunfish and carp. In bluegill sunfish, bioconcentration factor (BCF) values between 1,124 and 4,013 were determined, while in carp, the BCF values were determined to be between 200 and 1,500.

Conclusions of the UK RER based on EU Assessment Criteria

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.[24] The values obtained were 1124 (edible), 4103 (non-edible) and 2796 (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 σg/l exposure and 200-1500 at 2 σg/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 2800 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 fish-eating animals.

3.3.4 Toxicity Properties of PFOS

OECD Conclusions

PFOS demonstrated acute toxicity to aquatic organisms such as the fathead minnow, and aquatic invertebrates such as *Daphnia magna* and shrimp species. Acute toxicity data for PFOS as determined in tests with fish are provided in Table 3.5, while Table 3.6 provides a comparison of the acute and chronic toxicity characteristics of PFOS for fish, invertebrates and algae.

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[24] The robust summary in the OECD HAR 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.

Table 3.5: Acute Toxicity Data for PFOS Determined in Tests with Fish			
Medium	**Species**	**Results**	**Test Substance**
Freshwater	Fathead Minnow	96-hour LC_{50} = 9.5 mg/L 96-hour NOEC = 3.3 mg/L	PFOS potassium salt
		96-hour LC_{50} = 4.7 mg/L	PFOS lithium salt
		96-hour LL_{50} = 200 mg/L 96-hour NOEL = <170 mg/L	Mixture of didecyldimethylammonium salts, water and up to 5% residual perfluorochemicals
	Bluegill Sunfish	96-hour LC_{50} = 7.8 mg/L 96-hour NOEC = 4.5 mg/L	PFOS DEA salt
	Rainbow Trout	96-hour LC_{50} = 11 mg/L 96-hour LC_{50} = 7.8 mg/L 96-hour LC_{50} = 22 mg/L	PFOS potassium salt
Saltwater	Sheepshead Minnow	96-hour LC_{50} > 15 mg/L	PFOS potassium salt
	Rainbow Trout	96-hour LC_{50} = 13.7 mg/L	
Source: OECD (2002)			

Table 3.6: Toxicity Characteristics of PFOS		
Acute	Fish	Fathead minnow (*Pimephales promelas*) (96-h): LC_{50} = 4.7 mg/L
	Invertebrates	*Daphnia magna* (48-h): EC_{50} = 27 mg/L Mysid shrimp (*Mysidopsis bahia* - saltwater) (96-h): LC_{50} = 3.6 mg/L
	Algae	*Skeletonema costatum* (96-h): NOEC > 3.2 mg/L
Long-term	Fish	Fathead minnow (*Pimephales promelas*) (42-day): $NOEC_{survival}$ = 0.3 mg/L
	Invertebrates	*Daphnia magna* (28-day): $NOEC_{reproduction}$ = 7 mg/L Mysid shrimp (*Mysidopsis bahia* - saltwater) (35-day): $NOEC_{reproduction}$ = 0.25 mg/L
	Algae	Duckweed (*Lemna gibba*) (7-day): NOEC = 15.1 mg/L
Source: OECD (2002)		

PFOS was not found to be toxic to sewage sludge micro-organisms, and data were not available regarding soil-dwelling or sediment-dwelling species. However, the OECD Hazard Assessment indicates that further investigation was needed regarding these pathways, due to the possibility of soil exposure through the spreading of sewage sludge on agricultural land. Subsequently an acute toxicity test on earthworms in an artificial soil substrate has been carried out (3M, 2003). The test is considered to be valid, and the 14-day LC_{50} value determined was 373 mg/kg dwt.

Toxicity testing of PFOS on honey bees (*Apis mellifera*) suggests a low acute oral 72-hour LD_{50} of 0.40 µg/bee (ingestion) and a 72-hour NOEL of 0.21 µg/bee. The contact test yielded a 96-hour LD_{50} of 4.78 µg/bee and a 96-hour NOEL of 1.93 µg/bee. These results from acute oral and contact toxicity tests on honey bees (using PFOS potassium salt) indicate moderate and high levels of toxicity to the bees. The hazard of PFOS levels in honey was not considered in the OECD Hazard Assessment.

Conclusions of the UK RER based on EU Assessment Criteria

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

The lowest aquatic NOEC value (from the OECD and 3M reports) 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. It should be noted that although bird toxicity data can be used in this assessment, the criterion is for NOEC values (as <30 mg/kg in food), whereas the available data are from acute studies (LC_{50} 220 mg/kg in food).

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 were also noted in rats fed diets containing 100 ppm PFOS (6 mg/kg bw/day)[25]. 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 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 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;

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[25] It should be noted that the criteria for the classification of a substance as 'Toxic' with a risk phrase R48 is based on observations of serious damage to health at concentrations Ω5.0 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 Ω50 mg/kg bw/day in a 90-day study.

- 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.

Overall it is therefore concluded that PFOS should be classified as 'Toxic' and carry the Risk Phrase R48.[26] It therefore meets the T or 'Toxicity' criterion for PBT.

3.4 Summary of PBT Characteristics

3.4.1 Overall Findings of the OECD HAR on PBT Characteristics of PFOS

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
- 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.

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[26] PFOS may also have classification for carcinogenicity and reproductive toxicity (development), but the data require more expert review.

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.

3.4.2 Overall Conclusions of the UK RER on PBT Characteristics of PFOS

In conclusion, PFOS meets the **PBT** criteria. It should be noted that in the UK, when a substance is classified as a PBT, the Environment Agency has an obligation to act, and the complete cessation of emissions or zero emissions is the target or aim of any risk reduction measure. This has implications for the risk reduction measures to be considered in the rest of this report.

3.4.3 Overall Conclusions of the 3M Risk Assessment

In August 2003, 3M completed an environmental and health assessment for perfluorooctane sulphonic acid and its salts (3M, 2003). The report provides an assessment of the human and environmental risks associated PFOS and its salts, and addresses human and wildlife exposures to PFOS and the potential environmental and health effects on the basis of information available to 3M as of 30 June 2003. The report follows the methods and procedures outlined in the Screening Information Data Set (SIDS) Manual of the OECD Investigation of High Production Volume Chemicals.

The summary conclusions of the risk assessment are provided here:

Environment: the observed levels of PFOS from a wide variety of environmental samples would not be expected to result in adverse health effects to aquatic organisms or wildlife. Calculated ratios comparing actual exposure levels to no-effect concentrations from laboratory toxicity studies for a large number of species indicate a wide margin of safety. While uncertainty exists in this analysis, use of serum and liver data as a measure of internal dose reduces some of the uncertainty in inter-species extrapolation. The use of actual rather than modelled concentration data and the substantial size of the exposure and toxicity databases add further confidence to the assessment (3M, 2003).

Human Health: margins of exposure (MOE) for non-occupational human populations based on serum PFOS were found to range from 310 to 1550. For the most sensitive endpoint, pup weight gain during lactation, the MOE based on mean population serum PFOS values was 775, and this decreased to 310 using the upper-bound estimate for population serum PFOS concentration (95th percent bound of the 95th percentile of individual serum PFOS concentrations measured in studies of children, adult blood donors, and an elderly cohort (0.1 ppm)). MOE values comparing the liver value selected for risk assessment (the 59 ppm NOAEL from the monkey study) with estimated liver values in humans range from 341 for the upper bound of exposure to 868 for the representative mean exposure.

Occupationally-exposed populations have higher exposure levels and, hence, narrower margins of exposure compared to the animal no-effect levels, but these populations have been monitored for over 25 years without evidence of adverse health effects attributable to PFOS. In summary, the observed levels of PFOS in human serum demonstrate adequate margins of exposure and should not be associated with increased health risk (3M, 2003).

3.5 Environmental Risks of PFOS

3.5.1 Pathways into the Environment

The OECD Hazard Assessment states that there is currently little information concerning the ways in which PFOS is released into the environment.

Generally speaking, manufacturing processes (particularly fluorochemical production sites) constitute a significant source of PFOS in the environment. During the ECF process, various waste products containing PFOS based substances are released into the atmosphere or into wastewater treatment systems, as well as by-products many of which are incompletely fluorinated with hydrogen atoms. These incompletely fluorinated by-products can be recycled in the ECF process or partially degraded in stabilisation processes and eventually discharged to controlled, in-house waste water treatment systems. The resulting treatment sludge is either landfilled or land incorporated (3M, 1999). The cessation of production of PFOS by 3M is, therefore, most likely to have resulted in a reduction in environmental discharges. Direct atmospheric release of perfluorinated surfactants such as PFOS during production are thought to be unlikely as they are not sufficiently volatile, although there may be potential emissions into the atmosphere as a result of incomplete combustion of PFOS.

Given the wide range of applications and products that PFOS compounds are used in, sources other than their manufacture could result in emissions to the environment. These 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 PFAS 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. Significant quantities of aqueous AFFF (known to contain PFOS) have been known to be used in training exercises, which tend to occur frequently and in the same place. The amount of PFOS in the environment increases significantly where the resulting wastewater is left to simply soak away into the soil (although industry suggests that this practice is now discouraged).

In some cases, wastewater from these training exercises may be impounded and treated on-site (e.g. through precipitation, coagulation and adsorption onto activated carbon) prior to discharge into the environment. It is, however, understood that the discharge of such treated wastewater to the environment may still be problematic due to the resistance of the fluorosurfactants (particularly the perfluorocarbon back bone of PFOS) to chemical or biological degradation. Given that they are chemically inert, resist photo-oxidation and are soluble, it is possible (although there is no supporting evidence) that the discharge of wastewater containing PFOS into the environment will result in some passing through into the mains water supply, thereby constituting a potential source of human exposure to PFOS related substances. It should, however, be noted that no data are available on the efficiency of water treatment processes to remove perfluorinated surfactants.

Although, current information indicates that PFOS or its salts cannot be broken down further chemically under normally occurring environmental conditions, it is known that the PFOS anion can form salts with monovalent metallic cations under appropriate conditions. The OECD Hazard Assessment indicates that its presence in the environment suggests a cause for concern.

3.5.2 Environmental Monitoring

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. The ranges of PFOS levels in these cities are provided in Table 3.7.

Table 3.7: Environmental Levels of PFOS in Six US Urban Centres in the US

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

Source: OECD, 2002
Note: ND: not detected

The control cities’ samples generally inhabited the lower end of the above ranges, except for the municipal wastewater treatment plant effluent and sludge findings for one of the control cities (Cleveland), which were intermediate in their ranges, and the ‘quiet’ water samples at the control city (Port St. Lucie), which were the highest. In the same study, measurable quantities of PFOS (up to 0.852 ng/g) were found in four milk samples and one ground beef sample. One of the four milk samples was from a control city, although cities with fluorochemical substances production or use tended to give measurable PFOS levels. The testing included produce such as green beans, apples, pork muscle, cow’s milk, chicken muscle, chicken eggs, bread, hot dogs, catfish and ground beef.

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 ± 11 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 ± 19 ng/L.

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 highest concentration in surface water was measured 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).

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.[27] Values of $\log K_{oa}$ (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^3 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.

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 3.8) have taken place in a variety of locations around the globe and have shown concentrations exceeding 2 ppm in birds and 4 ppm in minks.

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[28] 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).

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

[28] UNECE-LRTAP: United Nations Economic Commission for Europe - Long-range Trans-boundary Air Pollution Convention.

Table 3.8: 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, California, Alaska, northern Baltic Sea, Mediterranean Sea, Arctic, Sable Island (Canada))	OECD, 2002	Bottlenose dolphin: 1,520 ng/g wet wt (liver)	Florida
		Ringed seal: 475 ng/mL (blood)	Northern Baltic Sea
US Fish & Wildlife Service survey of piscivorous fish	A	Bald eagle: 1,047 ppb (plasma)	US
		Six bird species: 2,055 ppb (liver)	US
Survey of fish-eating water birds (US, Europe, North Pacific Ocean, Antarctic)	B	Fish: 923 ng/g wet wt. (muscle)	Belgian estuary
		Carp: 296 ng/g wet wt. (muscle)	US Great Lakes
Survey of fish-eating birds (US, Baltic Sea, Mediterranean Sea, Japanese coast, Korean coast)	C	Bald eagle: 2,200 ng/mL (plasma)	Midwest US
		Brandts cormorant: 1,780 ng/g wet wt. (liver)	US
Survey of mink and river otter in the US	D	Mink: 4,800 ng/g wet wt. (liver)	US
		River otter: 994 ng/g wet wt. (liver)	US
Survey of oysters in the US (Chesapeake Bay & Gulf of Mexico)	E	Oysters: 1,225 ng/g dry wt.	US
Clam and fish samples upstream and downstream of 3M facility in Decatur, Alabama, US	F	Fish: 59.1 µg/kg wet wt. (whole body - upstream) Fish: 1,332 µg/kg wet wt. (whole body - downstream)	Decatur, 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	H	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: **A**: 3M (2000c); **B**: Giesy JP & Kannan K (2001a); **C**: Giesy JP & Kannan K (2001b); **D**: Giesy JP & Kannan K (2001c); **E**: Giesy JP & Kannan K (2001d); **F**: Giesy JP & Kannan K (2001e); **G**: Taniyasu S et al (2002); **H**: Jarnberg U & Holmstrom K (2003)*

3.5.3 Environmental Emissions

The Draft UK RER (2004) has reviewed the environmental risks arising from current and historic uses of PFOS related substances. A broad overview of the types of environmental emissions arising from the use of PFOS related substances in the various use sectors has been provided in Annex 4. This includes a quantification of these risks.

A summary of the conclusions[29] of the Draft RER (2004) shows that the risks posed by the current uses of PFOS related substances are as follows:

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[29] These conclusions must be interpreted in the light of the discussions in Annex 4 and the calculations in the Draft UK RER (2004).

- **Chromium plating**: risks for secondary poisoning for the freshwater, marine predator, and marine top predator endpoints;

- **Fire-fighting foams (formulation)**: risks to the aquatic compartment; risks to the terrestrial compartment; risks for secondary poisoning for the freshwater, terrestrial, marine predator and marine top predator endpoints;

- **Fire fighting foams (use)**: risks to the aquatic compartment (use pattern B), risks to the terrestrial compartment (use pattern B), risks for secondary poisoning for the freshwater, terrestrial (use pattern B), marine predator and marine top predator endpoints;

- **Photography (formulation)**: risks for secondary poisoning for the freshwater, marine predator, and marine top predator endpoints and the terrestrial food chain for some scenarios;

- **Photography (developing)**: risks for secondary poisoning for the freshwater, marine predator and marine top predator endpoints;

- **Photolithography**: risks for secondary poisoning for the freshwater, terrestrial, marine predator, and marine top predator endpoints (assuming instant breakdown of PFOS-substances to PFOS); and

- **Aviation**: risks for secondary poisoning for the freshwater, marine predator, and marine top predator endpoints and the terrestrial food chain for one scenario.

The calculated background concentrations are sufficiently high to indicate a risk for secondary poisoning without the local contributions from the specific use patterns. However, the local releases also make a significant contribution in most cases. Calculations performed for each use area (i.e. without the contributions from the other uses) give results substantially the same as those above, the main exception being photography (developing) for which no risks are identified.

With regard to historic uses, emission estimates show that releases from continuing uses in textile are significantly higher than those from the existing fire fighting foams under Scenarios 2 - 6 of the model calculations (See Table A4.13). Given the likely relative magnitude of emissions from such historical uses, any risk reduction measures that are implemented in relation to known current uses should be accompanied by measures to prevent further use in historical use sectors.

4. POTENTIAL SUBSTITUTES FOR PFOS RELATED SUBSTANCES IN SECTORS OF CONCERN

4.1 Introduction

As noted in Section 3, when a substance is classified as a PBT, the complete cessation of emissions is the target or aim of any risk reduction strategy.

In considering any strategy for a reduction in such risks, it is important to consider the availability of substitutes in the sectors of concern, where this includes direct (‘drop in’) substitutes as well as alternative processes. Such considerations are important since any proposed restrictions (whether on the use or method of use/disposal) may instigate a shift to such alternatives. The TGD requires that the use of substitutes should not result in greater or equal risks to humans and the environment.

In this regard, the replacement of a PFOS related substance by another chemical or an alternative system needs to take account of:

- the existence and cost of the substitute or alternative system;
- the technical suitability of the substitute or alternative system;
- the environmental and human health effects of the substitute or alternative system; and
- the capability of the substitute or alternative system to meet the required safety standards.

A discussion of the availability and suitability of substitutes for the ‘continuing uses’ of PFOS related substances is provided below against the above criteria. The discussion focuses on continuing uses (rather than historical uses[30]) as substitution is considered to already have taken place in the other sectors.

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

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[30] It should also be borne in mind that for some of the use sectors, there is no evidence of actual use in the EU or UK and as such there is no need for any assessment of substitutes.

4.2 Potential Substitutes to PFOS Related Substances in Metal Plating Applications

4.2.1 Availability of Potential Substitutes

PFOS related substances are used in the following main applications:

- decorative chromium plating; and
- hard chromium plating.

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

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

For hard chromium platers, information received indicates that the direct substitution of Cr (VI) is not currently a viable option as Cr (III) is not suitable for the deposition of thick chromium layers, as used in hard chrome applications. Substitutes such as the nickel-tungsten-silicon carbide composites are still in the research phase, although there exists the possibility of other substitutes such as electroless nickel coating in specific applications (CETS, 2002 as cited in BREF, 2003). A detailed assessment of the options available for substituting the use of Cr (VI) in hard chromium plating may need to be explored in more detail in other studies. The BREF (Best Available Techniques reference document) on the surface treatment of metals and plastics which is currently being prepared[31] and the Risk Reduction Strategy for Chromates (also on-going) are of particular relevance.

While Cr (III) is not technically suitable for hard chromium plating applications and there is no known alternative to PFOS related substance-based chemical mist suppressants, a number of options for mechanical mist suppression and improved ventilation exist. The longer time periods of immersion in the electrolyte required to obtain the necessary thickness of coating provide the opportunity for greater tank enclosure compared with decorative applications (where immersion times are measured in minutes rather than hours/days). Whilst causing some interruption to the process of

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[31] A BREF is a Best Available Techniques reference document produced as a result of an information exchange between Member States and an IPPC industry sector. This exchange is legally required by the IPPC Directive and the various BREFs inform regulators and industry of BATs for permitting and operating IPPC-controlled installations.

immersing and 'dragging-out' articles, this would eliminate the need for chemical mist suppression to meet the occupational exposure levels of 0.05mg/m^3 (as Cr 8 hr TWA) when combined with suitably adjusted ventilation extraction. In addition, ventilation extraction can be used to maintain levels of exposure to Cr (VI) mists below occupational exposure levels, the key area of difficulty being extraction of mists from the centre of the tank.

It should be noted that the future use of Cr (VI) is currently limited in the automotive[32], electrical and electronic industries[33] under various EU Directives.

4.2.2 Technical Suitability of Potential Substitutes

For decorative chromium plating, information received from a number of industry groups and regulatory authorities indicates that the substitution of Cr (VI) with Cr (III) does not result in any significant technical difficulties and, indeed, has a number of technical advantages. Historic problems with colour difference and variation during processing have also been overcome.

Technical advantages of using Cr (III) over Cr (VI) in decorative chromium plating applications (SEA, 2003) include:

- production of less rejects and freedom from burning (almost impossible to burn);
- better metal distribution, good throwing power and good covering power resulting in better corrosion protection;
- easier draining due to the lower viscosity and lower chemical concentration of Cr (III) electrolytes, resulting in less staining of the work;
- uniform surface coverage without build up on high current density areas; and
- maintained plating rate and deposit appearance over a very wide current density range.

For hard chromium plating applications the use of greater physical tank enclosures presents some operational disadvantages over the use of chemical mist suppressants. These include the need to remove and replace the enclosure between operations; the advantage of chemical mist suppressants being that they effectively provide a floating chemical enclosure through which articles can be raised and lowered. Such disadvantages do not occur with the use of improved ventilation extraction alone. However, while these may present operational disadvantages over chemical mist suppressants, there are no technical disadvantages from the perspective of product quality/production standards.

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[32] Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end of life vehicles (ELV Directive).

[33] Directive 2002/95/EC on the Restriction of Hazardous Substances in Electrical and Electronic equipment (ROHS Directive)

4.2.3 Cost Implications of Potential Substitutes

Information received from industry groups and regulatory authorities suggests that the substitution of Cr (VI) with Cr (III) in decorative plating processes, whilst requiring some initial capital expenditure, provides significant operational cost savings.

Initial one-off costs and capital expenditure are required for disposal of the Cr (VI) solution, re-lining the process tank with PVD (after removing and disposing the contaminated lead), and replacing the lead/antimony anodes with carbon, plus an ion exchange system (BREF, 2003; SEA, 2003). However, improvements in ion exchange resin technology have recently resulted in much lower operating costs.

Operating cost savings for the Cr (III) plating process are associated with both improvements in the production process and product quality (e.g. pitting), and with reduced regulatory compliance costs and associated controls. These cost advantages include:

- reduction in the need for air scrubbers and mist suppressants;
- reduction of up to 90% in the cost of treating rinse water;
- significantly lower costs of treating and disposing of waste[34]. The use of Cr (III) renders the need for a tank for storing the waste Cr (VI) prior to it being taken off the site redundant;
- lower health surveillance requirements. One company has reported that as a result of using Cr (III), its work force is required to be seen by the medical profession once a year rather than four times a year when using Cr (VI);
- greater system efficiency and increased production yield. Cr (III) has better throwing power, a higher current capacity, greater plating efficiency (up to 50% better) and about 30% less energy consumption than Cr (VI); and
- possibility of lower insurance premiums (given that the number of workers seeking compensation for health problems in general is rising).

The net effect is that, although the base chemicals are more expensive (about the same as a nickel process), the costs are more than offset by the savings made due to reduced waste treatment costs, reduced air monitoring costs, record keeping, and the reduced reject rate. The major benefit however relates to the significantly reduced risk of employee ill health induced by working with hexavalent chromium. Trivalent processes may require more effort to operate (i.e. regular monitoring of ampere-hours, pH, density, electrolyte cooling, and electrolyte samples must be sent away for analysis), but industry

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[34] It should be noted that the cost of Cr VI disposal was also beginning to rise due to environmental regulations.

indications are that the labour costs are the same for Cr (III) and Cr (VI). It is of note that in the UK, the Health and Safety Executive (HSE) will be starting an initiative to promote the adoption of Cr (III) processes in decorative chromium applications later in 2004.

For hard chromium applications and the adoption of improved enclosure and extraction ventilation, information received to date indicates that costs of up to £40,000 may be required for installing/upgrading extraction systems in a single unit.

4.3 Potential Substitutes to PFOS Related Substances in Fire Fighting Foams

4.3.1 Availability of Potential Substitutes

In discussing the availability of potential substitutes to PFOS based fluorosurfactants, it should be noted that the manufacture or production of PFOS based foam concentrates does not take place in the UK. Of particular interest are, however, the PFOS based foams that are currently in the inventories of a number of private and civil stockpiles of fire fighting foam. These constitute the focus of this risk reduction strategy.

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

- non-PFOS based fluorosurfactants;
- silicone based surfactants;
- hydrocarbon based surfactants;
- fluorine-free fire fighting foams; and
- other developing fire fighting foam technologies that avoid the use of fluorine.

The suitability of these various types of surfactants and foams as potential substitutes to PFOS based fluorosurfactants in fire fighting foams is discussed below.

4.3.2 Technical Suitability of Potential Substitutes

Since the 1960s, fire fighting foams used against fires of flammable liquids (Class B foams) have been based mainly on the use of fluorosurfactants. 3M (prior to its withdrawal) made its fluorosurfactants using the ECF (electro-fluorination) process, while other manufacturers produced fluorosurfactants using the telomerisation process (based on six and eight carbons mainly). Most of the fluorocarbon surfactants currently marketed in the UK are produced using the telomerisation process and result in C6 telomer based fluorocarbon surfactants.

As a result of many years of continuous development, telomer based fluorosurfactants have been indicated as providing an equal and comparable performance to the PFOS based fire fighting foams and are reported to be highly reliable. In fighting Class B fires, these telomer based fluorosurfactants exhibit a number of key performance characteristics including:

- rapid knockdown and extinguishment;
- effectiveness in extinguishing spill and storage tank fires;
- long shelf life (stable in long storage);
- ability to secure fuel spills and provide post fire security;
- minimised fuel pick-up in foam blanket; and
- ease of foaming with conventional nozzles.

Telomer based foams also have a lower fluorine content than PFOS based foams. In general, for a 3% type AFFF product manufactured in the UK, the amount of fluorine used in the concentrate would be approximately 0.5 - 0.8%, compared with concentrations of approximately 1.5% - 1.8% found in the PFOS based foams produced by 3M (BFPSA, 2003a).

Fluorine-free foams are a relatively new technology (compared with the fluorosurfactant technology), particularly fluorine-free foams for use on Class B fires. These newly developed foams for use on Class B fires do not contain any fluorosurfactant. For fire suppression, they rely on a fast moving foam blanket spreading over the surface of a burning liquid rather than on the film forming properties of AFFF fluorosurfactant solutions (pers. comm.).

The essential properties of these newly developed fluorine-free foams include slow drainage, high heat resistance, slow coarsening, low shear viscosity and low yield stress. Information received indicates that the fluorine-free foams may not currently achieve the standards of the PFOS based Class B fire fighting foams on a few chemical properties, however, work is currently ongoing towards achieving even higher levels (comparable to those achievable with PFOS based fire fighting foams). This does not suggest or imply that some of these foams are currently not suitable for use on Class B fires.

It should be stressed that the quality of foams is not based on the individual chemical properties of a foam but on certified test standards. Various industry sectors have in fact developed a range of tests which are used to independently verify the suitability of a fire fighting foam for their sector. Examples of tests applied by industry sectors include the ICAO Level A and B testing for the Aviation sector and the MIL-F testing for Military applications, while National test standards include Dutch Milieukeur criteria and Swedish P-labelling in addition to the European Standard (EN1568) tests[35] and UL (Underwriters Laboratories Standard).

While the majority of these tests are voluntary, they are applied by the industry sectors as a way of establishing the suitability of a fire fighting foam for that sector. In some sectors, the testing requirements are (or are linked to) regulatory requirements. For

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[35] The EN 1568 is a European Standard for fire fighting foams accepted by 18 countries and applied by most European Notified Bodies and government organisations.

instance, the ICAO test has been agreed and applied by several aviation authorities globally and is required if a foam is to be used in civilian airports.

Information received indicates that fluorine-free foams have attained a number of the above testing standards and are available in the global fire fighting market. Companies within and outside the UK are currently involved in various forms of fluorine-free technology. One UK producer of foams indicates they have produced fluorine-free foams which have achieved a UL listing, an ICAO Level A performance and exceeded the requirements of EN 1568 part 3. Work is currently on-going by this producer to achieve higher foam performance in this area.

Another European foam producer indicates that it has produced fluorine-free foams which have achieved the ICAO Level B testing (higher than the Level A) requirements and have also passed the EN 1568 testing requirements (which makes them comparable to PFOS based foams). The company has indicated that these foams are widely used in Australia, Singapore, New Zealand and other parts of the world.

Consultation with the UK Civil Aviation Authority (CAA) indicates that several foams which claim to be fluorine-free are utilised by aerodromes in the UK. The UK CAA accepts fluorine-free foams and actively encourages fire fighting agents to use foams which are more environmentally friendly.

There has been no extensive assessment of the suitability of hydrocarbon and silicone based surfactants as information received from industry indicates that these types of foams are often combined with fluorosurfactants to achieve higher performance levels in actual fire situations. Information received from consultation also indicates that hydrocarbons provide the lowest technical suitability of the various potential substitutes, with the silicon based foams providing a slightly higher level of performance. This does not mean that there are no pure silicon or hydrocarbon based surfactants or that foams based on these do not have future relevance in fire fighting foams, particularly from an environmental standpoint.

4.3.3 Cost of Potential Substitutes

Fluorine-free foams are approximately 5 – 10% more expensive than the fluorosurfactant based foams (including those PFOS based foams marketed previously). The manufacturers, however, indicate that prices for fluorine-free foams would reduce if the market size increased. It is, therefore, assumed that prices are broadly comparable.

As the transition from PFOS-based products has already taken place, there are no development or operational costs associated with the substitution of PFOS based foams by foam manufacturers or users.

4.3.4 Environmental and Health Impacts of Potential Substitutes

In assessing the environmental and health impacts of the alternatives to PFOS based fire fighting foams, it should be noted that the inherent properties of these foams result in a number of impacts on the environment. These properties include biological oxygen demand (BOD), chemical oxygen demand (COD), aquatic toxicity, foaming, effects on wastewater treatment plants, etc. The major issues with PFOS-based fire fighting foams, however, are related to their persistence and bioaccumulative/toxicity potential. These form the focus of the analysis of the environmental impacts of potential substitutes.

AFFF foams which are based on fluorosurfactants are now known to degrade to various types of perfluorocarboxylates (PFCs). Research has demonstrated that these PFCs are extremely long lived in the environment, surviving at appreciable concentrations for at least 10 years (Moody and Field, 1999). Perfluorocarboxylates containing six to eight carbons have been detected in groundwater samples collected from fire-training facilities in two sites in the US (a Naval Air Station and an Air Force Base) with concentrations ranging from 125 to 7090µg/L (US EPA, 2004). This detection of PFCs after 7-10 years of no fire-fighting activity indicates that PFCs are inherently stable and persist in the environment.

It should be noted that the PFC profile found in the environment is typical of the particular method of manufacture of the fluorosurfactants used (i.e. the presence of odd and even number homologues (PFC6, PFC7 & and PFC8) are usually typical of the fluorosurfactants produced by the ECF process, whereas only even homologues result from fluorosurfactants produced by telomerisation process) (Moody and Field, 1999).

With regard to biological toxicity, literature has suggested that PFCs are biologically toxic with PFOA and PFDA known to cause peroxisome proliferation and hepatocarcinogenesis (liver cancer). PFCs are indicated to act as hepatocarcinogens as a result of increased oxidative stress and tumour promotion. The inhibition of intercellular gap-junction communication is indicated to be chain length dependent with the maximum effect for PFCs with 7-10 atoms. PFC2-PFC5 had no appreciable inhibitory effect (Upham *et al*, 1998; Klein and Harman, 2000). This does not however conclude one way or another on the bioaccumulative and toxicity potential of telomers used in fire fighting foams and this should constitute the subject of research in another study[36].

It should also be noted that at a meeting organised by the US EPA, it was accepted based on the results of groundwater monitoring data presented, that telomer based fire fighting foams are not likely to be a source of PFOA (a PFC) in the environment (because they predominantly contain the C_6 fluorosurfactants[37]) and are no longer being considered as part of their PFOA ECA (Enforceable Consent Agreement) investigation. The US EPA,

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[36] Klein and Harman (2000) have summarised many of the issues relating to the breakdown of fluorosurfactants used in fire fighting foams which result in end-products which are persistent, bioaccumulative and potentially toxic.

[37] Consultation suggests that telomers based on C_8 building blocks are used mainly for surface protection treatments while the C_6 are used for fire fighting foams. When the telomer has as a basic building block an alcohol that contains a C_8 group, it is possible (as a number of studies have shown) that it may degrade biologically to PFOA. On the other hand, when the telomer is based on C_6 building blocks, this kind of degradation cannot occur (because the octyl group is not present). It has, however, not been confirmed that C_8 building blocks have not been used in recent years in fire fighting foams in the UK.

however, noted that it continued to be interested in these telomer products as well as in stockpiles of older fluorochemical foams (US EPA, 2003a).

However, the above concerns have in part driven much of the interest in non-fluorosurfactant based foam formulations that are biodegradable, have lower toxicity and are non-bioaccumulative in the environment. In addition, there is the possibility of further regulations and restrictions on the use of fire fighting foams containing fluorosurfactants as global interest in the effects of PFOS, the environmental persistence and toxicity of fluorosurfactant degradation products and the use of fluorosurfactants in dispersive applications (such as fire fighting foams) come under scrutiny by environmental agencies in various countries.

Under the Groundwater Regulations of 1998 (Statutory Instrument 1998 No. 2746), classes of compounds are listed into List I (most harmful) and List II (slightly less harmful). It should be noted that since the fluorosurfactants in modern fire fighting foams are by definition organohalogen compounds, they have been provisionally determined[38] as being in List I. This means that disposal of spent foam solution onto or into ground, with the likelihood that it will reach groundwater, may be prohibited under the regulations.

In Canada, the Evaluation Division of CCEB has recently prepared a list of 100 chemicals in use in Canada that, in the opinion of an expert panel, may meet criteria for persistence, toxicity and in some cases bioaccumulation. The criteria for inclusion are based on Canada's Toxic Substances Management Policy and include evidence for transport to remote regions, long persistence in water, soil or sediment, octanol-water partition coefficients >5000 and potential toxicity. Perfluorocarboxylates (PFCs) are listed in the top 100 potential persistent organic pollutants in current use in Canada.

It should also be noted that OSPAR intends to assess the group of perfluorocarboxylic acids when the full dataset is available from the further testing programme on PFOA (see Section 5.5.5).

With regard to the toxicological and ecotoxicological suitability of non-PFOS based fluorosurfactants, the evidence indicates that they are probably not more persistent, bioaccumulative or toxic than PFOS based fluorosurfactants. As such, they probably provide (at least) a slight incremental improvement in environmental and health terms compared to PFOS based foams. Whether telomers represent a significant concern for human health and the environment is under review elsewhere and conclusions are awaited. However, (until there is information to the contrary), it must be recognised that these fluorinated alternatives may not provide a major reduction in environmental risks compared with PFOS based foams as all fluorosurfactants will ultimately degrade to environmentally persistent fluorinated derivatives.

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[38] Formal consultation for full listing is currently underway and this process should be completed towards the end of 2004.

With regard to fluorine-free foams, current information indicates that compared to PFOS based foams, they do not persist or bioaccumulate in the environment (due to the absence of fluorine). With regard to acute toxicity, fluorine free foams appear to have a slightly lower acute toxicity, although the information provided to date is not conclusive (and this issue is still under review by the Environment Agency). Data on chronic toxicity are not available, although this applies to all of the substitute fire fighting foams.

4.4 Potential Substitutes to PFOS Related Substances in the Photographic Industry

4.4.1 Availability of Potential Substitutes

Chemicals or classes of chemicals that may be considered alternatives to PFOS related substances on an industry-wide basis (or even a company-wide basis) are reported as not currently being available for the photographic industry (although efforts are being made to identify alternatives). This is because PFOS substances have properties that are not known to be reproduced by other individual chemicals or chemical classes.

The basic technology for most imaging products involves silver halide chemistry. However, the dyes, couplers, stabilizers, antioxidants and other components of the emulsion can be (and typically are) different from company to company. The amounts or proportions of the various ingredients also vary from company to company, as does the manufacturing equipment used to coat the base material (i.e. film, paper, plates). Each manufacturer and each product development team must therefore assess replacements for PFOS related substances in reference to its own formulations[39]. For imaging products which are not silver halide based, energy capture systems (i.e. photon, X-ray, etc.) used also vary from manufacturer to manufacturer and product to product. The surfactant and antistatic packages used in imaging products must also vary to meet the product-specific requirements caused by differences in chemical composition, manufacturing process, and type of product.

Based on these differences and other critical properties required in imaging products, the development of alternatives to PFOS involves laboratory scale evaluations of:

- many different candidate replacements (alternative chemicals or alternative formulations);
- small volume formulation evaluations on a research and development scale;
- chemical interaction studies to define chemical and imaging interferences;
- film coating experiments to gain an understanding of how an altered coating will behave while being coated by machine;
- high-speed film transport studies to understand how coatings will behave when moving through manufacturing and processing machinery; and

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[39] It should be noted that manufacturers differentiate their products using proprietary emulsions made with proprietary ingredients, and dispensed by proprietary processes; therefore, formulation and manufacturing differences are the norm, not the exception.

- full-scale internal trials using processes and equipment that will actually be used to make and process a product, and trade trial evaluations to learn how a product will behave during customer use.

Successful alternatives to PFOS materials have included non-perfluorinated chemicals such as hydrocarbon surfactants, chemicals with short perfluorinated chains (C_3 - C_4), silicones, telomers, and in very few cases it has been possible to reformulate coatings so that they are inherently less sensitive to static build-up.

Replacement efforts as a result of these alternatives have resulted in an 83% decrease in the total amount of PFOS related substances used in imaging products since 2000 and the elimination of the following uses of PFOS related substances in imaging products:

- defoamer used in the production of processing chemicals for films, papers, and printing plates;

- photoacid generators in photolithographic processing solutions used in the manufacture of printing plates; and

- surfactants in photolithographic processing solutions used in the manufacture of printing plates.

The industry also notes that some of the alternatives that have successfully replaced uses of PFOS are telomer products that are currently under review in the US. The industry notes that if restrictions are placed on telomers, it may become significantly more difficult to further reduce or eliminate PFOS use.

4.4.2 Technical Suitability of Potential Substitutes

To meet the technical requirements for use in photographic products any alternatives to PFOS related substances must provide equivalent properties.

For those applications where substitution has not yet been possible, options explored to date have failed because they did not meet one or more of the following requirements for effective coating aids:

- absence of photoactivity and lack of interference with the imaging process;
- promotion of uniformity of photoprocessing results by controlling surface wetting properties;
- control of splicing tape adhesion properties;
- compatibility with photo-retouching materials;
- improvement of camera, projector, and printer transport to eliminate unwanted photographic effects; and
- prevention of the build-up of particles that can clog magnetic strip readers.

The imaging products/applications where there are currently no alternatives to PFOS related substances and which represent critical uses are as follows:

- surfactants for mixtures used in coatings applied to films, papers, and printing plates; The ability to control surface tension in imaging materials is a critical aspect of the use of PFOS substances as coating aids. Imaging materials must be coated with multiple (up to 18) layers of light sensitive materials at high speed to prevent the drying of materials as they are laid down. PFOS chemicals are critical for creating coatings of high complexity in a highly consistent manner, thus avoiding the creation of large amounts of waste due to irregularities in coating thickness;

- surfactants in a limited number of solutions used in the processing of films. This use involves incorporation of a PFOS material into a mixture that is used as a photoprocessing solution where its surfactant properties function to prevent discoloration of films while the films are being processed through the solution;

- electrostatic charge control agents for mixtures used in coatings applied to films, papers, and printing plates. PFOS coating aids also have unique properties at low concentrations for controlling static charge during the manufacture and use of imaging materials. This is particularly important for imaging materials that have a high sensitivity to light (i.e., high speed), as these products are unusually sensitive to light produced by static discharge during transport of imaging materials. Coating aids must not be photoactive; otherwise, unacceptable fogging or speed effects may occur in the coatings;

- friction control and dirt repellent agents for mixtures used in coatings applied to films, papers, and printing plates. Excessive friction during the transport of imaging materials and contamination of imaging materials by dirt or clogging of magnetic strip readers with debris can lead to significant waste of imaging materials during manufacturing and use; and

- adhesion control agents for mixtures used in coatings. Adhesion control is a property imparted to film coatings as a result of the use of PFOS materials as coating aids. Control of adhesion of various tapes to imaging materials is important because tape is the primary way in which imaging materials are attached to spools and to each other during processing. The strength of the bond between the tape and the imaging materials must be controlled so that imaging devices (e.g., cameras, photoprocessors) and imaging materials are not damaged during transport (i.e., the adhesive bond between the tape and the imaging material must be broken by a force that will not damage devices or materials being transported).

Additional critical imaging uses for PFOS/PFAS chemicals involve the fabrication of semiconductors for imaging devices such as digital cameras, cell phones, printers, scanners, etc.

4.4.3 Cost of Potential Substitutes

The cost for replacement of PFOS materials is estimated to be in the range of € 20-40 M for the full range of imaging products[40]. These costs are based on the estimated cost of achieving the current reduction of 83% in the use of PFOS related substances.

In some cases, product formulations have been changed solely to replace PFOS materials while in other situations, PFOS replacement has been incorporated into other product reformulation activities. As product reformulation activities are typically spread across multiple departments or multiple product lines in a single company, the complete cost of PFOS replacement is typically not calculated.

The cost to be incurred from further work on replacements (for the remaining 17%) is expected to be significantly higher than the above figure as the replacement work is increasingly more difficult.

4.4.4 Environmental and Health Impacts of Potential Substitutes

The potential health, safety, and environmental impacts of PFOS replacement chemicals are assessed by each manufacturer as part of their product commercialisation processes. All manufacturers have, as an overarching objective, the use of progressively less hazardous materials wherever possible in order to reduce any health, safety of environmental risks arising from the manufacture, use and disposal of their products. The potential impacts of each individual substitution are evaluated across the life cycle of each product or product family, and all of these data are brought together and assessed so as to protect the large amount of proprietary information provided by each manufacturer.

PFOS materials play a key role in minimizing manufacturing waste by contributing to the technology for creating coatings of high complexity in a highly consistent manner. The coating aid must allow the rapid uniform spreading of the layers so that irregularities in the coatings are avoided. It is reported that any irregularity in coating thickness makes imaging materials useless and increases manufacturing waste significantly.

4.5 Potential Alternatives to PFOS Related Substances in Photolithography and Semiconductors

4.5.1 Availability of Potential Substitutes

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

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[40] Some of the cost may include photolithographic uses but does not include the replacement of materials used for semiconductors.

Photoresists

The operation of PFOS based PAGS is critical to the semiconductor industry in the photolithography process. PAG's are based on PFOS related substances due to the resultant optical characteristics (uniform exposure), sensitivity, speed, low acid volatility, resolution and depth of focus and high yield (low incidence of contamination or defects). ESIA indicates that there are currently no substitutes known that give the same level of critical functionality to cause effective, efficient transformation in leading edge photoresists and which can be used in volume manufacturing.

In limited cases, resist suppliers can formulate chemically amplified resists without PFOS PAG. This is the case with photoresists designed for 248nm wavelength. It is estimated that about 50% of the suppliers are currently using PFOS PAG at this wavelength for improved performance. These suppliers may encounter some difficulties in maintaining current performance levels in the event of a change. It should be noted that the semiconductor industry continues to make many products with 436nm and 365nm photolithography for which further miniaturisation is no longer cost effective. These products do not require PFOS PAG (ESIA, 2003).

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

The next generation lithography includes electron project lithography (EPL), extreme ultraviolet lithography (EUVL), ion projection lithography (IPL), and x-ray proximity lithography (XPL). These technologies are at differing stages of development but all are currently unsuitable for use in manufacturing because they still face significant challenges. For example, EUVL is not expected to be available before 2007 and XPL which had made significant strides in development has not been able to overcome specific difficulties. EPL originated at IBM and Bell Laboratories in the USA, and is gaining acceptance in other parts of the world while IPL which is being strongly considered in Europe has not gained acceptance elsewhere. ESIA however indicates that the two favourites are EPL and EUVL although this decision is far from final (ESIA, 2003).

Resists for EPL and EUV are typically modified formulations of 248nm resists. ESIA indicates that it is too early to determine whether they will require PFOS PAG resist. IPL on the other hand works well with most resists and is unlikely to require a PFOS PAG. XPL needs a more sensitive resist than currently available and this is currently an unresolved issue for this technology (ESIA, 2003).

Anti-reflective Coatings

For anti-reflective coatings used in combination with deep ultra violet (DUV) photoresists, ESIA indicates that there is also no alternative available which fulfils the critical technical requirements necessary (ESIA, 2003).

For uses of PFOS related substances in top (TARC) and bottom (BARC) resist coatings, suppliers are said to be working on polymeric replacements. However, high fluorine content and polymeric nature are relatively incompatible properties. The semiconductors industry indicates that replacement could take up to five years, if it can be done at all (ESIA, 2003).

Developer Applications

In developer applications (including EBR's, RER's), strippers and etch mixtures, there are surfactants which are not PFOS based which could serve as alternatives.

4.5.2 Technical Suitability of Potential Substitutes

Photolithography steps are frequent and critical to the success of the final wafer product. Photoresists performance must be tailored to respond reliably and robustly to these repetitive and complex demands.

Information provided by ESIA indicates that the identification of substitutes for these PFOS applications would require an 'invention' and then a significant lead-time for qualification of such an 'invention' which itself could take between three to four years.

Developing or 'invention' of new photoresists requires a significant amount of research and development, engineering and qualification effort. Qualification involves actually producing circuits using the new resist for some photolithography patterns. This is usually carried out at the customers manufacturing site and often involves a side-by-side comparison of the new resist with the incumbent material. The new resist must be compatible with the customer's processing equipment, must not perturb previous and subsequent processes, and must be compatible with the customer's hazardous waste management system. The resist must perform flawlessly, otherwise the final yield of integrated circuits may deteriorate.

ESIA argues that PFOS related substances should remain available while research towards identifying PFOS substitutes continues. They also argue that any potential marketing and use restriction for use in critical applications in Europe would jeopardise the long term continued presence of the semiconductor industry in Europe. The photolithography process and the use of PFOS photo-acid generators within this process remain the key aspect of cutting edge semiconductor manufacture and development for future generations of technology.

4.5.3 Cost of Potential Substitutes

In developer applications, the technical performance of the non-PFOS based surfactant is comparable to the PFOS based surfactant. Although there is no need for new equipment, significant costs arise from labour, engineering and qualification. Industry estimates for the phase-out of PFOS in developers is estimated at around €1.5-2 million. Potentially higher developer costs could arise if down time, opportunity cost, logistics and yield loss are included.

4.5.4 Environmental and Health Impacts of Potential Substitutes

For developer applications, ESIA indicates that non-PFOS based substitutes will be selected that have no known environmental, safety or health impact.

It should also be noted that during the chemical formulation of photolithography products, worker exposure potential is very low. Chemical formulation of photolithography products occurs under highly automated, largely closed system conditions. The same process for electronics fabrication is similarly automated, with a low volume of *PFAS* used, and use of protective equipment. Chemical isolation is also an intrinsic part of quality control procedures.

Additionally, environmental release potentials are deemed to be low. Due to the low vapour pressure of PFOS, and the nature of the process, no emissions to the air are expected. Waste products, including 93% of the resist formulation (PAG’s and surfactants) are incinerated. Releases to water are also considered to be negligible.

4.6 Potential Alternatives to PFOS Related Substances in Hydraulic Fluids

4.6.1 Availability of Potential Alternatives

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

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

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

4.6.2 Technical Suitability of Potential Substitutes

Making formulation changes in aviation hydraulic fluids requires extensive review, testing, and approval by all airframe manufacturers of substitute formulations prior to use in commercial aircraft. In the industry’s view, even if an acceptable alternative to these perfluorinated anionic surfactants is found, the extensive qualification process designed to ensure safe operation of the aircraft would result in an extended time frame before it could be used. It has been suggested that the process of qualifying a new fluid for use in commercial aircraft has historically taken about 10 years from concept to actual commercial manufacture. There are several steps involved in this process which must be followed sequentially.

Broadly speaking, the hydraulic fluid would be required to go through:

- an evaluation stage: This is intended to satisfy the producers of the hydraulic fluid that they have a fluid mixture that will meet all of the performance criteria required. It would have to be ensured that the use of any ‘substitute’ additive would improve erosion resistance without adversely affecting the other important properties of the fluid; and

- a qualification stage: Once the fluid supplier offers a new candidate fluid, airframe manufacturers go through extensive ground evaluation. Once they are satisfied the candidate fluid will meet all performance properties, they offer the fluid to an airline for a highly monitored flight service evaluation, where the new fluid is actually flown in commercial aircraft for up to two years. If all this testing shows the fluid to be acceptable, the airframe manufacturers then qualify the fluid for commercial use in aircraft they manufacture.

Information received with regard to the suitability of telomers as replacements for PFOS related substances in hydraulic fluids indicates that, while the chemistries are similar, telomer based products are not able to demonstrate the technical performance required by the industry.

4.6.3 Costs and Environmental and Health Impacts of Potential Substitutes

As there are no current alternatives to PFOS substances currently being used in aircraft systems, there is no information on costs or environmental/human health attributes.

5. EXISTING RISK REDUCTION MEASURES

5.1 Overview

The following sections provide an overview of the various legislative and non-legislative risk reduction measures that are in place, or are likely to be implemented, to control the risks associated with PFOS related substances.

Firstly, an overview of the legislative controls and the voluntary action by 3M is provided. This is followed by a consideration of existing risk reduction measures in various use sectors. Finally, there is a consideration of international and national initiatives of relevance.

5.2 Overview of Legislative Controls

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.

The Danish EPA notes that 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 2 of this report has confirmed that none of them are included.

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

5.3 Voluntary Phase Out of Production by 3M

As discussed in Section 1, the main producer of PFOS compounds voluntarily decided to phase-out production in 2000[41]. Production ceased completely by the beginning of 2003 (see also Table 2.3). Although it is recognised that 3M was the largest global producer of PFOS, other producers do exist. The Danish EPA study on PFOS (Danish EPA, 2001-2) notes that, in the European market:

> "*..many consumers have switched to other suppliers who base their deliveries on producers who have continued their production of PFOS-compounds/perfluorocompounds*".

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[41] It has to be noted that the US EPA had already singled out perfluorooctane sulphonic acid and its potassium, lithium and ammonium salts for in-depth evaluation.

This view has to be considered in the light of information obtained through consultation according to which a number of companies may have stockpiled significant quantities of PFOS related substances upon the announcement of the voluntary phase out by 3M. We have not been able to obtain information on the quantities of PFOS related substances still in production or what the response/action of producers other than 3M has been since the announcement of 3M's decision.

5.4 Voluntary Risk Reduction Measures and Current Practices in Certain Industry Sectors

5.4.1 Risk Reduction Measures in the Metal (Chromium) Plating Industry

Formulators of preparations used in the chromium plating industry have advised that the following precautions are in place to prevent spillages of PFOS related substances and associated exposures during the preparation of the final product[42]:

- local exhaust ventilation is used to prevent exposure from spray emissions (including PFOS related substances);
- raw materials may be pumped directly into mixing tanks to prevent spillages;
- product mixing tanks (which are sealed) are conical in shape to allow for collection of the maximum possible quantity of final product from the tanks. This also helps in using only a small quantity of water for the cleaning of the tanks; and
- production areas are bunded to prevent any spillages ending up in the sewerage or contaminating the soil. A company has indicated that a separate run-off container is used to prevent entry of lost material to the sewer.

Small amounts of PFOS related substances go through the on-site wastewater treatment facilities as a result of washing the mixing tanks after a batch is prepared. The on-site treatment may include removal of solids, streaming of soluble metal waste and adjustment of the pH levels but does not target PFOS related substances.

Substitution of Hexavalent Chromium (Cr VI) by Trivalent Chromium (Cr III).

The substitution of hexavalent chromium (Cr VI) with the less hazardous trivalent chromium (Cr III) in decorative plating applications is a risk reduction measure which is of relevance to the use of PFOS related substances in metal plating. This recommendation has been advocated in the past by industry (suppliers of hexavalent chromium), industry associations (SEA and BSTSA) and government departments (for example HSE, who are starting an initiative this year (2004)).

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[42] It has to be noted that the formulators usually merely dilute the PFOS based preparations they are supplied and then forward them downstream.

The need for Cr (VI) in ‘bright’ decorative-chrome plating could be eliminated by substitution with the less hazardous trivalent form, Cr (III). Early attempts to encourage this substitution were not successful, mainly because Cr (III) deposited a different colour to Cr (VI) which was unacceptable to customers, particularly those purchasing chrome bathroom and kitchen fittings in the domestic market. However, most of these barriers to substitution have now been overcome and, in most cases, in ‘bright’ decorative-chrome plating it is now reasonably practicable to substitute Cr (VI) by Cr (III) (SEA, 2003).

Exposure to chromium and its compounds results in adverse effects on health, which vary according to the valency and water-solubility of the Cr compounds. The Cr (VI) compounds are of the most concern as they are classified as Category 1 carcinogens under the Chemicals (Hazard Information and Packaging for Supply) Regulations 2002 (CHIP). Other health effects experienced by platers include burns to and ulceration of the skin and mucous membranes, and skin and respiratory sensitisation. Perforation of the nasal septum and ulcers in the nose are ill effects which have been equally associated with persons employed at chromium plating baths (SEA, 2003).

It has been suggested that there are approximately 100 metal plating installations using Cr (III) worldwide (compared to 3,000 decorative plating installations) with 20 of such installations located in the UK. France and Spain are also indicated to have Cr (III) users (pers. comm.).

For hard chromium platers, while substitution with Cr (III) may not be an option, employers are still required under COSHH to ensure that their employees are handling hexavalent chromium safely. The SEA advises that Inspectors should ensure that employers have not only adequately assessed and controlled inhalation exposure but also dermal exposure, which in some circumstances is just as important. For Cr (VI) compounds, exposure should be reduced so far as is reasonably practicable and, in any case, below the occupational exposure level (OEL) of 0.05mg/m^3 (8-hour time weighted average (TWA)). For chromium (III) compounds, the exposure should be reduced to an OEL of 0.5mg/m^3 (8-hour TWA). In such processes where substitution of Cr (VI) is not practicable, or change of process feasible, the benchmark should be considered as nil/negligible likelihood of serious health effect (SEA, 2003).

5.4.2 Risk Reduction Measures in the Fire Fighting Foam Industry

Fire fighting foams containing fluorosurfactants are held in storage until required and are only used in emergency situations for fighting flammable liquid fires and in associated training exercises. It is suggested that training takes place in designated and controlled areas and usually is of limited scale and duration. The fire industry is encouraging fire fighting foam users to use fluorine free training foams for non-essential discharges and personnel training. The aviation sector is suggested to be moving in this direction to be able to satisfy both environmental and aviation regulators, and other users are considering going down a similar route in some regions in the UK.

BFPSA recommends foam users (2003a) to:

- avoid the unnecessary discharge of foams but where discharge is necessary to establish performance, foam amounts should be minimised and contained in catchment areas;

- pay particular attention to releases that could threaten conservation areas, drinking water reserves, aquifers or controlled waters (i.e. areas where rivers, lakes or ponds are present); and

- collect and dispose of in a controlled and responsible manner the foam concentrate and/or foam solution, as well as fire effluents. Prior to the release/discharge of foam in any form, consultation with the Health & Safety Officer of the facility and the responsible sewerage undertaker (usually water companies) should take place to ascertain the disposal procedures and advise on the intended use of foam and the expected releases.

Foam solution or small spills of foam concentrate, can be diluted with water to 250 ppm (i.e. 120 litres water per litre of foam solution or 4,000 litres per litre of foam concentrate) and then released to waste water treatment facilities in consultation with the receiving authorities. Larger volumes of foam concentrate must be disposed of through licensed disposal companies (BFPSA, 2003a). It should be noted that the Environment Agency and the Fire Services reportedly have a joint protocol (effective from November 1999) concerning the use of fluorine containing foams.

Current Practices at Facilities Using Fire Fighting Foams

It is understood that in live fire training facilities when fire fighting foam is applied to a controlled burning flammable liquid surface (e.g. kerosene), it is drained-off or run-off to the facility water treatment plant, if such a facility exists. The plant will usually consist of an oil/water separator or interceptor which levels off the hydrocarbons (contained in the foam) and a pump which transfers the wastewater off-site for re-use or disposal to private or public sewerage undertakers (usually water companies in the UK). The hydrocarbons are pumped off when the level reaches a specified design height.

Several live fire training facilities use retention basins to hold discharged firewater and foam solutions. However, this is not necessarily to reduce the environmental impact, but is more for firewater recycling reasons. This ‘spent’ water can be re-used for training purposes, however, the continued addition of foam solution will eventually render the fluids useless for producing foam. When this occurs, the storage basin is again drained or pumped out to private or public sewerage undertakers without foam separation. At present, there is no evidence to suggest fire training facilities have the capability to treat the recovered fluids from live fire fighting exercises by removal or treatment of the foam concentrate/produced foam and the surfactants (Ramsden, 2002).

There appear to be only limited procedures in place at fire training facilities to treat the negative effects of fire fighting foam run-off. The impact of fluorochemicals are being reduced by storage and release to wastewater drain and sewer, but this just tends to relocate the problem (i.e. sewage treatment works) rather than comprehensively solve it.

Use of Training Foams

Consultation indicates that there are foams specifically designed and intended for use in training exercises by relevant bodies (e.g. Fire Brigades, aviation fire fighters, etc.). These foams behave like real foams with the same characteristics (e.g. foam expansion, drainage time, fluidity, etc.). They are, however, not intended for use on real fires as they would not form a sealing film on the burning surface and do not generally provide good post fire security[43].

Information suggests that training foams available in the UK are currently protein based. They are generally cheaper than the real foams[44] as they contain neither fluorosurfactants nor preservatives (fluorinated surfactants are expensive raw materials). They are also more environmentally friendly with particular regard to biodegradation, due to the absence of the fluorosurfactants.

There are indications that these types of foams are currently used in both the UK aviation sector and Fire Brigades. Consultation, however, suggests that the uptake of these training foams in the aviation industry has not been significant. One of the reasons is because aviation fire fighters tend to deal only with Class B fires and as such prefer to use the real foams in practice, so as to avoid a mix up in actual fire situations. Aerodromes within the UK are also reported to have worked towards introducing significant control measures to prevent contamination or release of foams into the water table (CAA, 2003).

With regard to Fire Brigades, information received suggests that UK Fire Brigades are currently carrying out little to no training exercises due to the environmental impacts of fire fighting foams, as well as UK legislative requirements.

5.4.3 Risk Reduction Measures in the Photographic Industry

Film and Paper Manufacturing Operations

Controls of occupational exposure include:

- use of personal protective equipment by workers employed at the formulation stage (uniforms, eye shields, and gloves, also respirators where necessary);

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[43] This may be an advantage in training exercises as the same fire could be used for repeated training exercises. The feasibility of this is however not known.

[44] In a few cases, the training foams may be slightly more expensive than the real foams, for instance, where foams are built to specifications.

- after mixing, the diluted PFOS containing mixtures are transferred via automatic piping from the mix preparation area to the production area where they are added to coating machines; coating operations need to be conducted in a clean environment, therefore access of personnel to coating machines is very limited. If the presence of workers is necessary (for instance, if a mechanical failure occurs), the use of personal protective equipment is necessary. Exposure to PFOS materials during mechanical failures is expected to be minimal as the PFOS materials are bound in coating media, some products have surface overcoats that cover PFOS containing coatings, and contact is at most limited to the hands, if gloves are not worn; and

- during finishing operations, imaging materials are slit to commercial sizes, films are perforated as needed, quality assurance tests are performed, and finished product is spooled, wrapped, and boxed. Operators use bulk handling equipment to transfer light sensitive materials to the slitting and perforating machines. These operations are automated to maintain the light sensitive nature of the product and avoid contamination with dust or other debris that can make the product unusable. Contact with the product is minimal but may occur during machine set-up, machine failure, and quality control sampling. Some dusts may be present during cutting and perforating operations; dust masks are available for use to reduce exposure.

EPCI advises that monitoring for occupational exposure was conducted in the USA in four different workplaces operated by one company where PFOS related products are handled and mixed with the co-operation of 3M. In all cases, the results showed that airborne concentrations in the workplace were below detectable levels (<0.013 mg/m^3) (EPCI, 2003).

Controls of environmental releases include:

- waste produced during the coating stage includes containers that originally held the PFOS product and coating waste. The containers are disposed of through high temperature incineration in a rotary kiln or placement in a secure landfill. Coatings that are excess or not suitable for use are sent for silver recovery where the waste is incinerated at high temperature. PFOS material that is not used amounts to 1-3% of the available PFOS material. Coatings that cannot be used amount to 5 - 28.5% of the available PFOS material; and

- wastes from the finishing stage are all solid and are either incinerated or sent for recovery. Ultimately, all of the PFOS waste is incinerated. Waste from finishing operations is in the range of 5 - 15% of the available PFOS.

Printing Plate Manufacturing Operations

Controls of occupational exposure include:

- employees use personal protective equipment (uniforms, eye shields and gloves);

- the coating process is fully automated and controlled to maintain a clean environment;
- automatic diluting and dispensing systems minimise human intervention; and
- products are typically packaged and boxed using automated equipment that minimises human contact. Where this is not possible, gloves are used to protect workers and the products from damage.

Controls of environmental releases include:

- waste produced during the coating stage includes containers that originally held the PFOS product and coating solution waste. These drums are disposed of by incineration. The coating waste is drummed and removed as solvent waste, which is incinerated at high temperature in a rotary kiln. Waste from this operation is in the range of 1 - 10% of the available PFOS; and

- waste produced during the packaging of the finished plates is essentially solid sheets of coated aluminium. The aluminium sheets are sent for incineration and recovery of the metal. Waste from this operation is in the range of 10-24% of the available PFOS; and

- under EC Hazardous waste directives, photoprocessing solutions are classified as hazardous and are typically hauled away by a licensed company for appropriate treatment. The most common treatment for photographic waste (incineration) prevents releases into the environment.

Film and Paper Processing Operations

Photoprocessing involves the development of latent images and fixation, bleaching, and washing of the film prior to printing, scanning, or direct viewing as in the case of medical X-ray film. Handling of film or paper is expected to provide only negligible contact with PFOS materials.

Approximately 5-10% of one PFOS material may be released from film into film developer. None of the other PFOS materials used in imaging would be expected to be released into photoprocessing solutions.

Printing Plate Processing Operations

Controls of occupational exposure include:

- operators are recommended to wear cotton gloves to handle plate bundles when loading the plates into an automated platesetter cassette; and

- operators responsible for the addition of developer solution in the photoprocessor use eye shields, rubber gloves and aprons. The operator does not come in contact with the developing solution since there are valves on the processor that are opened to release the developer directly into the wastewater collection and neutralisation system. Therefore, EPCI expects that occupational exposure to PFOS materials from use of printing plates does not occur.

Controls of environmental releases include:

- The aqueous developer in the processor is exchanged with fresh developer at regular intervals. It is estimated that 10 - 26.4% of the available PFOS material is removed during the developing process. Typical processor developer capacity is 2 or 3.2 litres (7.5 or 12 gallons), depending on the processor model. For waste handling, customers work with their local waste collectors. In addition, 12-34% PFOS is incinerated when the printing plates are sent for aluminium recovery (EPCI, 2003).

5.4.4 Risk Reduction Measures in the Semiconductors Industry

According to ESIA (2003), PFOS containing solutions for applications relevant to the semiconductors industry are used in closed systems with no human exposure during normal operation. Coated wafers are not touched by humans for a number of reasons including that this would destroy the product. Equipment maintenance is also performed with appropriate personal protective equipment.

The vast majority (92%) of PFOS related substances in photoresist is collected in solvent waste. Photoresist containing solvent waste is typically either sent for incineration (with or without energy recovery) or sent for distillation for recycling of some of the chemicals in the mixed solution. In the case of distillation, it is assumed that PFOS related substances (with a very high boiling point) remain in the undistillable bottom sludge.

ESIA believes that incineration of photoresist-containing solvent waste or of distillate sludge (from solvent waste recycling) by certified companies occurs at sufficiently high temperature to insure PFOS destruction. Antireflective coatings (ARCs) may or may not be included in the same solvent waste stream (ESIA, 2003).

5.4.5 Risk Reduction Measures in the Aviation Industry (Hydraulic Fluids)

Hydraulic fluids used in aviation are usually phosphate ester based fluids. Because they are good solvents, they can dissolve fatty acids of the skin, cause drying of the skin and in extreme cases, result in dermatitis or secondary infection from bacteria. Mechanics also have to take precautions when dealing with these fluids as phosphate ester fluids are strong irritants, particularly to the eyes. This means that the fluids have to be handled and disposed of carefully, by virtue of the phosphate esters (without particular regard to the presence of PFOS related substances).

Aircraft hydraulic fluids are used in closed loop systems, either in an aircraft or in a shop test stand, and routine exposure to people and the environment is kept to a minimum. In addition, normal airline safety practices establish that any leaks that do occur in a hydraulic system are quickly repaired. During the normal use of the fluids in an aircraft, the PFOS related substances do not undergo degradation and, upon completion of their useful life in an aircraft, spent hydraulic fluid is drained and incinerated. Any spills or leaks that may occur during blending or container filling are also absorbed on oil, dried and incinerated.

A potential pathway to the environment is during aircraft maintenance. Hydraulic system parts are routinely removed from an aircraft and tested in the shop, and fluid is occasionally drained from an aircraft for complete replacement. When drained from an aircraft, used fluid is collected and normally combined with other waste fluids for incineration. There exists the possibility for leakages and spills to the environment from these areas.

The PFOS related substances used in aviation hydraulic fluids are present at a concentration of about 500 ppm, and are thought to have a very low exposure potential. Serum PFOS concentrations were measured in 12 blood samples from workers blending fluid ingredients in a hydraulic fluid manufacturing plant. The results did not show elevated levels of PFOS in their blood serum, with the mean concentration of 91.5 ppb. The manufacturer believes that these values are within the 50-100 ppb range that are to be expected as background levels from population studies carried out by 3M (Industry, pers. comm.).

5.5 Other Initiatives

5.5.1 Overview

This section considers a number of recent regulatory and other initiatives that relate to the use of PFOS related substances. These are in addition to the studies that have been carried out by the Danish EPA and the Dutch Royal Institute of Coasts and Seas (RIKZ) reported in Section 2.2.

5.5.2 United States

Following the announcement by 3M in May 2000 to phase out the production of PFOS, the US EPA proposed a significant new use rule (SNUR) under section 5(a)(2) of the TSCA for 90 PFOS related substances on 18 October 2000 (US EPA, 2000).

A SNUR is not a ban. It requires companies to file a notice (a SNUN) with US EPA 90 days before beginning the new manufacture or import of listed PFOS chemicals. The US EPA could grant, deny or impose restrictions on the intended use. The required notice is intended to provide the US EPA with the opportunity to evaluate any intended new use and associated activities and, if necessary, to prohibit or limit that activity before it occurs. Persons who intend to import any chemical substance governed by a final SNUR would also be subject to import certification requirements as well as other regulations. As a result of the proposed SNUR of October 2000, a final SNUR was published in the US Federal Register on 11 March 2002 for 13 substances including polymers, that are derived from perfluorooctane sulphonic acid and its higher and lower homologues (see

Annex 2 for list of substances relevant to this SNUR). This rule became effective from April 2002 (US EPA, 2002a).

In December 2002, another SNUR was issued for 75 substances, including perfluorooctane sulphonic acid (PFOSA) and certain of its salts, perfluorooctane sulphonyl fluoride (PFOSF), certain higher and lower homologues of PFOSA and POSF, and certain other chemical substances, including polymers, that are derived from PFOSA and its homologues. This rule came into effect on 8 January 2003, and it incorporates a number of derogations for specific *PFAS* chemicals that are essential to their specific uses in the semiconductor, aviation hydraulics and imaging industries. The SNUR does not apply to (US EPA, 2002b):

∉ use as an anti-erosion additive in fire-resistant phosphate ester aviation hydraulic fluids;

∉ use as a component of a photoresist substance, including a photo acid generator or surfactant, or as a component of an anti-reflective coating, used in a photomicrolithography process to produce semiconductors or similar components of electronic or other miniaturised devices. The use of *PFAS* in developers is outside the scope of the exclusion, as is its' use in polyimides;

∉ use in coatings for surface tension, static discharge, and adhesion control for analogue and digital imaging films, papers, and printing plates, or as a surfactant in mixtures used to process imaging films. The use as a surfactant in mixtures to process papers and printing plates would be considered a significant new use under the rule; and

∉ use as an intermediate only to produce other chemical substances to be used solely for the uses above.

As mentioned earlier, the US EPA in related activities in fluorinated chemicals released a Preliminary Risk Assessment on the developmental toxicity of PFOA in April 2003. The US EPA is currently working to develop information on sources of PFOA in the environment and the pathways leading to human and environmental exposures to PFOA (US EPA, 2003).

5.5.3 Canada

Information received from Environment Canada, indicates that in the three years prior to 3M's May 2000 announcement of a voluntary phase out of PFOS related substances, the most prominent uses of *PFAS* in Canada were repellents for fabrics, packaging and carpets (it was not possible to determine the percentage of *PFAS* that were PFOS related substances).

Table 5.1 below provides an overview of the Canadian market between 1997 and 2000. The survey suggests that PFAS are not manufactured in Canada. Instead, a total of fifteen Canadian companies imported PFAS from the US, France, Germany and Japan during the period 1997-2000 (Windle *et al*, 2003).

Table 5.1: Survey Identified Uses of PFAS in Canada (for years 1997-2000)

Application area	**Percentage of *PFAS* Market**
Water, oil, soil and grease repellent for fabrics	43.6%
Water, oil, soil and grease repellent for packaging	28.2%
Water, oil, soil and grease repellent for rugs and carpets	14.2%
Fire fighting foams	6.0%
Surfactant-detergent, emulsifier, wetting agent, dispersant	2.8%
Chemical formulation component	1.8%
Coating and coating additive	1.7%
Water, oil, soil and grease repellent for paper	0.7%
Processing aid	0.4%
Water, oil, soil and grease repellent for stone, tile and concrete	0.2%
Other (including pesticides and insecticides)	0.2%
Polymer additive	0.1%
Water, oil, soil and grease repellent for leather	0.1%
Component of formulations for polymer manufacture	0.0%

Source: Windle (2003)

Approximately 256 *PFAS* have been identified so far as ever being in commerce in Canada (Windle *et al*, 2003).

In 2000, the Canadian Government required industry to provide data on certain *PFAS*, their derivatives and polymers. This required any person manufacturing, importing or exporting more than 100 kg of such substances (whether alone or in mixture) during the period 1997-2000 inclusive to notify the Minister of Environment of such activity by 11 July 2000 and to provide information on use patterns and environmental effects by 7 September 2000. The list of substances included 182 entries; and the information was intended to be used for the assessment of whether the substances or the classes of substances listed in Schedule 1 are toxic or are capable of becoming toxic, or for the purpose of assessing whether to control, or the manner in which to control the listed substances or classes of substances (Environment Canada, 2000).

Canada has prepared a draft list of PFOS related substances (precursors) . The draft list will be available in the draft screening assessment report on PFOS and its Precursors that the Departments of Environment and Health Canada will publish in early 2004 (Windle, 2003).

5.5.4 Australia

Information collected by Australia’s National Industrial Chemicals Notification and Assessment Scheme (NICNAS, 2003) indicates that:

- PFOS and *PFAS* based chemicals are not currently manufactured in Australia, however, products containing these chemicals have been made and are used in the country. PFOS has been the favoured group of the PFAS chemicals used in Australia;

- voluntary phase out agreements by Australian industries since 2000 have resulted in a rapid decrease in the use of PFOS chemicals;

- only three remaining uses of PFOS chemicals exist. These uses are in some Class B fire-fighting foams and in specialised industrial products used for processing rubber and in the production of paints and coatings. These PFOS products are not expected to be available after December 2003;

- there is only one other use of a *PFAS* chemical currently identified by NICNAS. This use is an adhesive which is expected to be phased out by 2004 when the existing stock is exhausted. The adhesive is used to bond timber for applications in the building and construction industry. The timber product can also be used by domestic consumers; and

- the phase out in Australia means old stocks of PFOS and *PFAS* based products may still be found in Australia or be held by consumers and industrial users.

NICNAS believes it has identified all the applications of PFOS in Australia. It is likely that some importers and users may not know that products contain these chemicals because PFOS and PFAS based chemical ingredients may not be mentioned on Safety Data Sheets.

On the basis of the above findings and taking into account work undertaken in the US, Canada and elsewhere, NICNAS has recommended that (NICNAS, 2003):

- PFOS and related *PFAS* based chemicals be restricted to only essential uses, for which no suitable and less hazardous alternatives are available, such as certain Class B fire fighting foams;

- PFOS based fire fighting foam not be used for fire training purposes to limit environmental release;

- PFOS users exercise caution in selecting PFOA as an alternative, as PFOA may have the same environmental and health concerns as PFOS (as described elsewhere in this report, work on PFOA is still ongoing);

- all labels and Safety Data Sheets include details of the *PFAS* and PFOS chemicals in the product; and

- information on the safe use and handling of all these chemicals of concern be provided to fire fighters in the relevant and most recent Safety Data Sheets available from the suppliers of these chemicals.

NICNAS is now working on the collection of information on the import, manufacture, use and health effects of the PFOS alternatives perfluorooctanoic acid (PFOA) and perfluorinated telomer chemicals and products (NICNAS, 2003).

5.5.5 OSPAR Convention

At a ministerial meeting of the Contracting Parties to the OSPAR Convention in Sintra in 1998, it was agreed that man-made hazardous substances should not occur in the marine environment and that naturally occurring hazardous substances should not exceed natural background concentrations. To this end, it was agreed to make every endeavour to cease all discharges, emissions and losses of hazardous substances that could reach the marine environment by the year 2020 (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[45].

An associated fact sheet could also be developed for PFOS based 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:

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[45] 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).

- **perfluorooctanyl sulphonamide and sulphonyl compounds and derivates (PFOS type)**: all PFOS based 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 list 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;

- **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 4.3 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 4.3 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)[46] 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 5.2 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.

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[46] The Working Group on Priority Substances (SPS) convenes an intersessional correspondence group called Informal Group of DYNAMEC (Dynamic Selection and Prioritisation Mechanism for Hazardous Substances) Experts (IGE).

Table 5.2: List of Perfluorinated Chemicals which are either MPV Chemicals, on IUCLID and/or on the OSPAR List of Chemicals of Possible Concern	
CAS Number	**Name of Compound**
Perfluorinated 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
Perfluorinated Alkyl Sulphonyl Compound and Derivates	
375-72-4	1-Butanesulphonyl fluoride, -nonafluoro-*
423-50-7	1-Hexanesulphonyl fluoride, -tridecafluoro-*
Perfluorooctanoic Acids and Salts	
335-67-1	Octanoic acid, pentadecafluoro-
3825-26-1	Octanoic acid, pentadecafluoro-, ammonium salt*
Perfluorinated 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
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
Perfluorinated 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)-
Perfluorinated Alkanes with Single Iodide 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*	

6. POSSIBLE FURTHER RISK REDUCTION MEASURES

6.1 Risks to be Addressed

When considering the need for further risk reduction measures and what these measures may be, it is important to focus on the risks of concern. The results of the Review of Environmental Risks (RER) presented in Annex 4 provide some indication of the magnitude of releases, where the risks of concern may lie and for what sectors. However, as the RER also concludes that PFOS is a PBT, (near) zero emissions are the objective for this risk reduction strategy. It is therefore necessary to consider the full spectrum of uses of PFOS and their possible routes to the environment.

The discussion in Section 2 indicates that the cessation of production of PFOS by 3M has led to a significant move away from the use of PFOS in certain applications (notably carpets, paper and packaging). In considering the need for further risk reduction measures, it is useful therefore, to draw a distinction between the control of risks associated with continuing (existing) uses and those associated with historical uses.

As a result, the focus for the risk reduction strategy can be partitioned into two principal objectives:

- reducing risks associated with the current uses and any stockpiles of PFOS containing materials (such as fire fighting foams); and

- ensuring that the risks associated with historical uses do not ‘re-occur’ should an alternative source of PFOS become available.

Table 6.1 provides a summary of uses on this basis.

6.2 Identification of Possible Measures

6.2.1 Identification of Available Measures

Types of risk reduction measures that can be applied for a given chemical are outlined in the Technical Guidance Document (CEC, 1998).

The measures relating to manufacture, industrial and professional use of substances are summarised in Box 6.1, while Box 6.2 outlines the measures related to domestic and consumer use and those related to waste management. The measures identified in Box 6.1 and 6.2 have been screened (in early stages) in order to eliminate from consideration those that are not relevant to PFOS and its uses.

Table 6.1: Use Applications of PFOS Related Substances and Risk Reduction Measures

Applications/Sector	**Possible Pathways to the Environment**
Existing Confirmed Uses	
Fire Fighting Foams	Training
	Fire fighting
	Waste/Old Stock
Photographic Chemicals	Manufacture
	Processing
	Waste
Photolithography and Semiconductors	Manufacture
	Waste
Hydraulic Fluids	Aircraft maintenance
	Factories testing new components
	Waste
	Accidental loss
Metal Plating	Manufacture of preparations
	Metal plating process
	Waste
Historical Uses (Evidence of Use in UK and EU)	
Textiles	
Leather	
Carpet	
Paper and Packaging	
Coatings	
Historical Uses (Evidence of Use in EU (but not UK))	
Industrial and Household Cleaning Products (Surfactants)	
Pesticides and Insecticides	
Historical Uses (No evidence of use in UK and EU)**	
Medical Applications	
Mining and Oil Surfactants	
Flame Retardants	
Adhesives	
**As there is no evidence of the use of PFOS related substances in the following applications in the UK and EU more generally, these uses would not be considered any further in this risk reduction strategy.	

Box 6.1: Possible Risk Reduction Measures for Manufacture and Industrial/Professional Use

- Controls on manufacture;
- restrictions on the marketing and/or use of the substance under Directive 76/769/EEC;
- re-designing the process itself, or changing the substances or materials used in it;
- safe systems of work, such as specified standards of physical containment or extraction ventilation;
- application of good manufacturing practice, for example, under ISO standards;
- classification and labelling;
- separation of personnel;
- monitoring and maintenance of equipment;
- dust suppression methods, such as the use of substances in tablet or pellet form;
- occupational exposure limits and/or air monitoring in the workplace;
- accurate hazard information (for example, safety data sheets), and/or better delivery of safety information, such as clearer labelling or the provision of warning signs in the workplace;
- biological exposure indices and/or biological monitoring of workers;
- medical surveys of workers;
- training;
- use of personal protective equipment;
- licensing of operators of certain operations;
- ‘end-of-pipe’ controls to minimise, neutralise or render less harmful any emissions than cannot practicably be avoided otherwise;
- limit values for emission and effluent monitoring; and
- environmental quality standards and/or environmental monitoring.

Source: CEC (1998)

Box 6.2: Possible Risk Reduction Measures for Domestic Use and Waste Management

Domestic and Consumer Use

- Restrictions on the size of container;
- design of containers including non-spill or narrow-neck containers;
- limits on concentrations of components;
- product design changes, e.g. encapsulation;
- limits of the overall quantity available to each user;
- addition of an emetic, a stanching agent or a colorant;
- restrictions on use;
- classification and labelling;
- hazard warnings and/or use instructions on packaging;
- tactile danger warnings; and
- child resistant closures.

Waste Management

- Classification as hazardous waste;
- labelling which encourages responsible disposal;
- producer responsibility schemes;
- use of recycling banks;
- duty of care systems;
- compulsory acceptance of returned products; and
- specified disposal methods and/or conditions, for example, incineration (temperature and time).

Source: CEC (1998)

In terms of the measures that are applicable to PFOS, the following can be removed from the list relating to the professional and industrial use of PFOS (Box 6.1):

- use of dust suppression methods (though occasionally supplied as solids, perfluorochemicals are typically used in liquid form);

- monitoring and maintenance of equipment (PFOS is a breakdown product of perfluorinated chemicals, hazards (or risks) associated with exposure to PFOS related substances are not a result of lack of maintenance);

- classification and labelling (there is no classification of PFOS related substances at present; proposing suitable classification and labelling, if necessary, is outside the remit of a Risk Reduction Strategy, although the need for such classification and labelling can be recommended);

- biological exposure indices and/or biological monitoring of workers (could be useful for the identification of hazards and the quantification of the associated risks but cannot be considered as a risk reduction option); and

- medical surveys of workers (as above for biological monitoring).

The following can be removed from the list of measures relating to the domestic and consumer use of PFOS (Box 6.2):

- classification and labelling (for reasons as above);

- restrictions on the size of container (would not affect releases of PFOS related substances into the environment);

- design of containers including non-spill or narrow-neck containers;

- addition of an emetic, a stanching agent or a colorant (not relevant for PFOS related substances and their mode of use);

- tactile danger warnings (not of relevance based on identified hazards); and

- child resistant closures (not of relevance based on identified hazards).

With regard to waste disposal, the following can be removed from further consideration:

- the use of recycling banks (not of relevance on the basis of identified hazards, though it could be considered as part of a wider waste limitation/recycling component of industrial uses); and

- compulsory acceptance of returned products (has limited relevance to products that contain PFOS related substances).

6.2.2 Identification of Possible Measures

Given the above analysis, the measures of potential relevance to the hazards and risks associated with PFOS and its uses are:

Manufacture and Industrial/Professional Use

- Controls on manufacture;
- Restrictions on the marketing and/or use of the substance (for example, in the EU under Directive 76/769/EEC);
- Re-designing the process itself, or changing the substances or materials used in it;
- Safe systems of work, such as specified standards of physical containment or extraction ventilation;
- Application of good manufacturing practice, for example, under ISO standards;
- Occupational exposure limits and/or air monitoring in the workplace;
- Accurate hazard information (for example, safety data sheets), and/or better delivery of safety information, such as clearer labelling or the provision of warning signs in the workplace;
- Training;
- Exposure control including use of personal protective equipment;
- Licensing of operators of certain operations;
- ‘End-of-pipe’ controls to minimise, neutralise or render less harmful any emissions than cannot practicably be avoided otherwise;
- Limit values for emission and effluent monitoring; and
- Environmental quality standards and/or environmental monitoring.

Domestic and Consumer Use and Waste Disposal

- Limits on concentrations of components;
- Product design changes;
- Limits of the overall quantity available to each user;
- Restrictions on use;
- Hazard warnings and/or use instructions on packaging;
- Classification as hazardous waste;
- Labelling which encourages responsible disposal;
- Producer responsibility schemes; and
- Specified disposal methods and/or conditions, for example, incineration (temperature and time).

6.3 Means of Implementation

6.3.1 Possible Means of Implementation

The Technical Guidance Document (CEC, 1998) identifies a range of possible administrative, legal and/or other tools that could be used to take forward proposed risk reduction measures. These are as follows:

- information programmes and other EC/government initiatives;

- unilateral action by industry (the Technical Guidance Document indicates that additional risk reduction measures may be necessary unless unilateral action is taken by the majority of firms involved);

- voluntary agreements (such as negotiated agreements between industry and governments);

- technical standards and authoritative guidance (statutory, advisory or voluntary);

- regulatory controls, including more effective enforcement of existing controls, amendments to existing legislation or new legislation (such as uniform EU controls, target based controls - e.g. on the amount emitted to water - or restrictions on marketing and use); and

- economic instruments including taxes (such as emission taxes or product taxes), subsidies or tradeable permits.

These are discussed in more detail in the following sections. In considering these, information programmes are considered as a means of influencing industry self-regulation (for example, through unilateral action and voluntary agreements) for the eventual introduction of regulatory guidance and/or standards.

6.3.2 Unilateral Action by Industry

The TGD indicates that additional risk reduction measures may be necessary unless unilateral action is taken by the majority of firms involved. In this respect, the unilateral action by 3M can be considered to be a fairly unique example of a single company accounting for the majority of global production for a large group of substances.

As discussed earlier, the unilateral action taken by 3M has had a significant effect on the users and uses of PFOS. The knock-on effect of this has been a move towards alternatives in most sectors. However, this change in use patterns has been forced perhaps more by the lack of supplies than by a concerted and deliberate decision on the part of users to move away from PFOS. The fact that many of the users (and former users) of PFOS were not aware that they were using it would tend to support this viewpoint. In the main, these were uses where PFOS was not a safety or technology critical application.

6.3.3 Negotiated Voluntary Agreements

For uses where PFOS has safety and technology critical applications, 3M’s action has stimulated some voluntary action. The EPCI indicates that the companies in the imaging industry sector began programmes in mid-2000 to reduce and replace PFOS materials and, as a result, reductions in the usage of PFOS related substances are being made worldwide. The industry reports significant reductions (83%) in PFOS requirements on a global scale through voluntary efforts. The imaging industry is highly competitive and has an interest in driving manufacturing waste and photoprocessing solution waste down. This reduction in waste will consequently reduce releases of PFOS related substances further. Some of the products that still use PFOS related substances that have not been reformulated (and are non-critical uses) will be discontinued as changes in imaging technology make them obsolete (EPCI, 2003).

However, as noted earlier, the unilateral action by 3M will not guarantee that the potential risks associated with PFOS will continue to be addressed, baring in mind the presence of other potential manufacturers of PFOS related substances globally. In addition, whilst voluntary agreements are achieving some success, there may be a need to take steps to formalise the reductions in use to ensure that risks continue to be addressed.

One of the ways by which this could be achieved is via negotiated agreements between industry and government. Such agreements can potentially allow for tailor-made solutions to environmental risks to be adopted in a more timely and cost-effective manner than through traditional regulatory approaches. However, in order to avoid non-compliance amongst participating companies or associations, such agreements generally have to be supplemented by the threat of legislation. Thus, pre-requisites for the effective functioning of such agreements often include:

- a sufficient coverage in order to cover the bulk of emissions;
- clearly defined goals;
- public awareness of the agreement in order to provide an incentive for compliance;
- an effective means of monitoring compliance with the agreement; and
- legislative action to occur should there be non-compliance.

In the case of PFOS, such an agreement could take the form of one of the following:

- an agreement to modify the processes, such that emissions from PFOS are below a certain level (or are reduced to zero); or
- an agreement to phase-out the use of PFOS or to reduce and limit use to a certain level.

In terms of the former, in the UK, the joint Protocol concerning the use of fluorine containing foams which was agreed between the Environment Agency for England and Wales and the UK Fire Service goes some way towards meeting risk management objectives. However, this protocol as its stands will not achieve (near) zero emissions.

6.3.4 Legislation to Control Emissions and Exposure to PFOS Related Substances

A range of existing Community-level legislation (with implementing legislation in the Member States) applies to manufacturing and production processes, use and disposal of chemical substances, etc.

Legislation Predominantly Applicable to the Protection of the Environment

IPPC Directive

Under the IPPC Directive, a framework is provided for controlling emissions from certain industrial facilities. Sites should be operated according to the 'best available techniques' (BAT) which are, or will be, set out for the various process types covered in BAT Reference Documents. Emissions limits and process conditions for individual sites are then established by the Member States. The Directive 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).

Water Framework Directive

The Water Framework Directive (2000/60/EC) introduced a new framework for controls on certain 'priority substances' that present a significant risk to or via the aquatic environment. PFOS related substances are, however, not included in the list of priority substances or priority hazardous substances for which the Commission will submit proposals for a cessation or phase-out of discharges, emissions and losses.

Under the Groundwater Regulations of 1998 (Statutory Instrument 1998 No. 2746), classes of compounds are listed into List I (most harmful) and List II (slightly less harmful). PFOS-based fluorosurfactants used in various sectors (e.g. fire fighting foams, industrial and household cleaning products, etc.) are by definition organohalogen compounds and, as such, are List 1 substances. This means that the disposal of used solutions of such fluorosurfactants onto or into ground, with the likelihood that it will reach groundwater is prohibited under the regulations[47].

This applies except where authorisation is granted by the Environment Agency. Under the Regulations, a substance is not in List I if it has been determined by the Environment Agency to be inappropriate to List I on the basis of a low risk of toxicity, persistence and bioaccumulation. As PFOS is a PBT, it appears likely that any PFOS-based fluorosurfactant will not qualify to be removed from List 1.

It should be noted that organohalogen compounds are in the indicative list of main pollutants in Annex VIII of the Water Framework Directive.

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[47] Under the Regulations, an authorisation shall not be granted if it would permit the direct discharge of any substance in List I.

Packaging and Packaging Waste Directive

European Parliament and Council Directive 94/62/EC of 20 December 1994 on packaging and packaging waste aims to harmonize national measures concerning the management of packaging and packaging waste. Its purpose is, on the one hand, to prevent or reduce any impact on the environment of Member States (as well as of third countries) and, on the other hand, to ensure the functioning of the internal market and to avoid obstacles to trade.

It should be noted that Annex II, paragraph 1 to the Directive states that:

> *'packaging should be so manufactured that the presence of noxious and other hazardous substances and materials as constituents of the packaging material or of any of the packaging components is minimised with regard to their presence in emissions, ash or leachate when packaging or residues from management operations or packaging waste are incinerated or landfilled'.*

These provisions may be of relevance to placing controls on the future use of PFOS based formulations, for example in paper coatings.

Landfill Directive

The Landfill Directive (1999/31/EC) was adopted in July 1999 and sets out operational, regulatory and technical requirements for the landfill of waste. It sets out restrictions on the disposal of certain hazardous and liquid waste.

Waste Incineration Directive

Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste aims to prevent or limit the negative effects of incineration and co-incineration of waste on the environment and human health. This is achieved by means of operational conditions and technical requirements, through setting emission limit values for waste incineration and co-incineration plants within the Community and also through meeting the requirements of Directive 75/442/EEC (the Framework Directive on Waste by the European Council).

Directive on Hazardous Waste

Council Directive 91/689/EEC of 12 December 1991 on hazardous waste (as amended) was introduced in the general framework of Directive 75/442/EEC on waste and its aim is to approximate the laws of the Member States on the controlled management of hazardous waste.

The Directive includes a number of Annexes which describe:

- the categories or generic types of hazardous waste listed according to their nature or the activity which generated them (waste may be liquid, sludge or solid in form) (Annex I, parts A and B);
- the constituents of the wastes in annex I.B. which render them hazardous when they have the properties described in annex III (Annex II); and
- the properties of wastes which render them hazardous (Annex III).

It should be noted that some of the properties noted in Annex III (by way of example, ‘toxic’, ‘corrosive’, carcinogenic’) are based on the criteria laid down in Directives 67/548/EEC and 1999/45/EC on classification and labelling of dangerous substances and preparations. There is no classification and labelling for PFOS at present under 67/548/EEC or 1999/45/EC.

Legislation Applicable to the Protection of Human (Occupational) Health

At EU level, the following measures may be relevant to PFOS and the control of risks to occupational human health:

- Directive 67/548/EEC which approximates the laws, regulations and administrative provisions in Member States relating to the classification, packaging and labelling of dangerous substances;
- Directive 89/391/EEC which aims to ensure a higher degree of protection of workers against accidents and occupational diseases in the workplace, through the implementation of preventive measures, provision of information, consultation, balanced participation and training of workers and their representatives;
- Directive 89/656/EEC, which is the third individual directive within the meaning of Article 16 (1) of Directive 89/391/EEC, laid down minimum requirements for personal protective equipment used by workers at work; and
- Directive 1999/45/EC which approximates the laws on the classification, packaging and labelling of dangerous preparations to ensure protection of public health and the environment as well as free movement of such products.

Legislation Applicable to the Protection of Consumer Health

Directive 2001/95/EC of the European Parliament and of the Council of 3 December 2001 on general product safety (which replaced Directive 92/59/EEC) aims to ensure that products placed on the market are safe. In the context of the Directive, a ‘product’ means any product which is intended for consumers (or likely to be used by consumers). ‘Safe product ’means a product which does not present any risk or only the minimum risks compatible with the product’s use and taking into account, among others, its composition and packaging.

Legislation Requiring a Cessation or Phase-Out of Use

At the national (UK) level, restrictions on industrial and agricultural products can be introduced through the Technical Standards Directive (98/34/EC[48]). These restrictions could be introduced as either technical standards (voluntary technical specifications) or technical regulations (obligatory technical specifications). This Directive allows Member States to take measures for preventative or precautionary reasons, subject to clearance from EU authorities.

Member States are obliged to notify to the Commission the proposed technical regulations and are expected to observe a three month standstill period before the regulation is made or brought into force. This is to provide an opportunity for the Commission and other Member States to comment if they consider that the proposed regulation has the potential to create a technical barrier to trade. A number of substances have already been restricted under this Directive in various Member States[49].

At the EU level, the main established route for introducing restrictions on the marketing and use of substances is Directive 76/769/EEC concerning the marketing and use of certain dangerous substances and preparations.

A number of substances have already been restricted under this Directive and the procedures for implementing such restrictions are well established. A variety of different types of restrictions have been introduced for other substances, with derogations proposed in some applications. Marketing and use restrictions do not simply constitute a ban on use and can be very flexible in their approach to use and associated risk issues. It is important to note that conditions can be attached to any derogations, including time factors and process technologies.

6.3.5 Provision of Information (Technical Standards or Guidance)

There may be some scope to make recommendations for classification and labelling which would result in the production of official guidelines on PFOS. Alternatively, industry could be encouraged to adopt the appropriate risk phrases and labelling voluntarily. The provision of information in the form of industry technical standards and guidance could help as part of a wider strategy to reduce risks.

The protocol developed between the Environment Agency and the fire service in the UK on fire fighting foams represents an example of the use of such technical standards and guidance within a voluntary agreement.

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[48] Directive 98/48/EC of the European Parliament and of the Council of 20 July 1998 Amending Directive 98/34/EC Laying down a Procedure for the Provision of Information in the Field of Technical Standards and Regulations.

[49] For example, a notification by the Netherlands to introduce national measures concerning wood treated with copper substances was considered by CSTEE in 2002 and Denmark has introduced legislation banning the production of new materials containing cadmium, and draft legislation on recycling PVC containing lead.

6.3.6 Economic Instruments

Economic instruments can be applied to provide an ongoing financial incentive to achieve reductions in emissions from the use of substances. The following types of economic instrument may be relevant to the risk management of PFOS related substances:

- **emissions charge**: this type of scheme can be used to levy a per unit charge on emissions of substances to the environment. Clearly, as (near) zero PFOS emissions are required, this would not be an appropriate instrument;

- **product charge**: this involves levying a charge on the use of substances in all or certain applications to reduce use. As the charge is independent of emissions, such an approach requires that other measures are in place to ensure (near) zero emissions;

- **tradeable permits**: permit trading schemes can be developed to place a ceiling on the quantity of substances consumed in the EU, or on emission levels, within the various industry sectors, with users then able to trade permit quantities. Clearly, given that (near) zero PFOS emissions are required, this is not an appropriate instrument; and

- **liability based regimes**: instruments such as a performance bond could be used to reinforce voluntary commitments. Their operation within this context is likely to be highly complex, however, and this is unlikely to be an appropriate instrument in this case.

Whilst it is currently unclear how economic instruments could be given legal force through EU legislation, Directive 76/769/EEC may provide the most appropriate legal framework in the European context. In terms of action by the UK alone, however, a product charge could provide a means to encourage the development and uptake of alternatives and emissions control.

7. ASSESSMENT OF FURTHER RISK REDUCTION MEASURES

7.1 Introduction

7.1.1 Background

The TGD specifies that possible further risk reduction options should be examined against the following four decision criteria:

- **effectiveness**: the measure must be targeted at the significant hazardous effects and routes of exposure identified by the risk assessment. The measure must be capable of reducing the risks that need to be limited within and over a reasonable period of time;

- **practicality**: the measure should be implementable, enforceable and as simple as possible to manage. Priority should be given to commonly used measures that could be carried out within the existing infrastructure (though not to the exclusion of novel measures); and

- **economic impact**: the impact of the measure on producers, processors, users and other parties should be estimated; and

- **monitorability**: monitoring should be possible to allow the success of risk reduction to be assessed.

In the context of PFOS, as noted in Section 6, the focus for a risk reduction strategy can be partitioned into two principal objectives:

- reducing risks associated with the remaining uses and the stockpiles of PFOS containing materials (such as fire fighting foams); and

- ensuring that the risks from historical uses (or the uses themselves) do not 're-occur' should an alternative source of PFOS become available.

Table 6.1 provided this division in terms of the current uses of PFOS related substances and the historical uses in the UK and EU.

The following sections provide a semi-quantitative assessment of risk reduction options beginning with current uses. The remaining (historical) uses and associated risk reduction options are then discussed separately as a means of identifying the most appropriate options for preventing the recurrence of use (which is a different issue).

7.1.2 The Environmental Risk Review

Emissions from Current Sources

The RER identifies a risk of secondary poisoning for all uses and local risks to the terrestrial and aquatic environment for formulation and use of fire fighting foams. Table 7.1 summarises the risks identified in the RER for existing uses.

Table 7.1: Summary of Risks from Various Use Sectors of PFOS

Industry Sector	**Local Risk to the Terrestrial Compartment**	**Local Risk to the Aquatic Compartment**	**Risk of Secondary Poisoning**			
			Risk to Freshwater Food Chain	**Risk to Marine Predator (feeding on fish)**	**Risk to Marine Top Predator**	**Risk to Terrestrial Food Chain**
Chromium Plating			V	V	V	
Fire Fighting Foams (formulation)	V	V	V	V	V	V
Fire Fighting Foams (use)[1]	V	V	V	V	V	V
Photography (formulation)[2]			V	V	V	V
Photography (developing)			V	V	V	
Photolithography[3]			V	V	V	V
Aviation[4]			V	V	V	V

[1] Fire fighting foams (use): Risks to the aquatic compartment, terrestrial compartment and terrestrial food chain (secondary poisoning) for Use pattern B.

[2] Photography (formulation): Risk of secondary poisoning is for some scenarios.

[3] Photolithography: Risk of secondary poisoning assumes instant breakdown of PFOS-substances to PFOS.

[4] Aviation: Risk of secondary poisoning is for one scenario.

7.1.3 Existing Industrial and Professional Uses

Table 6.1 identified the following existing uses of PFOS based substances where these all represent industrial and professional uses:

- use of remaining PFOS fire fighting foam stock;
- photographic chemicals;
- photolithography and semiconductors;
- hydraulic fluids; and
- metal plating.

The possible measures identified in Section 6 are discussed with reference to their target and means of operation in as follows:

- manufacturing process changes (Section 7.2);
- environmental emissions control (Section 7.3);
- exposure control (Section 7.4);

- provision of information and guidance (Section 7.5);
- waste disposal (of PFOS containing products) (Section 7.6); and
- cessation or phase-out in use (Section 7.7).

7.1.4 Historical Uses

Table 6.1 identified the following historic uses of PFOS based substances:

- carpets, textiles and leather;
- paper and packaging;
- coatings and coating additives;
- industrial and domestic cleaning products; and
- pesticides and insecticides;

Domestic and consumer use is likely to represent a significant proportion of the total release of PFOS from the above applications and the possible measures are discussed in Section 7.8.

7.2 Manufacturing Process Changes

7.2.1 Available Measures

The relevant measures identified in Section 6 for application to existing industrial and professional users are as follows:

- controls on manufacture; and
- re-designing the process itself, or changing the materials used in it.

These measures reflect changes in the process itself to reduce/eliminate emissions of PFOS related substances. Table 7.2 provides an overview of the applicability of these measures to existing industrial and professional uses.

Further discussion of process changes is limited to their application to chromium (VI) metal plating.

7.2.2 Effectiveness

As discussed in Section 7.1, the emission estimates for PFOS from chromium plating vary, as there is uncertainty concerning the fate of PFOS related substances regularly added to plating solutions to provide mist suppression. The RER, and these proposals for risk reduction, assume that the emissions are of the higher magnitude at 500kg/year in the UK (or 250 kg/year regional).

Table 7.2: Applicability of Manufacturing Process Changes

Application	**Applicability**
Remaining stocks of PFOS based fire fighting foam	Process controls are irrelevant to the risks associated with fire fighting foams as PFOS is no longer used in the manufacture of such foams.
Photographic applications	Use of PFOS based materials is partly related to process safety as PFOS helps to prevent static discharge. The existing use of PFOS in the sector enables a number of the manufacturing operations to take place and, where it is used in manufacturing processes, the light and atmospheric sensitivity of the materials requires that it is used under highly controlled conditions. It is considered, therefore, that changes to the process used are unlikely to have any impact on process risks from this sector.
Photolithography and semiconductor applications	PFOS is used under highly controlled and contained atmospheric conditions due to the sensitivity of the product. Changes to these processes are therefore also unlikely to have any impact on process risks.
Aviation hydraulic fluids	Process controls are more relevant to containment and environmental emission of fluids during maintenance activities. These are considered in the section on emissions control.
Chromium VI plating	The substitution of hexavalent chromium (CrVI) with the less hazardous trivalent chromium (CrIII) in decorative plating applications would remove the need for the use of chemical mist suppressants in the decorative plating sector. Changes to hard CR (VI) plating processes are also available and involve mechanical mist suppression (for example, by tank enclosure) and the provision of extraction ventilation.

The discussion in Section 4 has identified the following options for alternative processes/operations (there being no alternative to PFOS in chemical suppressants):

- for **all platers** (decorative and hard plating), the provision of (additional) extraction ventilation;

- for **hard platers**, the provision of (additional) extraction ventilation and/or the provision of greater tank enclosure (due to longer immersion periods); and

- for **decorative platers**, a move away from the use of Cr (VI) processes to Cr (III) processes.

As the option involves substituting the use of chemical mist suppressants with tank enclosure and/or upgraded ventilation extraction systems, full implementation of the measure would provide total elimination of PFOS emissions associated with this sector (500kg/year reduction in the UK).

7.2.3 Practicality

Table 7.3 provides estimates of the percentage of companies of different size in the UK, where these have been applied to the numbers of platers (300 hard and decorative) in the UK, as reported in previous sections.

Table 7.3: Number and Size of Companies (after data from HSE)

Company Size (Number of Employees)	Percentage	Companies
>250	2%	6
10-249	38%	114
<10	60%	180
Total	**100%**	**300**

In 2007, chromium plating operations above a certain threshold will be covered by IPPC, which will require the consideration of the use of less hazardous substances and Best Available Technology (BAT). However, as can be seen from the data in Table 7.3, data would tend to suggest that at least around 60% of companies (180) are unlikely to be covered by IPPC. Actual estimates are that as the IPPC Directive has a 30 cubic metre vat capacity for this sector, even if all the process tanks in an installation are added together, IPPC will only affect about 10-20% of the installations in the sector. The size of tanks is not entirely related to throughput but also to the size of components treated. A small process line below the IPPC threshold could have a higher throughput and therefore consume and emit more materials (including PFOS) than an IPPC-controlled one.

In terms of implementation through IPPC, the smaller plating operations that make up the majority of companies would not be covered and, as such, it would be impractical to encourage the uptake of extraction ventilation and a move to Cr (III) processes by decorative platers through this route.

The alternatives are conditions on marketing and use. These could be based on a negotiated voluntary agreement or regulated at EU level under the Marketing and Use Directive (76/769/EEC). The latter would have to be focussed on restricting the use of the substance itself (i.e. PFOS) rather than on the introduction of the process controls that can be used to eliminate its use.

Probably, a pre-condition then, particularly in relation to hard plating, is the existence of occupational exposure levels (OELs) for Cr (VI) fumes. If these are not in place or robustly enforced, restrictions on use would not necessarily result in the introduction of the upgraded ventilation/enclosure systems required to maintain low occupational exposure.

For the UK situation it can be assumed that ventilation would be introduced to maintain the standards of the OELs (and this is what costs are based on). At an EU level it is not known whether all member states have (or enforce) occupational exposure levels for Cr

(VI). Care is required in this respect to ensure that any 'ban' on use does not result in an increase in occupational risks in Member States.

In terms of voluntary agreements, several initiatives have been attempted to encourage a shift from Cr (VI) to Cr (III) for decorative plating. These include industry and regulatory authority initiatives. To date these have had only limited success owing to a number of factors including platers having to respond to customer's specifications. This has been reported to us as a big obstacle to a voluntary approach, and to setting BAT in the BREF note under IPPC as customer's specifications need to be brought within the process. As such, restrictions on marketing and use (for example at EU level under 76/769/EEC) may be the only way of forcing the necessary shift in practices. The UK HSE will be starting a new initiative on Cr (III) this year (2004).

7.2.4 Economic Impact

Through consultation, the cost of upgrading ventilation extraction systems has been estimated as £40,000 per company. Annualised over 15 years (at the UK social discount rate of 3.5%) this equates to a maximum annual cost of £3,400 per company per year. It should be noted, however, that this figure does not include the operational savings from no longer purchasing chemical mist suppressants (containing PFOS related substances). The US EPA estimates operational costs of chemical mist supressants as being between £750 and £12,700 per year depending on the size of operation.

If these cost savings are subtracted from the annualised costs of £3,400 per company per year (calculated above), then this is reduced to a cost of between £2,700 per year to a **net benefit** of £9,200 per year. However, for the remainder of this analysis, these cost savings will not be included on the basis that there may be some additional operational costs associated with implementing improved extraction ventilation/tank enclosure and that these may be the same order of magnitude as the cost savings from no longer using chemical mist suppressants. The costs per company of the option are therefore taken as £3,400 per year.

Assuming that upgraded ventilation is not part of the emissions control systems maintained at present, the costs of additional extraction could be incurred by all platers (300). The total annualised costs across all platers are estimated at just over £1 million per year in the UK accompanied by a reduction in emissions of 500 kg per year if all platers (including decorative) employed the measure.

However, in practice decorative platers are likely to switch to the use of Cr (III) to avoid the costs and take up the potential net financial benefits from moving to this process.

In this case, the costs would only be experienced by hard platers who cannot (at present) take up Cr (III) technology or alternative processes. There are estimated to be 100 such companies that could not move to alternative plating technologies. On this basis, the total annualised costs of all hard (Cr (VI)) platers adopting improved ventilation for chemical mist suppressants are around **£350,000 per year**.

7.2.5 Monitorability

As indicated above, voluntary approaches have been limited in their success regarding the uptake of technologies in decorative plating. Once in place, the structure of the large number of smaller enterprises that make up the industry may mean that monitorability and enforcement of voluntary approaches is likely to be low. IPPC will not be able to help in this respect.

Conditions on marketing and use, for example at the EU level through Directive 76/769/EEC, would provide a robust means of achieving the necessary outcome, on the condition that there are OELs in place to ensure that there is no increase in occupational risks.

7.3 Environmental Emissions Control

7.3.1 Available Measures

The relevant measures identified in Section 6 are as follows:

- safe systems of work, such as specified standards of physical containment or extraction ventilation;
- licensing of operators of certain operations;
- limit values for emission and effluent monitoring;
- environmental quality standards and/or environmental monitoring; and
- ‘end-of-pipe’ controls to minimise, neutralise or render less harmful any emissions than cannot practicably be avoided otherwise.

Table 7.4: Applicability of Emissions Control

Application	**Applicability**
Remaining stocks of PFOS based fire fighting foam	Specified standards of physical containment are theoretically relevant to the use of fire fighting foams – in particular to their use under controlled conditions.
Photographic applications	The use of PFOS in the manufacturing stages of the photographic and semiconductor/photolithography sectors is highly contained due to the nature of these activities. In terms of safe systems of work and standards of containment, these are not relevant to the manufacturing processes as they are already achieved. Minimising the fate of the residual wastes containing PFOS is more likely to be an important route for reducing emissions from these processes.
Photolithography and semiconductor applications	
Aviation hydraulic fluids	Specified standards of physical containment are theoretically relevant to containment of spills during aircraft maintenance operations.
Chromium VI plating	The most likely source of emissions is likely to be from ‘drag out’ of articles and subsequent rinsing. End of pipe controls or simply rinsing articles over the tank itself may reduce these emissions.

7.3.2 Effectiveness

With regard to eventual environmental emissions, containment is a prerequisite which only becomes effective once combined with effective 'end-of-pipe' controls to minimise, neutralise or render less harmful any emissions than cannot practicably be avoided otherwise.

Fire Fighting Foams

As noted in previous sections, as PFOS based substances are no longer used in the manufacture of fire fighting foams, any current (and future) emissions in the absence of risk reduction measures are associated with the use of the remaining PFOS based fire fighting foam stock.

Containment and suitable treatment of firewater runoff is a condition for the operation of Hazardous Installations regulated under the Control of Major Accident Hazards (COMAH) Directive. Emergency planning and risk assessment at such installations requires consideration of worst case scenarios for fires, the availability of fire protection systems (such as foams through mutual aid packages with FAs) and sufficient containment to deal with the volumes of firewater. On these sites, then, the necessary pre-requisite for emissions control, namely containment, is available.

Outside these sites, containment is much less likely and environmental emissions control is not relevant.

Section 2 has provided estimates of the quantities of foams in storage by FAs and as part of MA packages at Hazardous Installations (HI) . These quantities are summarised in Table 7.5 (which reproduces Table 2.10).

Table 7.5: Estimates of Quantities and Use of Fire Fighting Foams in the UK

	All Foam Concentrates (Litres)	PFOS based Foam Concentrates (Litres)
Estimated current quantities in Fire Authority (FA) Inventories	986,347	76,187
Estimated current emergency stores at industrial complexes as part of Mutual Aid agreements	2,959,041	2,367,233
Quantity used by FAs (2002)	147,778	377
Total	**3,945,388**	**2,443,419**

In considering these quantities it is important to note that, under normal conditions, there will be no need to use the foams held by MAs. Emergency planning seeks to account for abnormal operating conditions and ensure that there is sufficient stocks of foam to tackle a major incident in the unlikely event that one should occur on one of the MA sites.

Use at HIs is thus difficult to predict. However, as containment is possible in the event of a fire, it is possible that emissions control could be applied on these COMAH sites to prevent emissions should there be a fire.

At present, the mode of release to the environment from such an installations in the event of a fire is via wastewater. In the UK, firewater containment and treatment is covered by COMAH Regulations and the Prevention of Pollution Guidance (PPG) notes (principally PPG 18). Disposal of fire water will be subject to the duty of care provisions under the Environmental Protection Act 1990 and may also be subject to control under the Waste Management Licensing Regulations 1994 depending on the constituents. In addition, where it contains hazardous substances it may be subject to the Special Waste Regulations 1996.

PPG 18 *Managing Fire Water and Major Spillages* requires that measures should be in place to dispose of, as soon as possible, any fire fighting water. It stipulates that, where re-use is possible, the material should be returned to storage on site. If off-site disposal is required, a registered waste carrier should be used, although if a foul sewer is available it may be possible to discharge to it with the approval of the local sewerage undertaker. Disposal needs to be documented with a transfer note under the Duty of Care Regulations 1991, or if it is a special waste, with a special waste consignment note under the Special Waste Regulations 1996. In the case of special waste consignments, there is normally a requirement for three days notice to be given to the Agency prior to movement.

Accordingly, options for emissions control for use of the remaining fire fighting foams in COMAH facilities would involve reviewing waste permissions to ensure that use of PFOS based foams in the event of fire is accompanied by suitable collection and treatment of contained water and by permitting of use at individual sites by the Agency. The measure could, in principle, be extended to FAs, if FAs were permitted to trade PFOS based stock for non-PFOS based stock within the MA. This would increase the amounts of PFOS stock at MAs by only 3%, but would eliminate use of PFOS on sites where containment is not possible.

Photographic and Photolithography/Semiconductor Applications

Industry inform us that environmental emissions control and appropriate waste treatment is already applied. Further measures are required to formalise these commitments to ensure that appropriate waste handling is applied in all cases, as some waste may currently go to waste water treatment.

Aviation Hydraulic Fluids

We have been advised by industry that there exists strict guidance on the collection and disposal of aviation hydraulic fluids via incineration. Further measures are required to formalise these commitments.

Chromium Plating

In 2007, chromium plating operations above a certain threshold will be covered by IPPC, which will require the consideration of the use of less hazardous substances and Best Available Technology (BAT).

It is possible that environmental emissions control will be employed by a proportion of platers under IPPC and that this may provide a closed loop system for zero (or near zero) emissions. As noted in Section 7.2.3, however, a large proportion (~80%) of companies are unlikely to be covered by IPPC. As such, if environmental emissions control were to be able to provide zero (or near zero) emissions of PFOS, the technology would have to be extended to cover smaller operations.

Also as discussed earlier, the emission estimates for PFOS from chromium plating vary, there being uncertainty concerning the fate of PFOS substances regularly added to plating solutions to provide mist suppression. The RER, and these proposals for risk reduction, assume that the emissions are of the higher magnitude of 500kg/year in the UK (or 250 kg/year regional). These emissions would be virtually eliminated under this option if closed loop systems were extended to all operations.

7.3.3 Practicality

There are several options for encouraging or requiring the adoption of containment and emissions control. These can be summarised as:

- regulatory controls;
- unilateral action by industry;
- voluntary agreements (such as negotiated agreements between industry and governments);
- technical standards and authoritative guidance (statutory, advisory or voluntary) and application of good manufacturing practice, for example, under ISO standards; and
- economic instruments such as a product tax.

In terms of regulatory controls, the following options are available for requiring containment and emissions control:

- ***IPPC Directive*** – setting emission limits may be theoretically possible for photographic applications (but possibly not development of film/paper and PFOS migration) and semiconductor applications. Emission limits could not be set for aircraft maintenance within IPPC. In addition, only a limited coverage (20% of companies) in the chromium plating industry would be possible under IPPC;

- ***The Water Framework Directive*** – as PFOS is not on either the PS or PHS list, it would take some time before environmental quality standards (EQSs) could be included or enforced for PFOS;

- ***Waste Incineration Directive*** – where wastes containing PFOS are incinerated, for example in the case of used aircraft hydraulic fluid, it may be possible to stipulate safe incineration temperature;

- ***Directive on Hazardous Waste*** – classification as hazardous waste would require inclusion of PFOS by the Directive. However, depending on the level of classification, the historical use of PFOS in textiles and leather would effectively make such PFOS treated products classifiable as hazardous waste; and

- ***Marketing and Use Directive*** – conditional use requirements could be applied to ensure that proper emissions controls (or any other appropriate measures) are adopted.

The Waste Incineration Directive could be used ensure that any waste streams from the use of PFOS related chemicals in the photographic, semiconductor and aviation (hydraulic fluids) sectors are disposed of through high temperature incineration. Assuming that PFOS is destroyed during such incineration processes, emissions from these sectors should be contained and reduced to near zero levels. This is important as these sectors have already indicated that they would seek a derogation (at least in the short term) from any proposals restricting the market and use of PFOS based substances.

IPPC is considered less practicable because not only may all operators in a given sector not be covered (for example in aviation and the majority of chromium platers), but implementation also takes into account site specific factors. As a result, what is the 'best available technology' at one site may not be 'best' at another site; unless strict requirements that cannot be varied from are set within the IPPC BREF notes, then consistent application of any proposed restrictions cannot be guaranteed across the EU.

In addition, as noted above, IPPC will not cover the smaller plating operations and, hence, without changes to the IPPC regulations to include them, emissions control technologies could not be implemented via this route. The alternative is conditions on use, which in the EU are achievable by means of marketing and use restrictions.

The Directive on Hazardous Waste would essentially translate into a ban on the use of these substances in consumer products (such as consumer use photographic products) and, thus, would be less practicable than placing restrictions on consumer applications (for example, at EU level under the Marketing and Use Directive 76/769/EEC).

In terms of regulatory approaches, it is likely that under the usual regulatory mechanisms (such as IPPC), the scope of controls in terms of coverage of industrial and professional uses is limited. In terms of coverage and enforcement to introduce appropriate clean technologies and emission limits, perhaps the only way to achieve robust coverage and controls is through controls on marketing and use (at EU level under Directive 76/769/EEC), with attached conditions for derogated uses. This is discussed further in Section 7.7.

Alternatives to regulatory control involve the use of voluntary agreements with associated technical guidance on clean technologies or the use of economic instruments. A voluntary agreement, accompanied by technical guidance, may be appropriate to aircraft maintenance. In this case, the agreement would focus on the adoption of strict hydraulic fluid handling and disposal requirements, to ensure that waste fluids were contained and were not emitted to either surface waters (e.g. through run-off) or to sewer. The industry has indicated that it already produces information on the handling of the fluids owing to other constituents; this option would see these strengthened and individual aircraft maintenance companies and airframe manufacturers signing up to a strict code of practice.

In terms of economic instruments, a product charge based on inputs of PFOS to processes may, in some cases (such as aircraft maintenance and use of fire fighting foams), be too disconnected from the emission to have the desired effect. A product charge would in theory be more applicable to the photographic and semiconductor sectors. In these cases, a charge would be aimed at providing users with an incentive to find alternatives to PFOS more quickly than they might otherwise do. However, as there is already the pressure of dwindling supplies of the PFOS based intermediates, placing an additional cost burden on these sectors is unlikely to speed up the process, and risks impeding it.

A product charge placed on the metal plating sector could theoretically be used to sponsor process changes in the hard plating sector and/or a shift away from the hexavalent chromium based processes in decorative plating. However, the level at which the charge would have to be set to sponsor a shift is problematic. In the case of hard platers, capital expenditure for process changes may be relatively high compared to costs of continued use of chemical mist suppressants. In the case of decorative platers, the potentially large savings in operational costs from moving to Cr (III) plating processes have, as yet, failed to produce a dramatic shift in the sector. As such, a product charge to further increase the operational costs of Cr (VI) might have to be very large to have any effect on decisions to undertake the necessary capital investments.

For fire fighting foams, the existing requirements to treat fire fighting water from hazardous installations as a waste (potentially under the special waste regulations) offers the potential to ensure that all fire waters containing PFOS are covered by permissions from the Agency and that the theoretical potential for only the permission of sewage undertakers to be sought is removed. This could ensure that fire waters containing PFOS cannot be discharged to sewer, where they may pose a risk.

7.3.4 Economic Impact

Fire Fighting Foams

The costs associated with maintenance of existing stocks of PFOS based fire fighting foams at COMAH facilities are zero in the event that there are no fires. 1991-2002 statistics on dangerous occurrences involving fire and/or explosions (defined as an event that results in a cessation of normal operations for more 24 hours) reveal an annual average of 27 occurrences across the whole of the UK. This equates to an annual frequency of 0.025 incidents per site per year (a one in 40 year event per site). It is thought that not all of these fires will have required the use of AFFF foams (such as the PFOS based foams).

For larger fires reportable to the EU under then COMAH Directive, based on a three year average for 1999/00 to 2001/02, the frequency is around 6 per year across the whole of the UK which equates to a frequency of 0.0015 per site per year (a one in 688 year event per site).

If PFOS based stocks were used to tackle these fires then, under the approach discussed above, the costs of treatment and disposal could be significant (though perhaps small to moderate compared with damage costs) depending on the method used. It is likely that

HIs would seek to avoid the need to treat fire waters for PFOS, choosing (where possible) to use the non-PFOS based stock first in the hope that the fire can be controlled using foams not subject to stringent treatment and disposal requirements.

It is estimated that, at present, some 80% of the MA stock may be PFOS-based. As such, it may be difficult for industry to reduce costs in this way initially. However, as foams have an average 15 year shelf life and if it is assumed that the 'newest' stock is, say, three years old, this would imply that the proportion of 'active' PFOS based stock would decrease through natural erosion over time as follows:

Year	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
PFOS	80%	73%	67%	60%	53%	47%	40%	33%	27%	20%	13%	7%	0%
Non-PFOS	20%	27%	33%	40%	47%	53%	60%	67%	73%	80%	87%	93%	100%

In the event that there was a fire, depending on the nature of the substances involved, there may be significant costs associated with the treatment of firewater to remove contaminants. As such, costs of treatment could be high whether or not PFOS based substances were amoung these contaminants. Given the unpredictability of fire frequency, type, size and outcome, it is not possible to come to a single value in an assessment of costs of treatment for firewater contaminated with PFOS related substances.

Photographic Applications

Industry inform us that environmental emissions control and appropriate waste treatment are already applied. No further costs should then be incurred should these activities be formalised.

Aviation Hydraulic Fluids

We have been advised by industry that there exists strict guidance on the collection and disposal of aviation hydraulic fluids via incineration. In principle, then, this option reflects (near) zero emissions for zero cost.

Chromium Plating

Table 7.6 provides costs from USEPA for the provision of emissions control at plating operations in the form of a packed bed scrubber (PBS) (in £ 2004). As can be seen from the table, the cost of a PBS ranges from £20,000 to £75,000 depending on the size of operation, with annual operating costs of between £1,700 and £6,500, again depending on the size of operation. The total annualised cost of emissions technology (over 15 years at a discount rate of 3.5%) ranges between £9,200 per year and £40,200 per year per operation.

Table 7.6: Costs of Environmental Emissions Control Option			
	Min	**Max**	**Average**
Cost of packed bed scrubber	£20,219	£74,887	£47,553
Annualised capital expenditure (CAPEX)	£1,756	£6,502	£4,129
Operational costs	£7,489	£33,699	£20,594
Total annualised costs	**£9,244**	**£40,201**	**£24,723**
All platers not covered by IPPC = 240	**£2,218,611**	**£9,648,242**	**£5,933,426**
Hard Platers not covered by IPPC = 80	**£739,537**	**£3,216,081**	**£1,977,809**

If it is assumed that all plating operations large enough to be covered by IPPC employ a PBS, then, under the emissions control option, an additional 80% of companies (240) would have to employ the technology to provide zero (or near zero) emissions control.

Taking the lower bound estimate of costs (for smaller operations), the total annualised cost of the emissions control option is £2.2 million per year if applied to **all** platers (hard and decorative) not likely to employ the technology under IPPC. However, given the size of the capital expenditure, it is unlikely that decorative platers would adopt such emissions control since there are, at present, likely to be net financial benefits from moving to the use of CR (III) plating processes (see Section 4). In practice, then, the technology may only be applied by the remaining (smaller) hard platers where a shift to Cr (III) processes is not possible.

It has been estimated in previous sections that 100 of the 300 platers are hard platers. Assuming that 80% of these would not be covered by IPPC, 80 companies would have to adopt the technology to attain zero (or near zero) emissions. Assuming, then, that the response of decorative platers to the option is to move to Cr (III) processes, then, applying the lower bound cost estimate, the total annualised costs of the option are **£0.74 million per year**. Assuming that 50% of emissions are from hard platers, the option is likely to result in the elimination of 250kg/year of releases and the control of 250 kg/year of releases.

7.3.5 Monitorability

Monitoring of IPPC based controls and any controls under the Waste Incineration Directive should be straightforward as systems already exist. Monitoring of waste permissions of firewater should be good because all HIs are tightly regulated by the Agency and others. We would expect monitorability to be a key issue with any product charge given the potential that PFOS related chemicals have been stockpiled.

To achieve robust containment and emission limits for PFOS, similarly robust monitoring and enforcement would be required. As such, voluntary approaches and associated guidance would require that agreements are negotiated in nature. Penalties for not following agreements are difficult to achieve on this basis. As such, because zero emissions (or close to) are required, it may be difficult to achieve this with voluntary approaches and economic instruments.

The use of marketing and use controls, for example at EU level under 76/769/EEC, with conditional derogations would provide a robust, monitorable and enforceable strategy for the adoption of (zero) emissions control.

7.4 Exposure Control

Available Measures

The relevant measures identified in Section 6 are as follows:

- use of personal protective equipment; and
- occupational exposure limits and/or air monitoring in the workplace.

Exposure control measures are more related to human health exposure but, depending on the measure, can indirectly reduce environmental exposure. However, as indicated in Table 7.7, exposure controls are already in place in the relevant applications.

Table 7.7: Applicability of Exposure Control Measures

Application	Applicability
Remaining stocks of PFOS based fire fighting foam	Exposure control is unlikely to be a means of reducing risks further.
Photographic applications	Photographic and photolithographic applications involving PFOS occur in tightly controlled environments. Human exposure may only occur during breakdown and maintenance operations and, here, protective equipment is used for the protection of the product line from contamination with dust etc. as much as for human health. There is no further exposure control of relevance to these applications.
Photolithography and semiconductor applications	
Aviation hydraulic fluids	We are informed that, as the base product is a skin irritant, personal protective equipment is already used and spillages prevented. Environmental emissions and containment have been described in Section 7.2.3.
Chromium VI plating	Containment and environmental exposure have been described in Section 7.2.2.

7.5 Provision of Information and Guidance

7.5.1 Available Measures

The relevant measures identified in Section 6 are as follows:

- application of good manufacturing practice, for example, under ISO standards;
- accurate hazard information (for example, safety data sheets), and/or better delivery of safety information, such as clearer labelling or the provision of warning signs in the workplace; and
- training.

7.5.2 Effectiveness

These measures apply to professional and industrial use of PFOS and PFOS based products. The use of guidance and training is implicit in the measures already identified under emissions control for application of PFOS.

However, in terms of delivery of reduced emissions, it was noted in Section 7.2.3 that it is unlikely that emission limits could be set for aircraft maintenance or controlled use of fire fighting foams under IPPC. The use of technical standards, guidance and training may provide a means of delivering of emissions control with regard to these sectors. The use of Pollution Prevention Guidance (in particular PPG 18) has been discussed with regard to fire fighting foams used on HIs. The discussion here relates to the use of such guidance by FAs during training.

7.5.3 Practicality

In terms of PFOS based fire fighting foams, a joint Protocol concerning the use of fluorine containing foams has already been agreed between the Environment Agency and the UK Fire Service with the aim of ensuring co-ordination and co-operation between the fire services and the Environment Agency in limiting the potential for pollution of controlled waters and the disposal of wastes.

The Protocol covers the disposal of foams during training. Following issuance of the Protocol, each brigade was advised by the HM Fire Service Inspectorate to contact the Environment Agency to make arrangements for the safe disposal of foam following training. The Environment Agency advises on the most suitable option for waste disposal from training exercises given local conditions, in a consultative exercise with the Fire Brigade (pers. comm., 2003).

Altering this protocol to ensure that the risks of PFOS are taken into account may provide a means of securing prevention of releases of PFOS in certain situations. However, as the protocol is ‘advisory’ and (it is assumed at present) covers the UK fire service alone, it’s advisory status would need to be upgraded in order to promote (near) zero emissions.

It is not known whether similar protocols apply or could be applied in other Member States, potentially limiting the value of this type of measure at the EU level.

In terms of the use of aviation hydraulic fluids, the delivery of similar protocols in the private sector effectively constitutes a negotiated voluntary agreement. As the vast majority of commercial aircraft are built by two major manufacturers and commercial aviation is tightly regulated by both industry and government, it seems likely that all aviation maintenance engineering works and component testing facilities must be approved and/or licensed by one or both.

7.5.4 Economic Impact

The economic impacts of these measures on the relevant industries will be similar to those discussed for emissions control.

7.5.5 Monitorability

With most forms of non-statutory industry guidance and standards, monitorability and enforcement is likely to be less robust than statutory conditions of use as the agreements are, in part, based on trust.

In the case of Environment Agency/UK Fire Service protocols, it could be expected that, as a government funded body, implementation by the UK Fire Service would be thorough. It is not possible to determine (at present) whether this would extend to private fire fighting companies and MAs.

It could be expected that the tight regulation of aircraft safety by the civil aviation industry and the aircraft manufacturers/operators would also permit thorough implementation of such an agreement for this sector.

7.6 Disposal of Waste PFOS Containing Products

7.6.1 Available Measures

The relevant measures identified in Section 6 are as follows:

- classification as hazardous waste; and
- specified disposal methods and/or conditions, for example, incineration (temperature and time).

The emphasis of these measures is on the disposal of final products of manufacture after industrial and professional use. Disposal and treatment of manufacturing and process wastes have been described in Section 7.3 in relation to environmental emissions. As such, the following waste streams from the professional and industrial use of PFOS have already been discussed:

- photographic chemicals;
- hydraulic fluids;
- photolithography and semiconductors; and
- metal plating.

Photographic and Photolithography/Semiconductor Applications

As part of emissions control for these sectors, the requirement to incinerate all PFOS related wastes generated would ensure that any potential for inappropriate treatment by local waste handlers is prevented. Whilst the industry sectors have informed us that the method of disposal is to incineration, the evidence in Sections 5.4.4 and 5.4.5 suggests that there is a small possibility that some waste may not have to go via this route. The costs of this requirement is negligible as it is already the expected mode of disposal.

Fire Fighting Foams

For fire fighting foams (which are the subject of the remaining discussion), there is an issue as to whether existing PFOS based stocks should be incinerated and replaced with newer, non-PFOS based foams. In considering this issue, it is worth noting that the substitute foams currently in the UK are based on the telomer technology with an environmental endpoint of perfluorocarboxylates. Whilst this represents a substitution, it is not presently clear whether this represents a significant reduction in risk compared to PFOS based foams as the risks associated with perfluorocarboxylates are currently under review in other parts of the world (the United States). This substitution issue has been discussed in more detail in Section 4.

The estimated quantities of fire fighting foams and their use in the UK have been provided in Table 7.5. There are obvious practical (and cost) considerations to be taken into account in proposing the incineration and replacement of the PFOS based stock. Options range from immediate replacement, through to delayed replacement with the conditions on use discussed in Section 7.3 on emissions control.

For the purposes of this Risk Reduction Strategy, the following options have been considered:

- **Option 1: Incinerate and Replace Immediately** – which involves the immediate incineration of existing PFOS stocks (mutual aid (MA) and FA stocks);

- **Option 2a: Conditional Delay of Five Years for Incineration and Replacement** which involves the 12 fire authorities with PFOS stock trading this stock with (industrial) mutual aid partners, in exchange for non-PFOS based stock. All stock would be permitted to be retained as part of mutual aid stock for up to five years, after which all stocks would be destroyed; or

- **Option 2b: Conditional Maintenance of Existing Stocks** – which is as Option 2a, but stock would be permitted to be retained as part of mutual aid stock until the end of service life (estimated as ~12 years).

7.6.2 Effectiveness

Under Options 2a and 2b, the emissions control measures described in Section 7.3 would need to be applied to ensure near to zero emissions. All options would require the incineration of PFOS based foams, with the timing of this depending on the option described above. Applying these criteria, emissions to the environment should be near to zero.

The variation in effectiveness between the options is associated with the risk that emissions control measures fail. As noted in Section 7.3, for those options involving delayed replacement, it is probable that HIs would seek to avoid the increased costs associated with collection, treatment and disposal after use by ensuring that non-PFOS based foams are used first in the event of fire. This suggests that MAs would effectively place the PFOS based stocks as back-up stocks only to be used where stocks of non-PFOS based foams have been exhausted in the event of fire. Such arrangements could be made more formal.

In such a scenario, the likelihood that PFOS based foams would actually be required will decrease with time since there will be an annual replacement of out of date stock. Replacement of stock over time under Options 2a and 2b is as follows:

Year	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Option 2a – Delayed Replacement (5 years)													
PFOS	80%	73%	67%	60%	53%	0%							
Non-PFOS	20%	27%	33%	40%	47%	100%							
Option 2b – Delayed Replacement to End of Shelf Life (~12 years)													
PFOS	80%	73%	67%	60%	53%	47%	40%	33%	27%	20%	13%	7%	0%
Non-PFOS	20%	27%	33%	40%	47%	53%	60%	67%	73%	80%	87%	93%	100%

This would suggest that the highest (but small) risk of failure of environmental emission controls in the event of a fire is within the first five years. Thus, the additional reduction in risk achieved through the destruction of the remaining stock after 5 years (as opposed to 12) is small compared to the reduction in risk achieved by destroying foams in year 0 under Option 1.

7.6.3 Practicality

The requirement to incinerate unused foams and waste containing PFOS related substances can be achieved through the Waste Incineration Directive. However, for fire fighting foams, the issue here is more related to when to incinerate rather than whether. Measures that could be used stipulate this timing are limited to negotiated voluntary agreements, technical standards, or use restrictions at EU level under 76/769/EEC.

In terms of implementation, the risks associated with remaining PFOS based stock are time limited. This means that any delay in implementation of any of the options could result in emissions. A voluntary agreement in the immediate term, may therefore provide an interim option in this case.

7.6.4 Economic Impact

The economic impacts of the options clearly relate to the need to either replace PFOS based fire fighting foams before their end of service life or adopt the alternative strategy of permitting controlled use until they reach the end of their service lives (or until a satisfactory alternative system gains further approval and acceptance).

The cost of safely disposing of 'waste' foams by incineration has been estimated by KemI (pers. comm., 2003) as being of the order of €1,000 per tonne (£600). Replacement costs are of the order of £3,000/tonne.

Option 1: Incinerate and Replace Immediately

As noted above, Option 1 involves the immediate destruction and replacement of stocks. In calculating the costs of this option, it should recognised that it involves incineration of all PFOS stocks. Replacement costs, however, are costs 'brought forward' as (it has been assumed) foams would have to be replaced with time anyway. In calculating the costs of this option, the Treasury social discount rate of 3.5% has been applied, so all costs are Net Present Value (NPV) total costs for the option.

Table 7.8 provides these NPV costs for Option 1 where these are reported for fire authorities and industrial mutual aid partners separately. **Costs are for the UK alone**[50].

From Table 7.8, the NPV costs of Option 1 are around £0.27 million for fire authorities and around £2.6 million for mutual aid partners.

Table 7.8: Option 1: Immediate Destruction (@ 3.5%)

		Costs (£)
Costs FA	Incineration	£45,712
	Replacement	£228,560
	Total	**£274,272**
Costs Private/MA	Incineration	£1,420,340
	Replacement	£1,182,698
	Total	**£2,603,038**
Total NPV Costs		**£2,877,310**
Total Emission (kg PFOS Acids)		**~ 0**

Option 2a: Conditional Delay of Five Years for Incineration and Replacement

Option 2a is based on the assumption that, on mutual aid industrial sites, even where PFOS stock are used in the event of an incident, emissions would be zero.

For this option, it has been assumed that the estimated 12 fire authorities with remaining PFOS based foams could exchange this for non-PFOS based stock. This would ensure that, in the event that the PFOS based stock was used, it would be in controlled and contained situations. As such, this (older) PFOS stock would be maintained as part of the mutual aid agreement for five years. The costs, therefore, are only associated with incineration of out of date stocks which will occur every year between years 0 and 4 and the costs of replacement 'brought forward' for the remaining stock with even distribution (and costs shared between fire authorities and mutual aid on the basis of tonnes exchanged). Total NPV costs for Option 2a are provided in Table 7.9.

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[50] Assuming the UK represents 20% of the EU, divide UK values by 2 for Regional costs/emissions and multiply UK values by 5 for Continental costs/emissions.

Table 7.9: Option 2a: Conditional Maintenance of Existing Stocks for 5 Years (@ 3.5%)

		Costs (£)
Costs FA	Incineration	£41,038
	Replacement	£14,697
	Total	**£55,735**
Costs Private/MA	Incineration	£1,275,131
	Replacement	£456,653
	Total	**£1,731,784**
Total NPV Costs		**£1,787,519**
Total Emission (kg PFOS Acids)		**~ 0**

Option 2b: Conditional Maintenance of Existing Stocks

Option 2b is the same as Option 2a except that the period for delayed replacement is extended to the shelf life of remaining stock.

On this basis, (older) PFOS stock would be maintained as part of the mutual aid agreement until it expired and was replaced as normal. The costs, therefore, are only associated with incineration of stocks which will occur every year between years 0 and 11 (it has been assumed) with an even distribution (with costs shared between fire authorities and mutual aid on the basis of tonnes exchanged). Total NPV costs for Option 2b are provided in Table 7.10.

Table 7.10: Option 2b: Conditional Maintenance of Existing Stocks (@ 3.5%)

		Costs (£)
Costs FA	Incineration	£38,099
	Replacement	£0
	Total	**£38,099**
Costs Private/MA	Incineration	£1,221,899
	Replacement	£0
	Total	**£1,221,899**
Total NPV Costs		**£1,259,998**
Total Emission (kg PFOS Acids)		**0**

7.6.5 Monitorability

Depending on the option selected, monitoring disposal and replacement of foams would be easy to achieve in the UK through the supervision and control of the UK Fire Service and HSE/Environment Agency inspectors, particularly at COMAH sites.

7.7 Use Restrictions

7.7.1 Available Measure

The remaining measure applicable to existing industrial and professional users is the substitution of PFOS based substances with alternative processes or substances by means of marketing and use restrictions or voluntary measures. The issues surrounding the potential for substitution have been discussed in Section 4. With regard to fire fighting foams, substitution and the timing of replacements has also been discussed above under environmental emissions control and disposal of waste PFOS containing foams. With regard to metal plating, substitution by changing manufacturing process is possible, where this has been discussed under manufacturing process changes.

The remaining existing industrial and professional users are:

- photographic applications;
- photolithography and semiconductors; and
- hydraulic fluids used in aviation.

These uses and the issues arising with the adoption of marketing and use restrictions are considered for each industry in the following sections.

7.7.2 Photographic Industry

A detailed discussion of the technical feasibility of substitution has been provided in Section 4.

As indicated, efforts to replace 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 costs of achieving this 83% reduction across the EU since 2000 have been estimated as € 20-40 million. (£12-24 million). This has involved the elimination of the following uses of PFOS related substance:

- as a defoamer used in the production of processing chemicals for films, papers, and printing plates;
- as photoacid generators in photolithographic processing solutions used in the manufacture of printing plates; and
- as surfactants in photolithographic processing solutions used in the manufacture of printing plates.

The current demand for PFOS chemicals is expected to be 1,500 kg/yr in the EU, with the UK expected to account for 270 kg/yr. The emission estimates in the RER (see Annex 4) are based on this level of use.

To meet the technical requirements for use in photographic products, any alternatives to PFOS related substances must provide equivalent properties (to PFOS related substances). There are no known technical issues arising from the successful replacement of PFOS related substances in the areas listed above.

The remaining imaging products/applications where no substitution has yet been made (which account for the current 1,500 kg/year usage in the EU) are reported to be as:

- 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.

There are, at present, no known substitutes for PFOS in these applications.

In terms of substitution, there are, at present, no substitutes available. As such, an immediate cessation in the use of PFOS based substances in the photographic industry (EU or UK) is likely to have extremely severe economic implications for the industry as it will interfere, indirectly with all processes in the industry. There is, however, an option to introduce provisions for a phase out over time. At an EU level, this would normally be achieved by means of marketing and use restrictions.

Under this proposal, a time limited derogation would be granted conditional on the use of environmental emissions control. As noted above, sophisticated environmental emissions control is already applied, but may need to be formalised as part of risk reduction measures. There may also be a need to ensure that research and development programmes are built into the derogation. Once the derogation expires, a need to review the industry's position and examine any trade issues arising from a complete ban on marketing and use for this sector.

An alternative may be a voluntary agreement, although, unless negotiated with the photographic industry globally, this will not prevent possible emissions from PFOS related substances in imported goods.

7.7.3 Photolithography and Semiconductors

A detailed discussion of technical feasibility has been provided in Section 4. To summarise the options in the context of a risk reduction strategy, PFOS based materials are reported as being critical in two applications within the photolithography process: photoresists and anti-reflective coatings (ARC's).

Photoresists

In terms of the former, the operation of PFOS based PAGS is reported to be critical to the semiconductor industry in the photolithography process. ESIA indicates that there are currently no substitutes known that give the same level of critical functionality to cause effective, efficient transformation in leading edge photoresists and which can be used in volume manufacturing.

The next generation of lithography includes electron project lithography (EPL), extreme ultraviolet lithography (EUVL), ion projection lithography (IPL), and x-ray proximity lithography (XPL). These technologies are at differing stages of development but all are currently unsuitable for use in manufacturing because they still face significant challenges. EPL is gaining acceptance in other parts of the world while IPL which is being strongly considered in Europe has not gained acceptance elsewhere.

In future, in this area of use, the industry may ultimately be moving away from PFOS in these new processes, not only on the grounds of the limit supplies of PFOS based substances, but also because of technical improvements in the process that may no longer require its use.

Anti-reflective coatings

For anti-reflective coatings used in combination with deep ultra violet (DUV) photoresists, ESIA indicates that there is also no current alternative to PFOS based substances available which fulfils the critical technical requirements necessary (ESIA, 2003).

For uses of PFOS related substances in top (TARC) and bottom (BARC) resist coatings, suppliers are said to be working on polymeric replacements. The semiconductors industry indicates that replacement could take up to five years, if it can be done at all (ESIA, 2003).

Developer Applications

In developer applications (including EBR's, RER's), strippers and etch mixtures, there are surfactants which are not PFOS based which could serve as alternatives.

Costs and Emissions

As noted above, the only substitutes for PFOS that are currently available are in developer applications. The identity of these is not known. There are no other substitutes currently available for the remaining processes. The costs associated with substitution in other applications in the industry are not known.

In terms of the costs of substitution in developer applications, the technical performance of the non-PFOS based surfactant is comparable to the PFOS based surfactant. Although there is no need for new equipment, costs arise from labour, engineering and qualification.

On the basis of these costs, industry estimates that a phase out of PFOS in developers would cost around €1.5-2 million (£0.9 to £1.2 million). Potentially higher developer costs could arise if down time, opportunity cost, logistics and yield loss are included.

Taking the higher bound cost (£1.2 million) to account for additional costs, this represents an annualised cost of £104,200 per year (annualised over 15 years at the discount rate of 3.5%).

Data presented in Section 2 suggests that the use of PFOS related substances in developer applications represents 41% of total use in the EU. Applying this to the emissions calculated in the RER model calculations provides the emission reductions indicated in Table 7.11, which vary by degradation scenario.

Table 7.11: Emissions and Emission Reduction from Substitution in Developer Applications

	Total Continental Release (kg/year)	**Emission Reduction (kg/year)**
Scenario 2 – PFOS-acid plus instant release of PFOS-substance	234	95.9
Scenario 3 – PFOS-acid plus PFOS-substance with 1 yr half life	30	12.3
Scenario 4 – PFOS-acid plus PFOS-substance with 10 yr half life	12	4.9

Applying the annualised cost of £104,200 per year to these emission reductions suggests costs of the order of between £1,100 and £21,200 per kilogram emission reduction.

Feasibility

Substitution in developers is the only substitution that can be made at present. For the remaining uses in the photolithographic and semiconductor industry, it has been estimated that the minimum time required for substitution is of the order of five years.

ESIA has stated that PFOS related substances should remain available while research towards identifying PFOS substitutes continues. They also believe that any potential marketing and use restriction on use in critical applications in Europe would jeopardise the long term continued presence of the semiconductor industry in Europe.

However, beyond a voluntary agreement to do similar, the most likely means by which these measures could be implemented throughout the EU would be marketing and use restrictions involving a time limited derogation, conditional on the formalisation of environmental emissions controls.

7.7.4 Hydraulic Fluids Used in Aviation

Feasibility

Given the lack of alternatives for aviation hydraulic fluids and the safety critical factors associated with their use, an immediate cessation in use is not an option. As such, if marketing and use restrictions (or similar) were introduced on PFOS related substances in general, a derogation is likely to be required. Whether this is time related is difficult to establish given the time to approve the safety characteristics of the alternative as well as the time taken to identify one.

7.7.5 Practicality of Measure

Restrictions on marketing and use can be very flexible in their approach to addressing risks. A total ban upon the marketing and use of PFOS would eliminate any environmental and human health risks from the substance itself (substituting the risks with those of another substance). Such a restriction could be worded so as to prevent the sale of finished products containing the substance in the EU (thus covering imported goods). However, to be effective, PFOS would have to be identified and identifiable in all products and associated documentation. This, in turn, suggests that some classification (and labelling) for PFOS may be required and that the presence of PFOS in articles can be monitored for.

In considering the advantages and drawbacks of the approach, the issues of substitution discussed in Section 4 require careful consideration (particularly with regard to telomer based substitutes). The key constraint on practicality is the need for derogations, as discussed above. It is proposed that these would be time limited and it may also be preferable to make them conditional on other activities relating to emissions control, waste management and research and development.

At an individual Member State level there are options to achieve cessation and phase out within their own territory (subject to clearance from EC authorities) under the Technical Standards Directive 98/48/EC[51] (TSD). Measures introduced under either could require industry sectors to cease use of PFOS by a certain deadline, could place phased requirements on reductions in use and cessation, or could set conditions on use, for example, only in closed systems for containment followed by incineration of wastes.

7.7.6 Monitorability

Monitoring the implementation of a ban upon the uses of concern should be relatively straightforward, given that suitable systems have been established through previous restrictions. However, whilst monitoring the success of a ban in relation to imports containing PFOS related substances into the EU should be relatively easy to accomplish, monitoring imports of finished products containing the substance may be more problematic.

There are various analytical methods which may be of relevance for determining the presence of PFOS in biological and environmental samples. These methods include:

- mass spectrometric detection;
- high-performance liquid chromatography (HPLC);
- gas chromatography followed by electron capture detection;
- neutron activation;
- X-ray fluorescence; and
- Nuclear magnetic resonance (19F NMR).

While these methods have been used in the determination of perfluorinated molecules in biological and environmental samples, it should be noted that in general, analytical methods for perfluorinated chemicals are currently under development and their optimisation is the subject of many ongoing studies. The validation and quality

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[51] For example, a notification by the Netherlands to introduce national measures concerning wood treated with copper substances was considered by CSTEE in 2002 and Denmark has introduced legislation banning the production of new materials containing cadmium, and draft legislation on recycling PVC containing lead.

assurance of analytical methods for PFAS is also indicated as an area of further work (RIKZ, 2002).

If conditional derogations were imposed, there would be a need to monitor compliance with these conditions for the industries concerned.

7.8 Measures for Applications where PFOS is No Longer Used

7.8.1 Available Measures

As has been identified in Figure 7.1 and elsewhere, all known historic uses in the UK and the EU are associated with emissions from consumer use. It is also probable that the emissions from historical uses, if allowed to re-occur, may be several orders of magnitudes higher than those emissions from current uses.

In the case of historical uses of PFOS, domestic and consumer use is likely to represent a significant proportion of the total release of PFOS from each of the following applications:

- textiles and leather;
- domestic cleaning products;
- pesticides and insecticides;
- paper and packaging; and
- coatings.

As has been described in previous sections, 3M's decision to cease manufacture of PFOS has forced a general movement towards alternatives where they are available. This has meant that the historical uses of PFOS identified above are believed to no longer occur, although this cannot be confirmed by some sectors or for all EU countries.

In commenting on the effectiveness of risk reduction measures and the enforcement issues, the TGD indicates that the introduction of controls on professional and industrial uses will often be the most effective way to reduce risks. This is because exposure/releases from consumer and domestic uses are, in general, unsupervised. Furthermore, waste management controls may be difficult to enforce if a substance is used domestically. Controls on professional and industrial use should therefore be given precedence if they appear to be more effective in addressing the potential risks from a substance.

Accordingly, the following product controls are theoretically applicable to the use of PFOS by domestic consumers:

- limits on concentrations of components;
- product design changes;
- limits of the overall quantity available to each user; and
- restrictions on use.

In the case of PFOS, limits on the overall quantity available to each user are synonymous with limits on concentrations in products for the consumer and domestic applications that have been identified. In terms of limits on the concentration in products, for all applications it is unlikely that any concentration above zero will be acceptable given that PFOS has been identified as a PBT and such uses would result in widely dispersed emissions to the environment.

As a result, cessation of use is the logical conclusion in relation to these historic consumer uses. This could best be achieved through one of the following measures:

- voluntary agreements, such as negotiated agreements between industry and governments; or
- regulatory controls, such as restrictions on marketing and use.

7.8.2 Effectiveness and Practicality

Voluntary Approaches

A voluntary agreement to maintain non-use of PFOS could be established for the various use categories. However, from responses received there is, at present, some unwillingness to commit to such agreements. This seems to be because of a general unwillingness to restrict options for products and processes. This suggests that a voluntary agreement would (at least) have to be negotiated with industry. A potential drawback of a voluntary agreement is that, unless it covers the international producers of finished goods (i.e. those outside the EU), there would remain the potential for emissions from imported goods.

Furthermore, where there is a large numbers of producers, it is difficult to ensure that an agreement will be adhered to by a sufficient percentage to meet risk reduction targets – in this case (near) zero emissions.

Regulatory Approaches

The alternatives to voluntary approaches include the use of regulatory controls to enforce the cessation in use of PFOS related substances. At an individual Member State level there are options to achieve cessation and phase out within their own territory (subject to clearance from EC authorities) under the Technical Standards Directive 98/48/EC (TSD).

At EU level, this could be achieved through the use of marketing and use restrictions under Directive 76/769/EEC which could address all applications. Alternatively, for some potential future applications, the use of PFOS could be limited within individual product legislation, for example, under Directive 2001/95/EC of the European Parliament and of the Council of 3 December 2001 on general product safety (which replaced Directive 92/59/EEC). Other examples include restrictions under Directive 94/62/EC on packaging and packaging waste. Clearly, however, this would only address one of the use categories.

Indirect Controls

To some extent, a shift back to the PFOS related substances by those industries that have already ceased use will be influenced by the controls that may eventually be implemented for those use categories where there is current (but reduced) use of PFOS related substances. The application and delivery of a (near) zero emissions policy, for example, would place an additional burden on any industry seeking to re-introduce use of PFOS.

7.8.3 Economic Impact

The economic impact of the measures, whether voluntary or regulatory, should be low, as the main costs would relate to the setting up of agreements/regulations and monitoring.

7.8.4 Monitorability

The necessarily high level of monitorability that would be required to ensure that historical uses did not re-occur can only be achieved robustly by restrictions on marketing and use. As discussed in Section 7.7.6, test methods to allow for the detection of PFOS related substances in a range of different article types are currently under development. Some of the existing methods are also undergoing optimisation and quality assurance procedures.

7.9 Summary of Measures and Implementation Issues

The discussion has identified a range of potential risk reduction measures that could be applied to reduce or eliminate the risks from emissions of PFOS to the environment. These range from voluntary measures through to regulatory mechanisms for controlling emissions and ceasing use of PFOS related substances.

Table 7.12 provides a summary of the controls discussed and a scoping of which releases they are likely to address. Combined with the discussion above, this provides for the following summary observations:

- process controls are applicable to the chromium plating industry, where these process changes are associated with the use of improved extraction and enclosure methods in hard chromium (VI) plating and a shift to chromium (III) processes in decorative plating – these changes can be viewed as a process change that substitutes the use of PFOS based substances. Marketing and use restrictions or measures under the Technical Standards Directive would be required to achieve this change;

- emission controls are applicable to all existing and professional uses, however it is difficult to obtain full coverage of industry sectors (and associated emissions) using IPPC, Incineration and Waste directives or other mechanisms on their own. Voluntary agreements are unlikely to provide the necessary guarantees of compliance, but may be a useful/essential interim measure to address the risks associated with emissions of remaining PFOS based fire fighting foams. Apart from this exception, marketing and use restrictions with associated conditional use derogations may be the only effective means of achieving the necessary reduction in risks. In the case of chromium platers, however, the costs of attaining the necessary emissions controls may outweigh the costs of adopting process controls that would eliminate the use of PFOS in this sector (described above);

- marketing and use restrictions (or similar) and associated conditional derogations would provide a means of achieving full coverage and a restriction on the import of goods containing PFOS related substances and would ensure that historical uses do not re-occur (or cease should consumer uses be on-going in the EU). Preventing these consumer uses from taking place can be viewed as essential to the success of the risk reduction strategy as a whole;

- conditions on use might include the use of fire fighting foams in contained situations with accompanying fire water collection, treatment and disposal requirements and the use of containment and disposal technologies in aircraft maintenance. Time limited derogations could be used to drive replacement with alternative substances and/or processes;

- product controls implemented through Directives on product safety and packaging and waste may offer a means of addressing emissions of PFOS from consumer uses (present and future). As product design changes are unlikely to be able to achieve the reduction in exposure/emission, this effectively represents a cessation in use driven by product safety and packaging and waste Directives; and

- negotiated voluntary agreements (supplemented with guidance) could be pursued in the immediate term, as a means to address some of the emissions. There is, however, an issue concerning the import of consumer goods containing PFOS from outside the EU and the potential for non-compliance by some firms within the various sectors.

Table 7.12: Summary Scoping of Possible Measures and Emission Pathways

Applications/Sector	**Pathways to the Environment and Likelihood of Pathway being a Significant Emission Source FOR THE SECTOR**	**Professional/Industrial Use Measures**					**Public and Consumer Use Measures**		**Implementation**				
		Manufacturing Process Changes	**Environmental Emissions Control**	**Exposure Control**	**Provision Of Information And Guidance**	**Waste Disposal (Of PFOS Containing Products)**	**Product Controls (Effectively a Cessation)**	**Provision Of Information**	**Voluntary Agreement**	**IPPC/ Limits**	**Directives on Product Safety/ Packaging, Waste**	**M&U**	**Need for Conditional Derogation**
Current Uses													
Fire Fighting Foams	Training	n/a			Y	Y			Possible interim measure	No		Yes	Possibly
	Fire fighting	n/a			Y	Y				No			
	Waste/Old Stock	n/a	Y		Y	Y				No			
Photographic Chemicals	Manufacture								Possible interim measure	No		Yes	Likely
	Processing									No			
	Waste		Y							No			
Photolithography and Semiconductors	Manufacture								Possible interim measure	No		Yes	Likely
	Waste		Y							No			
Hydraulic Fluids	Aircraft maintenance		Y		Y				Possible interim measure	No		Yes	Likely
	Factories testing new components		Y		Y					No			
	Waste		Y		Y					No			
	Accidental loss								No	No			
Metal Plating	Manufacture of preparations		Y						Unlikley	No		Yes	No
	Hard metal plating		Y							No			No
	Decorative metal plating		Y							No			No
	Waste		Y							No			

Historical Uses													
Textiles	No longer used	n/a	Indirectly	n/a	n/a	n/a	Y	n/a	Not compre-hensive	No	Possibly	Yes	No
Pesticides and Insecticides	No longer used	n/a	Indirectly	n/a	n/a	n/a	Y	n/a		No	Possibly	Yes	No
Leather	No longer used	n/a	Indirectly	n/a	n/a	n/a	Y	n/a		No	Possibly	Yes	No
Industrial and Household Cleaning Products (Surfactants)	No longer used	n/a	Indirectly	n/a	n/a	n/a	Y	n/a		No	Possibly	Yes	No
Carpet	No longer used	n/a	Indirectly	n/a	n/a	n/a	Y	n/a		No	Possibly	Yes	No
Paper and Packaging	No longer used	n/a	Indirectly	n/a	n/a	n/a	Y	n/a		No	Possibly	Yes	No
Coatings	No longer used	n/a	Indirectly	n/a	n/a	n/a	Y	n/a		No	Possibly	Yes	No

8. RECOMMENDED RISK REDUCTION STRATEGY

8.1 Overview

8.1.1 The Substance

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 are polymers of high molecular weights in which PFOS is only a fraction of the polymer and final product (OECD, 2002).

8.1.2 Uses

On 16 May 2000, 3M (the major global producer of PFOS based in the United States) announced that the company would phase-out the manufacture of PFOS voluntarily from 2001 onwards. This has resulted in a phase-out in the use of PFOS related substances in consumer applications within the UK[52] and/or EU applications (although some on-going use may take place across these sectors in the EU and accession countries) where all of these uses have a consumer end use and emission component:

- carpets;
- leather/apparel;
- textiles/upholstery;
- paper and packaging;
- coatings and coating additives;
- industrial and household cleaning products; and
- pesticides and insecticides.

Despite the 3M PFOS manufacturing phase-out, continuing use of PFOS related substances has been confirmed in the UK/EU for the following applications, where these all represent industrial and professional uses:

- metal plating;
- use of existing PFOS fire fighting foam stock;
- photographic industry;
- photolithography and semiconductors; and
- hydraulic fluids used in aviation.

8.1.3 Risks Associated with the Substance

Following the announcement by 3M that the company would phase-out the use of PFOS voluntarily from 2001, the OECD conducted a Hazard Assessment of PFOS. In November 2002, the final draft of the OECD Hazard Assessment of PFOS was endorsed

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[52] Note that there is uncertainty as to whether use in all of these applications has ceased in the UK although the general view is that it has.

at the 34th Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology.

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
- 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 2003, the Environment Agency for England and Wales, which is responsible for 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. The UK Review of Environmental Risks (RER) of PFOS related substances concluded that PFOS meets the **PBT** criteria. Risks have been identified for all uses.

As discussed in Section 3, when a substance is classified as a PBT in the UK, the cessation of present and future emissions is the target of any risk reduction strategy. The recommended risk reduction strategy for achieving near zero emissions is presented in the following sections.

8.2 Strategy to Address Risks from Historical and Other Possible Uses

8.2.1 Background

All known historic uses in the UK and the EU are associated with emissions from consumer applications. The RER has indicated that it is likely that the emissions from historical uses, if allowed to re-occur, would be several orders of magnitude higher than those emissions from current uses.

As noted above, use of PFOS related substances in the past has been confirmed either in the UK and/or the EU for the following applications (with some potentially ongoing although unconfirmed):

- carpets;
- leather/apparel;
- textiles/upholstery;
- paper and packaging;
- coatings and coating additives;
- industrial and household cleaning products; and
- pesticides and insecticides.

In addition to these, as noted in Section 2, evidence collected for this study suggests that there are potential uses that do occur/have occurred outside the EU. These uses have been identified as:

- medical applications;
- flame retardants;
- mining and oil surfactants; and
- adhesives.

8.2.2 Objective in Relation to Historical and Possible Future Uses

Preventing the re-occurrence of historical uses and the development of new uses can be viewed as essential to the success of the risk reduction strategy as a whole in reducing the environmental risks associated with PFOS.

8.2.3 Recommended Measures

For confirmed historical uses in the UK/EU, domestic and consumer use represents a significant proportion of the total release of PFOS. There are no controls on end-products or consumers which would be likely to prevent re-occurrence of use or (near) zero emissions in the event of re-occurrence of use.

There are no suitable controls other than marketing and use restrictions that can be placed on the potentially ongoing or possible re-occurring future uses.

Accordingly, it has been concluded that the only effective means of addressing the risks from such uses is through restrictions on the marketing and use of PFOS related substances.

This can be achieved:

- at National (UK) level through use of the Technical Standards Directive 98/48/EC (TSD) (subject to clearance from EC authorities); and

- at the EU level, through Directive 76/769/EEC concerning restrictions on the marketing and use of certain dangerous substances and preparations.

As a means of increasing the monitorability of trade in PFOS related substances, it is suggested, that marketing and use restrictions on PFOS could be supplemented by classification of PFOS as dangerous for the environment under the Classification and Labelling Directive, with the following risk phrases:

- R51 (toxic to aquatic organisms); and
- R53 (may cause long term adverse effects on the aquatic environment).

Additionally, PFOS could be classified as 'Toxic' and carry the Risk Phrase R48 (Danger of serious damage to health by prolonged exposure), based on the conclusions in Section 3.3. The suggested risk phrases (R51 and R53) are based on the findings of the Draft UK RER (RPA & BRE, 2004).

8.2.4 Economic Impact of Measures

There should be only a limited economic impact associated with these measures within the UK, although there may be a greater effect from the introduction of marketing and use restrictions in countries such as Sweden where some ongoing use of PFOS related substances may be taking place.

8.3 Strategy to Address Risks from Existing and Continuing Uses

8.3.1 Background

The following current uses of PFOS related substances represent industrial and professional uses:

- metal plating;
- use of existing PFOS fire fighting foam stock;
- photographic industry;
- photolithography and semiconductors; and
- hydraulic fluids used in aviation.

Given the risks associated with the use of PFOS related substances, the objective of the strategy in relation to these existing uses is to achieve, where possible, cessation or phase-out of use. Where this is not currently feasible, a balance must been struck between critical uses in certain sectors and the need for cessation. In striking this balance, the nature of the critical use must be considered alongside a cessation over a reasonable timescale and the feasibility of achieving (near) zero emissions from the critical uses in the interim.

8.3.2 Strategy for Metal Plating

Objectives and Actions in Relation to Metal Plating

Process changes that eliminate the need to use PFOS based fume suppressants in hard (Cr (VI)) plating are currently available (and applied elsewhere). The objective of the strategy is to apply these process changes to the UK/EU industry.

The process changes comprise the adoption of Cr (III) plating methods for decorative platers currently using Cr (VI) technologies. For continuing users of Cr (VI) plating technologies, the provision of additional extraction ventilation and/or the provision of greater tank enclosure can be used to adequately control mist and fumes from tanks within the Occupational Exposure Limits (OELs) for Cr (VI).

Recommended Measures

There are no emissions or product control based measures that can be applied to implement the above process changes.

The use of a Voluntary Agreement with the plating industry is considered unlikely to succeed on the basis that there have been a number of industry and regulator led initiatives to promote a shift to Cr (III) technology in the past and these have had limited effectiveness. This is partly because they cannot readily address the issue of customers' specifications stipulating the use of Cr (VI) plating processes.

It is concluded that the proposed actions can only be robustly implemented and monitored under the provisions of a regulated cessation and phase-out of use. Accordingly, metal plating applications of PFOS related substances should be included in the marketing and use restrictions already proposed for historical and possible uses. This can be achieved:

- at National (UK) level through use of the Technical Standards Directive 98/48/EC (TSD) (subject to clearance from EC authorities); and

- at the EU level, through Directive 76/769/EEC concerning restrictions on the marketing and use of certain dangerous substances and preparations.

Economic Impact of Actions

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

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

On this basis, assuming that upgraded ventilation is not part of the emissions control systems maintained at present, the total annualised cost of the actions in the UK is **£350,000 per year**. This is accompanied by total elimination of PFOS related emissions of 500 kg per year.

8.3.3 Risk Reduction Strategy for Stocks of Fire Fighting Foams

Objectives and Actions in Relation to Fire Fighting Foams

As PFOS based substances are no longer used in the manufacture of fire fighting foams, emissions from fire fighting foams in the UK are associated with the use of the remaining PFOS based fire fighting foam stock. The bulk of this is stored at facilities where containment of fire water runoff is required under the COMAH Directive and associated regulations. However, under the current regulatory controls at these sites, it is possible that fire water containing PFOS based substances could be discharged to waste water (with appropriate permission from the sewage undertakers); with a risk having been identified for such releases in the RER.

In relation to the (smaller) quantities of PFOS based foams retained by an estimated 11 of the 59 Fire Authorities (FAs), containment of firewater and appropriate treatment cannot usually be achieved. The RER has also identified that such emissions pose a risk.

The primary objective for the risk reduction strategy in relation to emissions from the remaining stocks of fire fighting foams is the safe destruction of these remaining stockpiles by high temperature incineration. However, in considering the actions to achieve this primary objective, the strategy must take into account that the substitute foams that are currently most available in the UK are based on telomer technology with an environmental endpoint of perfluorocarboxylates . Whilst this represents an existing and technically feasible substitution, it is not clear whether this represents a significant reduction in risks compared to PFOS based foams. The risks associated with perfluorocarboxylates are currently under review in other parts of the world (e.g. United States).

Accordingly, actions requiring the immediate destruction and replacement of PFOS based foams have been avoided in favour of a five year delay in destruction of the remaining foams, the application of emissions controls on firewater in the interim, and the high temperature incineration of any foams disposed of in the interim five year period. This five year delay should allow adequate time for greater data on the environmental and health risks of the substitute foams to be generated.

Recommended Measures

The specific actions required on the part of FAs and Mutual Agreement (MA) partners in respect of these objectives reflect Option 2a in Section 7 and are as follows:

- FAs are to trade remaining PFOS based stock for non-PFOS based stock held at MAs (increasing MA PFOS based stock by an estimated 3%);

- MAs are able to retain stock of PFOS based foams as part of reserves for a period of five years, whereupon all remaining stock will be destroyed by high temperature incineration;
- in the event that PFOS based foams are required within the five year period, contained fire waters are not permitted to be released to wastewater; and
- all future disposal of PFOS based foams is to be by high temperature incineration.

To achieve the objectives it is recommended that marketing and use restrictions are applied to ensure that any future marketing and import of PFOS based foams does not re-occur and to enforce, if necessary, the five year limit for incineration and conditions for use before this limit expires. This can be achieved:

- at National (UK) level through use of the Technical Standards Directive 98/48/EC (TSD) (subject to clearance from EC authorities); and

- at the EU level, through Directive 76/769/EEC concerning restrictions on the marketing and use of certain dangerous substances and preparations.

However, without the immediate introduction of controls, the bulk of emissions from remaining stocks of PFOS based fire fighting foams may occur in the short-term and before such measures can be implemented. Accordingly, it is recommended that a negotiated Voluntary Agreement should be pursued as quickly as possible (and within the next six months) to achieve the actions set out above. This will help safeguard the environment in the interim.

This Voluntary Agreement should include provisions for the consent of the Environment Agency to be obtained before contained (treated or untreated) firewater is disposed of and that all disposal of PFOS based foams will be by high temperature incineration. This could be included in Pollution Prevention Guidance note 18 (PPG 18) *Managing Fire Water and Major Spillages*

Both marketing and use restrictions and a Voluntary Agreement should be supplemented by:

- controls under the Waste Incineration Directive, requiring high temperature disposal; and

- reinforcing the duty of care provisions under the Environmental Protection Act 1990, the Waste Management Licensing Regulations 1994 and the Special Waste Regulations 1996 to ensure that PFOS contaminated fire water is disposed of appropriately.

Economic Impact of Actions

The costs of this proposed measure are associated with incineration of stocks which will occur every year over the five year phase-out period and the costs of replacement ‘brought forward’ for the remaining stock. The **total NPV cost of these actions is around £1.7 million** (where around 75% of this cost is associated with the requirement to incinerate remaining stock).

In the event that there was a fire, depending on the nature of that fire and the presence of other contaminants in the firewater, there could be significant costs associated with the treatment of firewater whether or not PFOS based foams have been used. Given the unpredictability of fire frequency, type, size and outcome, it is not possible to come to a single value in an assessment as to the costs of the treatment and disposal for fire water containing PFOS based foams.

8.3.4 Risk Reduction Strategy for the Photographic Industry

Objectives and Actions in Relation to Photographic Applications

The primary objective of the strategy in relation to photographic applications is a cessation or phase-out in use of PFOS related substances.

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

- as a defoamer used in the production of processing chemicals for films, papers, and printing plates;
- as a photoacid generators in photolithographic processing solutions used in the manufacture of printing plates; and
- as surfactants in photolithographic processing solutions used in the manufacture of printing plates.

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

- surfactants for mixtures used in coatings applied to films, papers, and printing plates;
- electrostatic charge control agents for mixtures used in coatings applied to films, papers, and printing plates;
- friction control and dirt repellent agents for mixtures used in coatings applied to films, papers, and printing plates; and
- adhesion control agents for mixtures used in coatings.

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

An immediate cessation in the use of PFOS based substances in the photographic industry (EU or UK) is likely to have severe economic implications for the industry as it will interfere, indirectly, with many of the processes used in the industry. It would also have significant worker safety implications.

The objective of the strategy is, therefore, to introduce provisions for a time limited derogation backed up with formal provisions for emissions control measures.

Recommended Measures

Photographic applications should be included in marketing and use restrictions with a time limited derogation for phase out of five years. Attached to this five year derogation should be conditions of permitted use, which should formalise provisions for suitable emissions and waste treatment via incineration. As noted earlier, this can be achieved:

- at National (UK) level through use of the Technical Standards Directive 98/48/EC (TSD) (subject to clearance from EC authorities); and
- at the EU level, through Directive 76/769/EEC concerning restrictions on the marketing and use of certain dangerous substances and preparations.

This should be supplemented by requirements under the Waste Incineration Directive for high temperature incineration of all waste streams.

In the interim, it is suggested that a Voluntary Agreement by the photographic industry to start such undertakings would smooth the transition and provide for swifter and more effective risk management.

It is also suggested that a review(s) of progress should be carried out at a suitable point(s) within the five year derogation. Evidence of research progress on substitutes should be presented at such a review(s) along with tangible evidence connected with any continuing problems for substitution that may impact on the deadlines.

Economic Impact of Actions

The cost to be incurred from further work on replacements is expected to be no less (and probably significantly higher) than the estimated figure of € 20-40 million (£12-24 million) spent on successful replacements to date.

Environmental emissions control and waste incineration already takes place (with the exception of some waste streams that may currently go through water treatment), hence this risk reduction option relates only to formalising these commitments. The costs to industry of such emission control are therefore assumed to be negligible.

8.3.5 Risk Reduction Strategy for Photolithography and Semiconductors

Objectives and Actions in Relation to Photolithography and Semiconductors

The primary objective of the strategy in relation to photolithography and semiconductor applications is a cessation or phase-out in use of PFOS based substances.

However, PFOS based materials are reported as being critical in two applications within the photolithography process: photoresists and anti-reflective coatings (ARC's). A detailed discussion of the technical feasibility of substitution in these applications has been provided in Section 4.

Persistent long-term growth in the semiconductor industry of 16% over the past decades (ESIA, 2002) has created an industry in UK with a turnover of £5 billion in 2000 employing around 40,000 workers in 2001 (Keynote, 2002). The UK forecast growth in the semiconductor sector is predicted at 44.8% between 2002 and 2005 (Keynote 2002), due to the increase in demand for end user products, such as third generation mobile phones and digital technology.

Semiconductors currently account for 63% of the market sector with related active components contributing a further 26% of the value of the market. An immediate cessation in the use of PFOS related substances in the sector is likely to adversely affect the industry and its competitiveness.

The objective of the strategy is, therefore, to introduce provisions for a time limited derogation backed up with formal provisions for emissions control measures.

Recommended Measures

Photolithography and semiconductor applications should be included in marketing and use restrictions with a derogation for phase-out of five years. Attached to this five year derogation should be conditions of permitted use, where this should formalise provisions for suitable emissions and waste treatment via incineration. As noted earlier, this can be achieved:

- at National (UK) level through use of the Technical Standards Directive 98/48/EC (TSD) (subject to clearance from EC authorities); and

- at the EU level, through Directive 76/769/EEC concerning restrictions on the marketing and use of certain dangerous substances and preparations.

This should be supplemented by requirements under the Waste Incineration Directive for high temperature incineration of all waste streams.

In the interim, it is suggested that a Voluntary Agreement by the photolithography and semiconductor industry to start such undertakings would smooth the transition and provide for swifter and more effective risk management.

It is also suggested that a review(s) of progress should be carried out at a suitable point(s) within the five year derogation. Evidence of research progress on substitutes should be presented at such a review(s) along with tangible evidence connected with any continuing problems for substitution that may impact on the deadlines.

Economic Impact of Actions

Environmental emissions control and waste incineration already takes place (with the exception of some waste streams that may currently go through water treatment), hence this risk reduction option relates only to formalising these commitments. The costs to industry of such emission control are therefore assumed to be negligible.

With regard to these deadlines, it is known that technical improvements through the adoption of new processes may mean that PFOS related substances are no longer required. The need to phase-out use of PFOS based substances within five years should be considered within the decision making processes concerning which of the new process technologies to adopt.

8.3.6 Risk Reduction Strategy for Hydraulic Fluids Used in Aviation

Objectives and Actions in Relation to Hydraulic Fluids

The substances used in aviation hydraulic fluids have not been identified in the list of CAS registered substances in Annex 2 that are PFOS related. Nonetheless, these substances are believed to be PFOS related.

The overall objective of the strategy is a phase-out and a cessation of use of these PFOS related substances in aviation hydraulics. However, given the lack of alternatives, the aviation safety critical factors associated with their use, and that these issues apply to the safety of the vast majority of the world’s civilian aircraft, an immediate cessation in use is not a feasible option.

The objective of the strategy is, therefore, to introduce provisions for a phase-out within a reasonable timescale backed up with formal provisions for emissions control measures.

Recommended Measures

Aviation hydraulic fluid applications should be included in marketing and use restrictions with a derogation. Attached to this derogation should be conditions of permitted use, where this should formalise provisions for suitable emissions control and waste treatment via incineration. This should be supplemented by requirements under the Waste Incineration Directive for high temperature incineration of all waste streams. In addition, it is suggested that the aviation industry should put forward a Voluntary Agreement in relation to the conditions of use to provide for swifter and more effective risk management.

As regards the definition of a reasonable timescale, as there are no candidate replacements at this time and safety testing and approval of new hydraulic fluids is rigorously applied over an extended timescale, it is difficult to set clear deadlines for a phase-out. Accordingly, it is suggested that reviews of research progress should be carried out at regular intervals. Evidence of research progress on substitutes should be presented at such reviews along with tangible evidence connected with any continuing problems for substitution. The first of these reviews should be timed to occur alongside the other reviews for derogated uses.

Economic Impact

In terms of environmental emissions control, the cost of implementing strict conditions of use should be negligible as we are informed that appropriate emissions control and waste incineration measures are already applied.

8.4 Summary of Recommended Risk Reduction Strategy

Table 8.2 provides a summary table of the proposed risk reduction strategy.

Table 8.2: Summary of Recommended Risk Reduction Measures

	Marketing and Use Restriction (TSD or 76/769/EEC) with classification and labelling suggested)		**Interim Voluntary Agreement**	**Waste Incineration Directive Requirements**	**Duty of Care provisions under Environmental Protection Act (1990), Waste management Licensing Regulations (1994) and Special Waste Regulations (1996)**
	Cessation	**Conditional Derogation (timescale and emissions control)**			
Historical Uses					
Carpets	Yes				
Leather/apparel	Yes				
Textiles/upholstery	Yes				
Paper and packaging	Yes				
Coatings and coating additives	Yes				
Industrial and household cleaning products	Yes				
Pesticides and insecticides	Yes				
Other Possible Future Uses					
Medical applications	Yes				
Flame retardants	Yes				
Mining and oil surfactants	Yes				
Adhesives	Yes				
Existing Uses					
Metal plating	Yes				
Use of existing PFOS fire fighting foam stock	Yes	5 years	Yes	Yes	Yes
Photographic industry	Yes	5 years with progress reviews	Yes	Yes	Yes
Photolithography and semiconductors	Yes	5 years with progress reviews	Yes	Yes	Yes
Hydraulic fluids used in aviation	Yes	Reviewed	Yes	Yes	Yes

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ANNEX 1

PROJECT SPECIFICATION

PROJECT SPECIFICATION

RISK REDUCTION STRATEGY AND ANALYSIS OF ADVANTAGES AND DRAWBACKS FOR PERFLUOROOCTANE SULFONATE (PFOS)

1. Objective

1.1 To assess the advantages and drawbacks of different risk reduction options, primarily for environmental concern, on the use of perfluorooctanyl sulphonate (PFOS) and substances that can degrade to PFOS in the environment, to:

i. enable judgement as to whether the benefits of adopting the restrictions, outweigh the consequences to society as a whole of imposing the controls;

ii. determine whether the chosen risk reduction strategy is the best option, and offers the greatest net benefits;

1.2 Precise details of the outline work plan are described below.

2. Background

2.1 During the ninth meeting of the Task Force on Existing Chemicals (29-30 May 2000) several OECD member countries agreed to informally work together to collect information on the environmental and human health hazards of PFOS to produce a hazard assessment. This followed an announcement by 3M, the largest US manufacturer of PFOS and PFOS related chemicals, to phase out production and use of these chemicals from 2001 onwards. The UK and US agreed to take the lead, assisted by the OECD secretariat, on this activity by requesting available exposure information from Member countries, as well as from non member countries through the Intergovernmental Forum on Chemical Safety (IFCS).

The Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology (November 2000) agreed that this matter was of sufficient interest to all OECD member countries, for the activity to be undertaken under the existing Chemicals Programme and overseen by the Task Force.

The UK now intends to produce a Risk Reduction Strategy (RRS) on PFOS (including those substances which degrade to PFOS) in accordance with the EU Existing Substances Regulation (793/93/EEC). In this Regulation, where any proposed control measures include recommendations for restrictions on the marketing and use of substances, an analysis of the advantages and drawbacks of the substance, and of the availability of replacement substances should be submitted. The implication is that benefits as well as risks should be taken into account in developing controls on hazardous substances in current use, while examining the likely effectiveness, practicability, economic impact, and monitorability of the risk reduction measure(s).

3. Risk Reduction Strategy

3.1 The aim is to recommend a strategy which effectively reduces risks, while imposing the minimum necessary burden on society as a whole. Attached as Annex A is an EU technical guidance document on development of risk reduction strategies.

3.2 According to the Existing Substances Regulation, where the risk reduction strategy recommends marketing and use restrictions, it must be supported by an analysis of advantages and drawbacks and the availability of alternatives, viz there is a balance to be struck between the benefits arising from the use of the substance, and the risks. Alternatives to be assessed include both alternative substances and alternative methods. Step 5 (Section 6) of the above-mentioned technical guidance document explains the approach to be taken should the risk reduction strategy recommend marketing and use restrictions. As further background enclosed at Annex B is the publication "Risk Benefit Analysis of Existing Substances" - guidance produced by a UK government/industry working group in February 1995.

3.3 Although the formal minimum requirement calls for the analysis of advantages and drawbacks only when marketing and use restrictions are recommended, the contractor should conduct such an analysis on all identified risk reduction options in order to provide a more complete basis for decision making. The advantages and drawbacks can be assessed in terms of qualitative or quantitative analysis as appropriate across the following range:

> i. a systematic qualitative assessment - risks and benefits should be described to allow the balance of advantages and drawbacks to be assessed, and the scope for further quantification established; which would largely depend on the availability of information following consultation. A qualitative assessment will include a systematic listing of risks and benefits to justify that the proposed control measures will offer the greatest net benefits;
>
> ii. a semi quantified assessment - applicable where more information is available, allowing as many factors as possible to be quantified. Partial quantification can provide a powerful aid in decision making. Quantified data can be expressed either in physical units (e.g. amounts of units affected, kg, etc.) or commensurate units (e.g. monetary values);
>
> iii. a fully quantified assessment: it will rarely be possible to produce a fully quantified analysis, e.g. cost benefit analysis which allows a degree of certainty or confidence about the impact of proposed restrictions. If a fully quantified assessment is undertaken, the economic consequences can often be approximated by measuring the likely effect on producer and consumer surplus. Valuing the environmental and human health advantages will be more difficult, and involve applying techniques for expressing advantages find drawbacks in a common form.

3.4 In summary, the analysis of advantages and drawbacks should always include a systematic qualitative analysis, and in most cases involve a semi quantitative or a fully quantified analysis. A key element will be the availability of replacement substances, and the analysis should demonstrate how this affects the balance of advantages and drawbacks of the recommended restrictions.

3.5 Once the likely reductions in risks to human health and the environment from the risk reduction measures have been established, described and possibly valued, they can be compared with the consequences of those control measures for producers and consumers. A decision must then follow on whether any overall increasing burden that would result from the adoption of the proposed risk reduction measures is justified by the reduction in risk to people and the environment. The basis for this decision will range from a purely subjective comparison between qualitative statements of changes of risk and effects of control measures, to a clear financial difference between monetary values on risk reduction. The outcome of the risk benefit analysis may conclude that:

i. restrictions are not likely to result in significant drawbacks, and are justified;

ii. there are significant drawbacks, but adoption is justified by probable reduction in risk;

iii. proposed restrictions are likely to result in significant drawbacks, and are not justified by probable reduction in risks.

4. Hazard assessment

4.1 The specific substance to be addressed by this contract is perfluorooctane sulfonate (PFOS). Where the term PFOS is used, this should be taken to mean both PFOS and any substance that can be degraded to PFOS in the environment. The OECD agreed and published hazard assessment (can be found at www.oecd.org/pdf/M00036000/MOO036809.pdf) has indicated the following for PFOS:

4.2 Human Health

- is persistent, bioaccumulative and toxic to mammalian species
- has been detected in the serum of occupational and general populations
- a statistically significant risk of death from bladder cancer
- an increased risk of episodes reported for neoplasms of the male reproductive system; and overall category of cancers, benign growths and neoplasms of the gastrointestinal tract (risk ratios highest in employees with the highest and longest exposures to fluorochemicals.

- not found to be genotoxic in a variety of assay systems

4.3 Environment

- persistent in the environment but there is currently little information on the life-cycle steps that may lead to releases into the environment
- does not hydrolyse, photolyse or biodegrade under environmental conditions and not expected to volatilise
- found in surface water and sediment downstream of production facilities
- is found in wastewater treatment plant effluent, sewage sludge and landfill leachate
- is distributed widely among several species of wild-birds and fish
- is detected in marine mammals at a number of locations world-wide
- has been shown to bioconcentrate in fish
- has high acute toxicity to honey bees

4.4 Conclusions

- PFOS related chemicals are used in a variety of products including surface-treatments of fabric for soillstain resistance, paper protection applications as part of a sizing agent formulation and in performance chemicals for applications such as fire fighting foams.
- the number of production sites is not clear but there is production in the US, Europe and Japan
- its persistence, presence in the environment and bioaccumulative potential indicate cause for concern
- given the apparent widespread occurrence of PFOS, national or regional exposure information gathering and risk assessment may need to be considered

A human health 1 environmental risk assessment has not been undertaken, although potential risks have been identified for man via the environment resulting from concerns about the bioaccumulative potential of PFOS. The current conclusion of the hazard assessment is that further information is required to better characterise the risk. As a result of gathering further information, more uses may be identified and these may be included in the contract leading to further work. This work may help to determine whether precautionary action is necessary.

If the scope of the analysis needs to be extended to uses of PFOS and PFOS related compounds beyond that of the hazard assessment (Le if this indicates information is required on other uses other than stated in the OECD hazard assessment) then these additional requirements will be

included in the contract on a time charge basis against limits agreed with the Nominated Officer.

5. Outline Work Plan - PFOS Risk Reduction Strategy

5.1 Preliminary Research

Since there is no agreed detailed risk assessment available, it will be necessary to identify, at the start, the use pattern and life-cycle of PFOS in order to fully evaluate any appropriate risk reduction measures. Previous Environment Agency research considered perfluoroalkyl substances (PFAS) in general, not just PFOS. Information is therefore needed on :

- what industries the PFOS-related chemicals (including polymers) are used in (industryluse categories), with an indication of the size and distribution of the industry in each case (some of this information is available in the Agency report, for a limited number of sectors)
- the tonnages involved, shelf-life of products and trends [the Agency report provided detailed data on tonnages of PFAS sold onto the UK market from three global producers, with one other providing data on one application area]
- the typical concentration of these substances that can degrade to PFOS in formulations, preparations and articles throughout the whole life cycle of the substance, with an indication of their degradation pathways and half-lives.
- what the likely emissions of these chemicals are at each stage in their life cycle (including e.g, upholstery cleaning and the possibility of release from landfill sites).

It is likely that much of this information will only be made available at the EU scale, in confidence. A good overview is likely to be difficult to achieve since the market for PFAS is extremely diverse and highly fragmented in end-product terms (there are thousands of consumer and industrial products on the global market, ranging from shoe polishes to optometry aids, which rely on low concentrations of highly fluorinated products). The main applications for PFAS in the UK are as protective treatments (e.g. for carpets, textiles, paper and board), surfactants (including fire fighting chemicals), and in paper/board treatment, with a market of around 400 tonnes of fluorinated active ingredient (in 2000), all of which is imported. Trade associations were unaware of PFAS use in certain sectors, even though PFAS manufacturers indicated that they sold into those sectors. In most instances trade associations and their members were not aware of the specific type of PFAS contained in their products. This implies that most of the consultation will need to rely on information provided by the primary producers. Due to the large number of chemicals likely to be involved, grouping will have to be considered.

Information about actual sites that import/process such chemicals in the UK should be included. Consultation should also take place with other regulatory authorities (e.g. a project concerning the use of PFOS in Denmark took place in 2001, and the Netherlands in 2002103). Close contact should be maintained with the Environment Agency who will be evaluating the potential for and significance of any risks that may be identified during this investigation of the use pattern and life-cycle.

5.2 The Risk Reduction Strategy aim is to produce a risk reduction strategy in accordance with steps 1-6 of the technical guidance (Annex A) for all identified risks of PFOS (and substances which degrade to PFOS) and if necessary, a Regulatory Impact Assessment (RIA) and Competition Assessment. The strategy should separately address both the environment risks and the implications of control measures that would be necessary to deal with the man via the environment concerns identified in the human health risk assessment. The need for any precautionary action to address the human health concerns would be a policy decision informed by the results of the strategy. The stages to be followed in the risk reduction strategy are set out below.

Stage 1

i. Data gathering and evaluation of PFOS uses of concern from the OECD hazard assessment and the preliminary work carried out as in 5.1. Establish the range of potential risk reduction options and current control measures in place. Stage 1 should be completed within up to 8 weeks of the instruction to proceed.

Stage 2

ii. a systematic qualitative assessment of the advantages and drawbacks for each option identified (subject to confirmation with the Nominated Officer at completion of stage 1). Recommendations will be required at the completion of this stage as to whether a semi quantified or fully quantified assessment can be justified. Completion of a draft stage 2 report will be required within 12 weeks of the instruction to proceed (for stage 1)

Stage 3

iii. a semi quantified assessment examining one or more options as appropriate for the current uses of concern; or

iv. a fully quantified assessment examining one or more options as appropriate for the current uses of concern. Justification for options requiring a quantitative approach (semi or full) should be demonstrated following completion of the qualitative assessment. The options to be considered for quantification or whether to move direct to Stage 4 should be agreed with the Nominated Officer before commencement of Stage 3. Completion of Stage 3 report will be required within 10 weeks of the instruction to proceed (for stage 3).

Stage 4

v. preparation of the final risk reduction strategy in accordance with Step 6, Annex A. All available cost information should be set out for each option considered and any assumptions made clear. The Stage 4 Final Report (Risk Reduction Strategy) will be required within 2 weeks of agreement to the Stage 3 report.

Stage 5

vi. if marketing and use controls are proposed, preparation of separate Regulatory Impact Assessments (RIA), for Great Britain and Northern Ireland, briefly describing the issue that has given rise to a need for legislation: the risks, costs and benefits of the proposal; who is affected and non-regulatory options. The RIA **must** include a Competition Assessment and Small Firms' impact Test. Guidance on preparing. a RIA can be found at the Cabinet Office web site http://www.cabinet-office.gov.uk/regulation/scrutiny/ The RIA should be a standalone document which summarises the key information and be a maximum of 15 pages referring to the risk reduction strategy as an annex. The two completed RIAs will be required within 4 weeks of the start of stage 4 and following formal instructions to proceed from the nominated officer (at the beginning of stage 4)

5.3 Consultation with producers, downstream users, consumers, the Environment Agency, Department of Health, other Government departments and Agencies and other Member States will be important, to ensure that all significant uses of PFOS have been taken into account, and that all the consequences of control measures or substitutes have been considered. At the outset of the studies a list of consultees, both in the UK and other Member States, should be prepared and maintained throughout.

5.4 At certain key stages of the analysis it will be necessary to consult, and peer review emerging findings/conclusions. Assistance should be provided to the Nominated Officer as necessary. Arrangements should be in place so that draft reports are distributed to consultees and can be placed on the Defra/chemicals web site. A table of comments will be required, summarising written comments made and actions taken. A separate comments table will be required for responses to views expressed by other Member States.

During the course of the contract the contractor may receive commercially confidential information. This information should be kept separate from the main publicly available report and provided to the nominated officer as a confidential annex. Where such information is needed to justify specific recommendations in the report it should be quoted in as generic a way as possible (agreed with the nominated officer).

5.5 The availability of substitutes is a key issue when considering potential control measures. There must be some assurance that steps taken to control the risk will not result in greater or equal risk to people or the environment from the use of substitute substances. It will therefore be important to engage in detailed consultation with all stakeholders (producers / formulators 1 users 1 scientific fora, etc.) to identify potential substitutes and to gain an understanding of the hazard profiles. The successful contractor will also be responsible for reviewing the available scientific data on substitutes with the Environment Agency, Health and Safety Executive, Department of Health and Department of Trade & Industry to determine the potential impact of substitutes. This may involve the need to collect sufficient data in order to apply relevant scientific modeling. The aim will be to ensure sufficient information is available to enable necessary assumptions to be made on the suitability of potential substitutes taking into account the likely effects on human health and the environment. Alternative processes should be also explicitly addressed.

5.6 Reports

An Interim report will be required at completion of each stage. A final (stand alone) report will be required at completion of Stage 4. All reports should be submitted in a format compatible with that set out in Annex A and include an Executive Summary. The Stage 4 final report should include a conclusion and recommendation which determines the most appropriate risk reduction strategy. Three copies of the final report should be provided (plus one unbound) with an electronic version in Word 2000 and as a PDF file.

5.7 Presentations

It will be necessary, both during the peer review process of the study as it develops, and on completion, to assist the Nominated Officer with the presentation of the conclusions. The contractor will be required to prepare and deliver formal presentations either to UK industry/government groups or to assist in subsequent negotiations with other EU Member States, or in other international fora as required.

6. Nominated Officer

6.1 The Nominated Officer for the contract is Hasmitta Stewart, Department for Environment, Food and Rural Affairs, Chemicals & GM Policy Division, Zone 3/F6, Ashdown House, 123 Victoria Street, London SW 1 E 6DE, Tel 020 7944 5867.

6.2 The management of the contract will be overseen by the Nominated Officer and a steering group with representatives from other Member State(s), Department for Environment, Food and Rural Affairs, other Government departmentslagencies and non -govern mental organisations (NG0s). A meeting will be called at the commencement of the contract, and prior to the formal completion of Stage 1, Stage 2 and Stage 3. Interim reports should be provided to each steering group member before each Steering Group meeting. Further ad hoc meetings will be called as required by the Nominated Officer. The contractor will be required to produce a draft written record of each meeting.

7. Tender Proposal

7.1 A tender proposal should to be made with costs broken down by each stage. The tender proposal for the contract should include a resume of how the requirement is to be approached, and the methodology proposed. Any proposals for sub contracting any elements of this contract should be specified in the tender proposal.

7.2 Contractors should provide time charge rates for each member of the team as well as their CVs. Proposals should show the division of man-days and costs between all stages.

Chemicals and GM Policy Division

ANNEX 2

DRAFT LIST OF COMPOUNDS POTENTIALLY DEGRADING TO PFOS IN THE ENVIRONMENT

ANNEX 2: DRAFT LIST OF COMPOUNDS POTENTIALLY DEGRADING TO PFOS IN THE ENVIRONMENT

Table A2.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

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

Table A2.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

Ref No.	CAS Number	PFOS related substance
22	24924-36-5	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-2-propenyl-
23	25268-77-3	2-Propenoic acid, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester
24	29081-56-9	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt
25	29117-08-6	Poly(oxy-1,2-ethanediyl), .alpha.-[2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl]-.omega.-hydroxy-
26	29457-72-5	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt
27	30295-51-3	1-Octanesulphonamide, N-[3-(dimethyloxidoamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
28	30381-98-7	1-Octanesulphonamide, *N*,*N'*-[phosphinicobis(oxy-2,1-ethanediyl)]bis[*N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt
29	31506-32-8	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-methyl-
30	38006-74-5	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl]amino]-*N*,*N'*,*N''*-trimethyl-, chloride
31	50598-29-3	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(phenylmethyl)-
32	52550-45-5	Poly(oxy-1,2-ethanediyl), Ŭ-[2-[[(heptadecafluorooctyl)sulphonyl]propylamino]ethyl]-ɤ -hydroxy-
33	56773-42-3	Ethanaminium, *N*,*N'*,*N''*-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulphonic acid (1:1)
34	57589-85-2	Benzoic acid, 2,3,4,5-tetrachloro-6-[[[3- [[(heptadecafluorooctyl)sulphonyl]oxy]phenyl]amino]carbonyl]-, monopotassium salt
35	58920-31-3	2-Propenoic acid, 4-[[(heptadecafluorooctyl)sulphonyl]methylamino]butyl ester
36	61577-14-8	2-Propenoic acid, 2-methyl-, 4-[[(heptadecafluorooctyl)sulphonyl]methylamino]butyl ester
37	61660-12-6	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[3-(trimethoxysilyl)propyl]-
38	67939-42-8	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[3-(trichlorosilyl)propyl]-
39	67969-69-1	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[2-(phosphonooxy)ethyl]-, diammonium salt
40	67939-88-2	1-Octanesulphonamide, *N*-[3-(dimethylamino)propyl]- 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, monohydrochloride
41	68081-83-4	Carbamic acid, (4-methyl-1,3-phenylene)bis-, bis[2-[ethyl[(perfluoro-C4-8-alkyl)sulphonyl]amino]ethyl] ester
42	68298-11-3	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl](3-sulphopropyl)amino]-*N*-(2-hydroxyethyl)-*N*,*N*-dimethyl-, hydroxide, inner salt

Table A2.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

Ref No.	CAS Number	PFOS related substance
43	68329-56-6	2-Propenoic acid, eicosyl ester, polymer with 2-[[(heptadecafluorooctyl)sulphonyl] methylamino]ethyl 2-propenoate, hexadecyl 2-propenoate, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate and octadecyl 2-propenoate
44	68239-73-6	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(4-hydroxybutyl)-*N*-methyl-
45	68310-75-8	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl]amino]-*N*,*N’*,*N’’*-trimethyl-, iodide, ammonium salt
46	68541-80-0	2-Propenoic acid, polymer with 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and octadecyl 2-propenoate
47	68555-90-8	2-Propenoic acid, butyl ester,polymer with 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl 2-propenoate, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate and 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate
48	68555-91-9	2-Propenoic acid, 2-methyl-, 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester, polymer with 2-[ethyl[(nonafluorobutyl)sulphonyl]amino] ethyl 2-methyl-2-propenoate, 2-[ethyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [ethyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and octadecyl 2-methyl-2-propenoate
49	68555-92-0	2-Propenoic acid, 2-methyl-, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester, polymer with 2- [methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and octadecyl 2-methyl-2-propenoate
50	68608-14-0	Sulphonamides, C4-8-alkane, perfluoro, *N*-ethyl-*N*-(hydroxyethyl), reaction products with 1,1'-methylenebis[4-isocyanatobenzene]
51	68649-26-3	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-, reaction products with *N*-ethyl-1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-1-butanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-*N*-(2-hydroxyethyl)- 1-heptanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-(2-hydroxyethyl)-1-hexanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,5-undecafluoro-*N*-(2-hydroxyethyl)-1-pentanesulphonamide, polymethylenepolyphenyleneisocyanate and stearyl alc.
52	68867-60-7	2-Propenoic acid, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester, polymer with 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2- [methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate and.alpha.-(1-oxo-2-propenyl)-.omega.-methoxypoly(oxy-1,2-ethanediyl)
53	68877-32-7	2-Propenoic acid, 2-methyl-, 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester, polymer with 2-[ethyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(tridecafluoro-hexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(undecafluoro-pentyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and 2-methyl-1,3-butadiene
54	68891-96-3	Chromium, diaquatetrachloro[.mu.-[*N*-ethyl-*N*- [(heptadecafluorooctyl)sulphonyl] glycinato-.kappa.O:.kappa.O']]-.mu.-hydroxybis(2-methylpropanol)di-

Table A2.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

Ref No.	CAS Number	PFOS related substance
55	68909-15-9	2-Propenoic acid, eicosyl ester, polymers with branched octylacrylate, 2- [[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl acrylate, 2-[methyl [(nonafluorobutyl)sulphonyl]amino]ethyl acrylate, 2- [methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl acrylate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl acrylate, 2- [methyl[(undecafluoropentyl)sulphonyl]amino]ethyl acrylate, polyethylene glycol acrylate Me ether and stearyl acrylate
56	68958-61-2	Poly(oxy-1,2-ethanediyl), .alpha.-[2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl]-.omega.-methoxy-
57	70225-14-8	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1)
58	70776-36-2	2-Propenoic acid, 2-methyl-, octadecyl ester, polymer with 1,1-dichloroethene, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl 2-propenoate, *N*-(hydroxymethyl)-2-propenamide, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate and 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate
59	71463-78-0	Phosphonic acid, [3-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]propyl]-
60	71463-80-4	Phosphonic acid, [3-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]propyl]-, diethyl ester
61	71487-20-2	2-Propenoic acid, 2-methyl-, methyl ester, polymer with ethenylbenzene, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl 2-propenoate, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2- [methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate, 2- [methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate and 2-propenoic acid
62	91081-99-1	Sulphonamides, C$_{4\text{-}8}$-alkane, perfluoro, *N*-(hydroxyethyl)-*N*-methyl, reaction products with epichlorohydrin, adipates (esters)
63	92265-81-1	Ethanaminium, *N*,*N*,*N*-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]-, chloride, polymer with 2-ethoxyethyl 2-propenoate, 2-[[(heptadecafluorooctyl)sulphonyl] methylamino]ethyl 2-propenoate and oxiranylmethyl 2-methyl-2-propenoate
64	94133-90-1	1-Propanesulphonic acid, 3-[[3-(dimethylamino)propyl][(heptadecafluorooctyl) sulphonyl]amino]-2-hydroxy-, monosodium salt
65	94313-84-5	Carbamic acid, [5-[[[2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethoxy]carbonyl]amino]-2-methylphenyl]-, 9-octadecenyl ester, (Z)-
66	98999-57-6	Sulphonamides, C$_{7\text{-}8}$-alkane, perfluoro, *N*-methyl-*N*-[2-[(1-oxo-2-propenyl)oxy]ethyl], polymers with 2-ethoxyethyl acrylate, glycidyl methacrylate and *N*,*N*,*N*-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]ethanaminium chloride
67	127133-66-8	2-Propenoic acid, 2-methyl-, polymers with Bu methacrylate, lauryl methacrylate and 2-[methyl[(perfluoro-C$_{4\text{-}8}$-alkyl)sulphonyl]amino]ethyl methacrylate
68	129813-71-4	Sulphonamides, C$_{4\text{-}8}$-alkane, perfluoro, *N*-methyl-*N*-(oxiranylmethyl)
69	148240-78-2	Fatty acids, C$_{18}$-unsatd., trimers, 2-[[heptadecafluorooctyl)sulphonyl]methylamino]ethyl esters
70	148684-79-1	Sulphonamides, C$_{4\text{-}8}$-alkane, perfluoro, *N*-(hydroxyethyl)-*N*-methyl, reaction products with 1,6-diisocyanatohexane homopolymer and ethylene glycol
71	160901-25-7	Sulphonamides, C$_{4\text{-}8}$-alkane, perfluoro, *N*-ethyl-*N*-(hydroxyethyl), reaction products with 2-ethyl-1-hexanol and polymethylenepolyphenylene isocyanate
72	178094-69-4	1-Octanesulphonamide, *N*-[3-(dimethyloxidoamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-,potassium salt

Table A2.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

Ref No.	CAS Number	PFOS related substance
73	178535-22-3	Sulphonamides, $C_{4\text{-}8}$-alkane, perfluoro, *N*-ethyl-*N*-(hydroxyethyl)-, polymers with 1,1'-methylenebis[4-isocyanatobenzene] and polymethylenepolyphenylene isocyanate, 2-ethylhexyl esters, Me Et ketone oxime-blocked
74	182700-90-9	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-methyl-, reaction products with benzene-chlorine-sulphur chloride (S_2Cl_2) reaction products chlorides
75	L-92-0151 (US Pre-manufacture notice)	2-Propenoic acid, 2-methyl-, butyl ester, polymer with 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [ethyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and 2-propenoic acid
76	P-94-2205 (US Pre-manufacture notice)	Polymethylenepolyphenylene isocyanate and bis(4-NCO-phenyl)methane reaction products with 2-ethyl-1-hexanol, 2-butanone, oxime, *N*-ethyl-*N*-(2- hydroxyethyl)-1-C_4-C_8 perfluoroalkanesulphonamide
77	192662-29-6	Sulphonamides, $C_{4\text{-}8}$-alkane, perfluoro, *N*-[3-(dimethylamino)propyl], reaction products with acrylic acid
78	251099-16-8	1-Decanaminium, *N*-decyl-*N*,*N*-dimethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulphonic acid (1:1)
79	306973-46-6	Fatty acids, linseed-oil, dimers, 2- [[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl esters
80	306973-47-7	Sulphonamides, $C_{4\text{-}8}$-alkane, perfluoro, *N*-(hydroxyethyl)-*N*-methyl, reaction products with 12-hydroxystearic acid and 2,4-TDI, ammonium salts
81	306974-19-6	Sulphonamides, $C_{4\text{-}8}$-alkane, perfluoro, *N*-methyl-*N*-[(3-octadecyl-2-oxo-5-oxazolidinyl)methyl]
82	306974-28-7	Siloxanes and Silicones, di-Me, mono[3-[(2-methyl-1-oxo-2-propenyl)oxy]propylgroup] -terminated, polymers with 2-[methyl[(perfluoro-C4-8-alkyl)sulphonyl]amino]ethyl acrylate and stearyl methacrylate
83	306974-45-8	Sulphonic acids, $C_{6\text{-}8}$-alkane, perfluoro, compounds with polyethylene-polypropylene glycol bis(2-aminopropyl) ether
84	306974-63-0	Fatty acids, C_{18}-unsatd.,dimers, 2-[methyl[(perfluoro-$C_{4\text{-}8}$-alkyl)sulphonyl]amino] ethyl esters
85	306975-56-4	Propanoic acid, 3-hydroxy-2- (hydroxymethyl)-2-methyl-, polymer with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol and *N*,*N*',2-tris(6-isocyanatohexyl)imidodicarbonic diamide, reaction products with *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-1-octanesulphonamide and *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-*N*-(2-hydroxyethyl)-1-heptanesulphonamide, compounds with triethylamine
86	306975-57-5	Propanoic acid, 3-hydroxy-2-(hydroxymethyl)-2-methyl-, polymer with 1,1'-methylenebis[4- isocyanatobenzene] and 1,2,3-propanetriol, reaction products with *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-1-octanesulphonamide and *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-*N*-(2-hydroxyethyl)-1-heptanesulphonamide, compounds with morpholine
87	306975-62-2	2-Propenoic acid, 2-methyl-, dodecyl ester, polymers with 2- [methyl[(perfluoro-$C_{4\text{-}8}$-alkyl)sulphonyl]amino]ethyl acrylate and vinylidene chloride
88	306975-84-8	Poly(oxy-1,2-ethanediyl), .alpha.-hydro-.omega.-hydroxy-, polymer with 1,6-diisocyanatohexane, *N*-(hydroxyethyl)-*N*-methyl perfluoro $C_{4\text{-}8}$-alkane sulphonamides-

Table A2.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment

Ref No.	CAS Number	PFOS related substance
		blocked
89	306975-85-9	2-Propenoic acid, 2-methyl-, dodecyl ester, polymers with *N*-(hydroxymethyl)-2-propenamide, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl methacrylate, stearyl methacrylate and vinylidene chloride
90	306976-25-0	1-Hexadecanaminium, *N*,*N*-dimethyl-*N*-[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]-, bromide, polymers with Bu acrylate, Bu methacrylate and 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate
91	306976-55-6	2-Propenoic acid, 2-methyl-, 2-methylpropyl ester, polymer with 2,4-diisocyanato-1-methylbenzene, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol and 2-propenoic acid, *N*-ethyl-*N*-(hydroxyethyl)perfluoro-C_{4-8}-alkanesulphonamides-blocked
92	306977-58-2	2-Propenoic acid, 2-methyl-, 3-(trimethoxysilyl)propyl ester, polymers with acrylic acid, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate and propylene glycol monoacrylate, hydrolysed, compounds with 2,2'-(methylimino)bis[ethanol]
93	306978-04-1	2-Propenoic acid, butyl ester, polymers with acrylamide, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate and vinylidene chloride
94	306978-65-4	Hexane, 1,6-diisocyanato-, homopolymer, *N*-(hydroxyethyl)-*N*-methyl perfluoro-C_{4-8}-alkane sulphonamides- and stearyl alc.-blocked
95	306979-40-8	Poly(oxy-1,2-ethanediyl), .alpha.-[2-(methylamino)ethyl]-.omega.-[(1,1,3,3-tetramethylbutyl)phenoxy]-, *N*-[(perfluoro-C_{4-8}-alkyl)sulphonyl]
96	306980-27-8	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*,*N*'-[1,6-hexanediylbis[(2-oxo-3,5-oxazolidinediyl)methylene]]bis[*N*-methyl-

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

ANNEX 3

HISTORIC DATA ON UK CONSUMPTION (IMPORTS) OF PFOS RELATED SUBSTANCES

ANNEX 3: HISTORIC DATA ON UK CONSUMPTION (IMPORTS) OF PFOS RELATED SUBSTANCES

Table A3.1: Summary Data on Applications of PFOS Related Substances Imported in the UK Prior to 2000

Application Type	**Percentage of Total Number of Products**	**Percentage of all CAS Nos. Available in the Market**	**PFOS Tonnage Range**	**Approximate Percentage of Total PFOS Imports**	**Percentage of Products with ROF***	**Maximum ROF Content in Preparations**	**ROF as a Percentage of Imported PFOS (in each application type)**	**ROF as a Percentage of Total ROF**
Paper & packaging protection	7%	9%	>25 t/y	32%	75%	1%	3.2%	42%
Carpet protection	10%	13%	>25 t/y	23%	-	-		-
Coatings (additives)	17%	30%	>10 t/y	18%	70%	7%	3.7%	28%
Apparel & leather protection	25%	37%	>10 t/y	15%	73%	2%	3.4%	21%
Fabric & upholstery protection	10%	22%	>10 t/y	10%	33%	2%	2%	9%
Fire fighting foams	18%	7%	>1 t/y	1%	-	-		-
Additives for household products	2%	2%	<1 t/y	1%	-	-		-
Chemical intermediates	7%	15%	<1 t/y	1%	25%	1%	0.7%	<1%
E&E** bath surfactants	5%	7%	<1 t/y	<1%	-	-		-
TOTAL	**100%**	**N/A**	**N/A**	**100%**	**40%**	**7%**	**2.4%**	**100%**

Source: Consultation

** ROF = "Residual Organic Fluorochemicals". This represents one or more of a reported total of 22 PFOS related substances*

*** E&E = electroplating and etching*

Note that the following tables do not provide full CAS Numbers of the PFOS related substances for reasons of confidentiality. The reference numbers for the chemical substances (1 - 46) do <u>not</u> represent the reference numbers for the substances in Annex 2 to this report. It should also be noted that percentages presented in the Tables A3.1 through to A3.4 have been rounded.

Table A3.2: Number of Products Containing Any Given PFOS Related Substance

No	Listed in Annex 2	Apprl & Leather	Carpet	Coatings	E&E Bath	Fabric & Upholst.	Fire Fighting	House-hold	Chem. Interm.	Paper & Packag.
1	V	1				1			1	
2	V			1					1	
3	V									2
4	V				1		11			
5	V							1		
6	V			1						
7									2	
8	V			1						
9									2	
10	V				1					
11	V			1						
12	V									2
13	V	2	2			1				
14				2						
15	V	1	1							
16	V			1						
17	V									2
18									1	
19				1						
20	V	1								
21	V	2	2			2				
22	V	1				1				
23		1	4			2				
24	V	2								
25				1						
26	V			1						
27	V	1								
28	V				1					
29				1					1	
30	V		5			2				
31	V									2
32	V			1						
33		1								
34							4			
35				1						
36		2	1			2				
37				1						
38		1								
39		1								
40		1		1						
41		1								
42		1				1				
43		1								
44							1			
45						1				
46						1				

Table A3.3: Sectoral Imports of CAS Numbers as a Percentage of the Total Imported PFOS Related Substances in Each Sector

No	Listed in Annex 2	Apprl & Leather	Carpet	Coating	E&E Bath	Fabric & Upholst.	Fire Fighting	House-hold	Chem. Interm.	Paper & Packag.
1	V	<1%				<1%			29%	
2	V			<1%					1%	
3	V									2%
4	V				**82%**		**75%**			
5	V							**100%**		
6	V			<1%						
7									24%	
8	V			<1%						
9									**35%**	
10	V				4%					
11	V			<1%						
12	V									**60%**
13	V	<1%	<1%			<1%				
14				<1%						
15	V	19%	4%							
16	V			<1%						
17	V									8%
18									12%	
19				12%						
20	V	**38%**								
21	V	4%	7%			8%				
22	V	5%				3%				
23		1%	6%			3%				
24	V	2%								
25				1%						
26	V			4%						
27	V	<1%								
28	V				14%					
29				6%					<1%	
30	V		**82%**			**42%**				
31	V									30%
32	V			<1%						
33		<1%								
34							5%			
35				<1%						
36		1%	1%			8%				
37				15%						
38		24%								
39		<1%								
40		3%		**61%**						
41		<1%								
42		<1%				18%				
43		2%								
44							20%			
45						16%				
46						<1%				
TOTAL		**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**

Table A3.4: Total Imports per CAS Number as a Percentage of the Total Imported PFOS Related Substances Across All Sectors

No	Listed in Annex 2	Apprl & Leather	Carpet	Coatings	E&E Bath	Fabric & Upholst.	Fire Fighting	House-hold	Chem. Interm.	Paper & Packag.	Total Across all
1	V	<1%				<1%			<1%		**<1%**
2	V			<1%					<1%		**<1%**
3	V									1%	**1%**
4	V				<1%		1%				**1%**
5	V							1%			**1%**
6	V			<1%							**<1%**
7									<1%		**<1%**
8	V			<1%							**<1%**
9									<1%		**<1%**
10	V				<1%						**<1%**
11	V			<1%							**<1%**
12	V									19%	**19%**
13	V	<1%	<1%			<1%					**<1%**
14				<1%							**<1%**
15	V	3%	1%								**4%**
16	V			<1%							**<1%**
17	V									3%	**3%**
18									<1%		**<1%**
19				2%							**2%**
20	V	5%									**5%**
21	V	1%	2%			1%					**3%**
22	V	1%				<1%					**1%**
23		<1%	1%			<1%					**2%**
24	V	<1%									**<1%**
25				<1%							**<1%**
26	V			1%							**1%**
27	V	<1%									**<1%**
28	V				<1%						**<1%**
29				1%					<1%		**1%**
30	V		19%			4%					**23%**
31	V									9%	**9%**
32	V			<1%							**<1%**
33		<1%									**<1%**
34							<1%				**<1%**
35				<1%							**<1%**
36		<1%	<1%			1%					**1%**
37				3%							**3%**
38		3%									**3%**
39		<1%									**<1%**
40		<1%		11%							**11%**
41		<1%									**<1%**
42		<1%				2%					**2%**
43		<1%									**<1%**
44							<1%				**<1%**
45						2%					**2%**
46						<1%					**<1%**
										TOTAL	**100%**

ANNEX 4

EMISSION ESTIMATES FOR THE VARIOUS USE SECTORS OF PFOS RELATED SUBSTANCES FROM THE DRAFT UK RER

A4. Environmental Emissions of PFOS Related Substances

A4.1 Approach to Calculating Environmental Emissions

A4.1.1 Overview

This Annex provides the results of the UK Review of Environmental Risks (RER) of PFOS related substances.

The aim is to describe and quantify the nature of the environmental emissions arising from the use of PFOS related substances in various sectors. In order to achieve this, the PFOS related substances have been grouped into various classes and a brief outline of the properties of these classes is provided (Section A4.1.3). This is followed by a quantification and discussion of the environmental emissions of these groups of PFOS related substances from the various use sectors (Section A4.2). Section A4.3 considers degradation of the groups of substances. Given the uncertainties associated with degradation and degradation rates of PFOS related substances, a number of breakdown scenarios have been included as model calculations to provide an analysis of the contribution of the various sectors to the overall burden of PFOS in the environment.

A4.1.2 Criteria for Grouping of PFOS Related Substances for Exposure Assessment

Annex 2 lists the various chemical substances which have been identified as having the possibility of degrading to PFOS in the environment. 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-acids**.

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[1]. Thus assumptions about the extent to which this happens, and the rate, have been made in the model calculations in Section A4.3. It is not possible to treat each substance of this group individually, so a generic set of properties have 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 and environmental behaviour, these substances will be called **PFOS-substances**.

The third group are polymeric materials, higher molecular weight polymers derived largely from the FOSE-type 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. 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 A4.3. These substances may contain residual PFOS-substances, and releases of these will also be considered. For the purpose of estimating releases and environmental behaviour, this group of substances will be called **PFOS-polymers**.

It has been assumed throughout that only substances and polymers derived originally from PFOSF have the potential to degrade to PFOS in the environment. Hence telomer-derived substances and materials are not included, nor are perfluorooctanoic acid (PFOA) related substances. It should however be noted that, in some sectors, it is not always possible to tell which specific type of material is being used. Similarly, the distinctions between the three groups (PFOS-acids, PFOS-substances and PFOS-polymers) are not always clear, and hence in some cases materials may be incorrectly allocated. In some cases the allocation has been simplified by assuming that all of the material used in a particular sector is of one group, where the reality may be that substances from different groups are used.

A4.1.3 Group Properties

PFOS-acids

The property values used are those of the PFOS acid potassium salt and are taken largely from the 3M Risk Assessment (3M, 2003).

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[1] The 3M report (3M, 2003) comments that in tests with a number of substances, N-EtFOSE was the only substance to lead to the formation of any PFOS, but no further information on these studies is included.

The log Kow value cannot be measured due to the surfactant properties of the substance. However, sorption to sediment and soils has been measured directly and these values can be used. The number of determinations in different soils and sediments is limited, and so the values derived should only be considered as indicative. They also do not provide any real information on the properties of the sorbing phases which are important in determining the degree of sorption. It is possible that other soils and sediments could exhibit very different sorptive behaviour[2]. Three soils were tested, and the sorption and desorption Kd values for each have been averaged. These give 32.7 for the clay, 12.8 for the clay loam and 35.1 for the sandy loam. The overall average value is 26.9, and this has been used for all soils. Only one sediment was tested, and the average of the sorption and desorption Kd values was 8.71. This value has been used for both sediment and suspended sediment. For sewage sludge, only one set of measurements were made[3]. The sorption and desorption values are almost an order of magnitude different (338 and 3130 respectively) so in this case the geometric mean has been used, which is 1028. This value has been used for all three sludge partition coefficients required in EUSES.

For bioconcentration, the whole body fish value of 2796 has been used for fish and aquatic biota. A bioconcentration factor for worms has been estimated from measurements during a toxicity test on worms (see the Draft Risk Evaluation Report (RPA & BRE, 2004)) and this has been used in the evaluation.

The use of the measured values for partition coefficients and bioconcentration factors means that a value for log Kow is not needed. Table A4.1 below provides a summary of values for PFOS-acids used in this analysis.

Table A4.1: Summary of Values for PFOS-acids

Property	**Value Used**
Solubility	570 mg/l
Vapour pressure	3.31×10^{-4} Pa at 20°C
Kd values (soil)	26.9
Kd values (sediment and suspended sediment)	8.71
Kd values (sewage sludge)	1028
Henry's Law constant	3.19×10^{-4} Pa m^3 $mole^{-1}$
Bioconcentration Factor (fish and aquatic biota)	2796
Log Kow value	Not required

PFOS-substances

Although there are a large number of substances which are included in this group, there is little or no readily available property information for any of them. The substance with the most data in RIKZ (2002) is N-EtFOSE (CAS 1691-99-2) and this has been used as

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[2] It should be noted that the values used are obtained from the robust study summaries in the 3M assessment rather than the main body of the text and are the 48-hour point values rather than those estimated using the Freundlich equation.

[3] The 48 hour point results are only presented as limit values, so in this case the Freundlich values have been used.

the model compound for this group. The properties of this group are shown in Table A4.2 below. Data are taken from RIKZ (2002).

Table A4.2: Summary of Values for PFOS-substances

Property	**Value Used**
Molecular weight	571.25
Melting point	57°C
Solubility	0.15 mg/l
Vapour pressure	0.5 Pa
Log Kow	4.4

Information on degradation rates is taken from the Draft Risk Evaluation Report (RPA & BRE, 2004). A degradation half life in air of 16 hours was estimated. For biodegradation, a rate constant of 0.0014 h^{-1} has been used. This rate will be used for water, soil and aerobic sediment in the model. An alternative half life of one year, to allow for the possible slower degradation of other substances, is also used in the same way.

The fraction of N-EtFOSE adsorbed to particulates in air was measured as 65% in outdoor air samples. This value is used in the calculations rather than estimating this percentage from the log Kow value.

It is recognised that other substance considered in this group may have somewhat different properties. These calculations are intended to give a rough idea of possible behaviour.

PFOS-polymers

There are no data on the properties of the polymeric substances. Therefore, properties have been chosen to represent the expected behaviour, i.e. low volatility, low solubility, and tendency to be associated with solid phases, as shown in Table A4.3 below.

Table A4.3: Summary of Values for PFOS-polymers

Property	**Value Used**
Molecular weight	10000
Melting point	when treated as a solid (100°C) used
Solubility	10^{-6} mg/l
Vapour pressure	10^{-6} Pa
Henry's Law Constant	10^{-5} Pa m^3 $mole^{-1}$
Log Kow	6

There are no data on degradation rates for the polymers, or on the extent to which PFOS may be produced, so again values have been selected to represent possible outcomes. The half lives for polymers are expected to be longer than those for the substances, so a half life of 30 years has been used. This is an arbitrary value. It should also be noted that the residual fluorocarbons present in the polymers have been treated as PFOS-substances and as such, this rate does not apply to them.

A4.2 Estimating the Environmental Emissions of PFOS Related Substances

A4.2.1 Overview

The emission estimates presented below are focussed mainly on the sectors identified as representing ‘continuing uses’ of PFOS related substances for which further risk reduction measures may be required. These sectors are:

- metal plating;
- fire fighting foams stock;
- photographic;
- semiconductors; and
- aviation.

In addition to these, special consideration is given to materials currently in use which were treated before the changes in use pattern (or the withdrawal by 3M). Releases from these applications have been considered and these include PFOS applications in:

- carpets;
- leather/apparel; and
- textiles/upholstery.

The historical uses of PFOS related substances in the following applications have been confirmed either in the UK or the EU. Emission estimates have been prepared for the confirmed historic uses in the UK (the first two) but no information was located to allow estimates for the other two applications to be made:

- paper and packaging;
- coatings and coating additives;
- industrial and household cleaning products; and
- pesticides and insecticides.

There are no emission estimates for uses of PFOS related substances in the following applications as there is no evidence of historical or current use in the UK or EU:

- medical applications;
- flame retardants;
- mining and oil surfactants; and
- adhesives.

For these emission calculations, the current use figures are generally based on the UK. The UK is assumed to account for 20% of each activity in the EU in order to estimate total use. It should also be noted that calculations assume that 10% of the activity takes place in the regional environment, with the rest in the continental environment. Exceptions to this are noted in the relevant sections.

A4.2.2 Metal Plating

The substances used in this sector are considered to be of the PFOS-acid type. The three example products included in Table 2.8 all contain the tetraethyl ammonium salt of PFOS.

Emissions to water are estimated using the approach taken in the risk assessment for chromium (VI) compounds under the Existing Substances Regulation (RAR, 2002). This approach was in turn based on an Emission Scenario Document on Metal Finishing (Environment Agency, 1997). It is assumed that a large scale processor treats 40 m^2 of metal per hour, over a 12 hour day for 240 days per year. Losses can occur from the treatment tank through solution remaining on the metal articles as they are removed from the tank – this is called drag-out. For a rack deposition system, the typical drag-out rate is 5 litres per 100 m^2 of surface treated. Hence for the site above, the drag-out rate would be 2 litres per hour. Information received indicates that PFOS-acid substances are present in the treatment bath at ppm levels (pers. comm.). Assuming a level of 10 ppm, then the removal rate for PFOS would be 20 mg per hour. Chromium plating takes place at ~40°C, and there is some evaporation of water from the tank, so some of the drag-out is returned to the treatment tank. A figure of 25% is suggested in the ESD, hence the loss of substance is 15 mg per hour. The drag-out is removed from the metal by rinsing, so this substance is diluted in the rinse water, but the rate of loss is not affected by this. For a 12 hour day, the daily loss to water is therefore 180 mg/day. Over 240 days the annual loss is 43 g/year.

There may also be the possibility of emissions to air from this process. This should be low, as the function of the substance is to prevent mist formation during the plating process, and the substance has a low vapour pressure. An approach to estimating such emissions is to consider the maximum limit for chromium (VI) in air of 0.05 mg/m^3, and to assume that all components of the treatment bath are present in any mist at their ‘working’ concentrations. From the ESD, the concentration of chromium (VI) in a hard hexavalent chromium bath is ~130 g/l. The volume containing 0.05 mg is therefore 3.8x10^{-7} litres. At a concentration of 10 ppm, this contains 3.8x10^{-6} mg of PFOS, hence the air concentration of PFOS is 3.8x10^{-6} mg/m^3. No specific information on air flow rates in chromium plating works is available, but a rate of 7,200 m^3/hour has been used for large lubricant blending sites (Environment Agency, 1997a) and is used here as an illustration. For a 12 hour day, this gives a daily removal of air of 86,400 m^3, and hence a release of PFOS of 0.33 mg/day. For a 240 day year, this is an annual emission of 79 mg.

From the calculations, the overall emission from the site is 43g/year. This appears to be too low to account for the amount of PFOS used in this industry in the UK, which is estimated at 500 kg per year (Table 2.8). It would require over 10,000 sites of the size for which the calculation has been performed to account for this amount of PFOS, whereas in Section 2.6.6 there are estimated to be around 300 platers in the UK. The reasons for this difference are not clear and consultation with the UK Health and Safety Executive (HSE) has identified that there is no information on why more chemical mist suppressant must be added periodically (every two weeks) despite the fact that drag-out alone is unlikely to account for the loss of active suppressant. This might suggest that there is some breakdown or deterioration of the suppressants during use (pers. comm). However, it is assumed that the 500 kg sold each year goes to replace losses (principally from drag-out). It is however possible that some material is lost when the contents of plating baths are disposed of, but the ESD indicates that such baths are maintained in use for long periods without such disposal. For this review, the daily emissions estimated above will be used to estimate local concentrations. On the larger scale, it will be assumed that all of the substances sold for use in this sector in a year are released to waste water during the course of a year. Emissions to air on this scale are neglected.

A company in Germany (Section 2.6.4) estimated that the market for this area in the EU was 8.6 – 10 tonnes. The upper figure is used to estimate releases on the larger scale. Table A4.4 below provides a summary of emissions from metal plating.

Table A4.4: Summary of Emissions from Metal Plating

Local (mg/day)	**Regional (kg/year)**	**Continental (kg/year)**
180 (waste water) 0.33 (air)	1000 (waste water)	9000 (waste water)
All as PFOS-acids		

A4.2.3 Fire Fighting Foams

No production or formulation of these foams occurs in the UK, but a calculation for the formulation of the foams has been carried out for information. New foams purchased will not contain PFOS related substances, but there is a stockpile of foams containing PFOS related substances which may be used over the next few years. In this section, estimates are made of the possible release of the PFOS from these fire fighting foams.

Section 2.8.4 presented information relating to a producer of foams, which gave a use level of 40 tonnes of PFOS related substances per year (the company no longer uses PFOS-based products). At a concentration of 1% in the foams this would make 4,000 tonnes of concentrate. This seems high in comparison to the UK stock figures below, but is used as an illustration. There are no specific data regarding emissions from the production of the foams, so the default values from the Technical Guidance Document are used, treating the process as a formulation. The relevant emission factors are 0.001 to air and 0.02 to water, with production over 300 days per year. The resulting emissions are 0.13 kg/d to air and 2.7 kg/d to water.

From data provided by fire services in the UK, the current stockpile of fire fighting foams containing PFOS related substances is 76,000 litres. The stocks held by major installations are not considered in this evaluation. These will be used in the event of a major incident, and such use is not considered to be part of the 'normal' use of the substances. The frequency of use by Fire Authorities is also expected to be much higher compared to major installations. The estimate of use of PFOS-based foams is therefore based on the amounts held by Fire Authorities (76,000 litres).

The fraction of the stock of foams (all types) used in 2002 was 15%, although the fraction of PFOS based foams used was only 0.5%. For the purpose of these calculations, it will be assumed that the higher rate of use is the normal rate, and that the remaining stock will be used at this rate. The shelf life of the foams is given in Section 2.8.4 as 10-20 years; a use rate of 15% would use up the existing stock within this time frame, whereas the reduced use rate would leave much of the stockpile to be disposed of. If the PFOS-based foams are not used then the releases below will be over-estimates.

Confidential information on the quantities and compositions of formulations imported into the UK in the past has been provided. From this, it is reasonable to assume a concentration of 1% PFOS related substance in the foams stored (i.e. corresponding to the volumes above). From the information provided the major part of the PFOS containing material was of the PFOS-acid type, and so this will be assumed for these calculations.

Assuming a density of 1 kg/l for the concentrates, the amount of foam is 76 tonnes, containing 760 kg of PFOS-acid. At a use rate of 15% per year, this is a use of 114 kg per year for the UK. It is assumed that all of this is released to the environment. As every fire will have different characteristics, there is probably no such scenario as a typical fire. As an illustrative calculation, it is assumed that 1% of this total is used at a fire. Two scenarios for the release to the environment are considered, as possible extremes. In the first (use A), there is no containment of the foam and water, and so 50% of the release (0.57 kg) goes to surface water without treatment and 50% (0.57 kg) to soil. In the second (use B), it is assumed that the foam and water are collected and passed to a waste water treatment plant, hence 1.14 kg to waste water treatment. The release is assumed to take place over one day.

The UK emissions are assumed to be 20% of those for the EU for these calculations, hence the EU release is 570 kg/year. This is assumed to be split evenly between surface water and soil. The regional emissions are 28.5 kg/year to surface water and to soil, and the continental emissions are 257 kg/year to surface water and to soil.

Table A4.5 below provides a summary of emissions from use of fire fighting foams.

Table A4.5: Summary of Emissions from Use of Fire Fighting Foams

Local (kg/day)	Regional (kg/year)	Continental (kg/year)
Use A: 0.57 (drain) 0.57 (soil) Use B: 1.14 (wwtp)	28.5 (surface water) 28.5 (soil)	257 (surface water) 257 (soil)
All as PFOS-acid		

A4.2.4 Photography

From Section 2.11, PFOS-based chemicals are used in coatings applied to photographic films, papers and printing plates. PFOS related substances have been used in developing solutions as well, but recent information suggests that they have been removed from such products. For these calculations it is assumed that the use is in the manufacture of film, paper and plates. The function of the substances appears to be largely as anti-static agents, so they are intended to remain in the film, including after processing.

Table 2.14 lists six substances which are used in this sector. Of these, one is of the PFOS-acid group, one of the PFOS-substance group and the other four are PFOS-polymers. The OECD assessment indicates that the carboxylate derivatives of N-alkyl-perfluorooctane sulphonamide are used as anti-static agents. For these calculations the substances used in this sector are assumed to be PFOS-acids for the production of film step, and PFOS-substances for subsequent steps. Information on the relative proportions of the various types would allow the estimates to be improved.

The amount of PFOS related substances used in the EU to make film is estimated as 850 kg/year, while the amount in film used in the EU is 750 kg/year. The Technical Guidance Document (TGD) for the Existing Substances Regulation in the EU has been used to estimate releases from the production of film, considered as a formulation step. The emission factors for a substance used in the production of films etc are 0.0001 to air (for vapour pressures below 1 Pa) and 0.002 to water (for any function other than control of crystal growth). The content of PFOS related substances in film is 0.1 – 0.8 µg/cm^2. PFOS related substances are considered by industry to be used mainly in medical applications, e.g. x-rays. According to the Emission Scenario Document on the photographic industry in the TGD, such film has a double coating of photographic material, and so the higher concentration of PFOS related substance will be assumed. Taking this as 0.8 µg/cm^2, and assuming the use of 850 kg per year, a total of 1.06x10^{12} cm^2 of film containing PFOS related substances could be produced.

The most common backing material for film is PET, according to Kirk-Othmer (1994). The material has a density of 1.39 g/cm^3. The depth of film in Kirk-Othmer is suggested as 45 µm, with 10µm of base layer (backing) and 35µm of coating. In the absence of other information, the density will be assumed to apply to the whole film. The mass per unit area is then given as 1.39 x 45x10^{-4} or 6.3x10^{-3} g/cm^2. For a production of 1.06x10^{12} cm^2 this gives 6,630 tonnes of film. This quantity of film can be used in the B tables of the TGD to estimate the amount produced at one site and the number of days of operation. This gives a fraction of 0.4 used at one site, applied to the total tonnage, and use over 300 days. The amount of PFOS-substances used in the EU is 850 kg, so 40% is 340 kg, at 1.13 kg/day. From the emission factors above, the releases to air are 0.11 g/day and to waste water 2.27 g/day. Overall EU emissions are 0.085 kg/year to air and 1.7 kg/year to waste water. As the site accounts for 40% of emissions, these are used for the regional releases. So the regional releases are 0.034 (air) and 0.68 (waste water) kg per year, and the continental releases are 0.051 (air) and 1.02 (waste water) kg per year.

There is little information on whether any of the substances are released from the film when it is processed. EPCI commented that approximately 5-10% of one PFOS material may be released from film into film developer. None of the other PFOS materials used in imaging would be expected to be released on developing. The substances are intended to remain in the film, in order to perform their function. Section 2.11.3 suggests that the use of PFOS related substance is linked to some extent to dry processing, where emissions to water will not occur. The Emission Scenario Document on the photographic industry in the TGD has a default release factor of 1 in the absence of information, i.e. all of a substance is removed on processing, but this is considered to be inappropriate for these substances. For the purpose of this evaluation, it will be assumed that any PFOS-substance present will be releases on developing, and that polymeric material will remain in the film.

From the Emission Scenario Document, the amount of film (taken as X-ray film) processed in one day at a representative site is 110 m^2. The concentration of PFOS-polymers in the film is 0.8 $\mu g/cm^2$, or $8x10^{-6}$ kg/m^2. Hence the amount of PFOS-polymers in the film processed in one day is 0.88 g. The amount of PFOS-substance is 1% of this, or 8.8 mg, and this is assumed to be released to water. Across the EU, the 750 kg of PFOS related substance in films used in this sector would give rise to 7.5 kg of PFOS-substance released to waste water, with 0.75 kg to the region and 6.75 kg to the continent.

The polymers not released at this time will remain in the film or other material and may be kept for considerable periods of time. At the end of their use, X-ray film, movie film and commercial films are typically collected by brokers, and sold for secure disposal (movie film) or recycling of silver and/or PET polymer. These usually result in the incineration of residual materials.

Table A4.6 below provides a summary of emissions from the photographic industry.

Table A4.6: Summary of Emissions from Photographic Industry

Step	Local (g/day)	Regional (kg/year)	Continental (kg/year)
Film production (formulation)	0.11 (air) 2.27 (waste water)	0.034 (air) 0.68 (waste water)	0.051 (air) 1.02 (waste water)
Film development (processing)	0.0088 (waste water)	0.75 (waste water)	6.75 (waste water)

Production emissions as PFOS-acid; developing emissions as PFOS-substance

A4.2.5 Photolithography and Semiconductors

For this sector, use has been made of a draft Emission Scenario Document (ESD) on photoresist use in semiconductor manufacturing produced by the United States Environmental Protection Agency. This document has been reviewed by the OECD Task Force on Environmental Exposure Assessment, and is intended for publication in the OECD Environmental Health and Safety Publications series on Emission Scenario Documents.

Section 2.12 describes the use of PFOS related substances in this area in the role of photo-acid generators in positive photoresists, as well as in antireflective coatings and as surfactants. The ESD mentions polyfluoromethacrylates in photoresists, which may or may not relate to PFOS. For this assessment it is assumed that the substances used are of the PFOS-substances type.

The ESD has information on the use of photoresists at sites in the USA, with up to 36 kg being used on site per day for larger sites, and for up to 360 days per year. These figures have been used here[4]. From Table 2.16, the content of PFOS-substances in the photoresists is up to 0.1%, hence the amount used per day would be up to 36 g. This assumes that all photoresists used at the site contain PFOS-substances; although this may not be the case, as there is no information relating to this the worst case assumption has been taken. This level of use over 360 days corresponds to an annual use of up to 13 kg. This would appear to fit reasonably with the total use of PFOS-substances in the EU, which is given as 471 kg/year in Table 2.16. However, this overall figures covers use in a range of areas and the specific use in photoresists only accounts for 46 kg/year. The estimated site use is still consistent with this, but may be a high estimate. For the calculation of releases on the regional and continental scales in this section, an overall EU use of 500 kg/year is applied.

The ESD estimates emissions from semiconductor manufacturing for a series of processes:

- **packaging/container residuals**: the loss from this step is estimated as 0.6%, with the losses gong to landfill or to incineration. For a use of 36 g/day, the loss is 0.22 g/day. For a use of 500 kg in the EU the overall loss is 3 kg/year, with 0.3 kg to the region and 2.7 kg to the continent;

- **equipment cleaning**: losses from this step are estimated as 1% again to landfill and incineration. The estimated loss for the site is 0.358 g/day. The total EU loss is 4.98 kg/year, with 0.498 kg to the region and 4.482 kg to the continent;

- **application excess**: an amount of resist is applied to the semiconductor wafer which is then spun. The percentage of resist adhering to the wafer is considered to range from 1% to 7%; an average of 4% is used here, hence 96% of the application goes as waste. For the site, the estimated waste is 34 g, which goes to incineration. The total waste for the EU is estimated as 472 kg/year, with 47.2 kg to the region and 425 kg to the continent;

- **loss in developer**: the ESD assumes that 50% of the resist on the wafer is removed in the developer. The amount released at the site is 0.72 g/day, this is considered to go to waste water. The total loss for the EU is 9.94 kg/year, with 0.994 kg to the region and 8.946 kg to the continent; and

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[4] For comparative purposes, the ESD has information from Germany that suggests a use of 11.25 kg photoresist per day, somewhat lower than the value chosen.

- **loss on etching and stripping**: the ESD assumes that the rest of the resist is removed at this stage. As 50% was removed at the previous stage, the emissions at this step are the same as those for developing: 0.72 g/day to water at the local site, 9.94 kg/year for the EU, 0.994 kg/year for the region and 8.946 kg/year for the continent. These emissions are to waste water or to recycling, release to waste water has been assumed as a worst case.

Table A4.7 below provides a summary of emissions based on the ESD.

Table A4.7: Summary of Emissions based on ESD

Step	**Local Emission (g/day)**	**EU (kg/year)**
Container residual (l/i)	0.22	3
Equipment clean (l/i)	0.358	4.98
Application excess (l/i)	34	472
Developer (ww)	0.72	9.94
Etching/stripping (ww)	0.72	9.94

l/i – landfill/incineration
ww – waste water

The overall breakdown of the fate of the PFOS-substances according to the ESD is ~20 kg to waste water and 480 kg to incineration/landfill. This is based on the use of 500 kg per year. ESIA and SEMI estimated a mass balance for the EU based on a use level of 471 kg per year, and concluded a larger proportional release to water, 251 kg/year to waste water and 218 kg/year to incineration. Examining the mass balance, the differences arise largely through the use of PFOS-substances in areas other than as photoresists. For the anti-reflective coatings, the mass balance assumes 40% is present on the wafer when it goes to the developing step, whereas the ESD has only 4% of the photoresist material. On developing, all of the remaining anti-reflective coating is removed, thus entering the waste water stream rather than going to incineration as in the ESD. Part of the PFOS-substances are used in the developer in the EU, and this is considered to go directly into waste water according to the mass balance. The net effect is that a greater proportion of the PFOS-substances used go into waste water.

The mass balance is considered to be more relevant for the EU, and so the overall emissions from this will be used for the regional and continental emissions.

These give 25 kg/year to waste water on the regional scale, and 226 kg/year to waste water on the continental scale. For the local scale, the emissions estimated with the ESD will be used, but with the addition of a release for the use of PFOS-substances in the developer. It is assumed that the site uses developer and resist materials containing PFOS-substances in the same proportions. The site used for calculations uses 13 kg of PFOS-substances as resists, etc. from a total of 276 kg for this type of use (or 4.7%). The amount of PFOS-substance in developers is therefore 4.7% of the total in developer (195 kg/year), or 9.2 kg/year. For 360 days of use, this is 25.6 g/day. Combined with the estimated releases from resist materials of 1.43 g/day, the local emission is 27 g/day. Table A4.8 below provides a summary of emissions from photolithographic processes.

Table A4.8: Summary of Emissions from Photolithography

Local (g/day)	Regional (kg/year)	Continental (kg/year)
27	25	226
All emissions are to waste water and are of PFOS-substances.		

A4.2.6 Aviation

PFOS related substances are used in hydraulic fluids in the aviation industry (Section 2.15). These are considered to be PFOS-acids for these calculations (see note on composition in 2.15.3). The manufacture of these fluids takes place outside the EU, so there is no need for a formulation step.

Information relating to emissions of hydraulic fluids is taken from an Emission Scenario Document on Lubricants and Lubricant Additives (Environment Agency, 1997a). Losses are most likely to occur on installation into equipment, during maintenance and on removal for disposal. Aviation systems are expected to be well sealed and so losses during use are expected to be low. It is assumed that all of the substances sold during a year go to replace the fluids lost during the same period, as the suggested replacement or reconditioning frequency for these types of fluids is one year. The suggested fate of the fluids is 2% loss to the environment (1.4% to soil, 0.6% to water) over the service life and 98% taken to chemical disposal from which no significant emissions are expected.

The world use of PFOS related substances in this sector is 2.2 tonnes, the EU is assumed to use one third of this, or 0.73 tonnes. The losses in the EU are therefore 4.4 kg/year to water and 10.2 kg/year to soil. In other work it has been assumed that 10% of the EU releases could relate to one large airport. Hence the local and regional annual emissions are 0.44 kg to water and 1.02 kg to soil. The local site emissions are assumed to take place over 300 days, hence the daily emissions are 1.5 g/day to waste water and 3.4 g/day to soil. Table A4.9 below provides a summary of emissions from hydraulic fluids used in Aviation.

Table A4.9: Summary of Aviation Releases

Local (g/day)	Regional (kg/year)	Continental (kg/year)
1.5 (waste water) 3.4 (soil)	0.44 (waste water) 1.02 (soil)	3.94 (waste water) 9.2 (soil)
All as PFOS-acids		

A4.2.7 Protective Treatment of Fabrics (Carpets, Textiles and Leather)

As noted earlier, the use of PFOS related substances in treatment of fabrics has effectively ceased in the UK. However, there are materials currently in use in articles which contain PFOS related substances from earlier treatments, and these may contribute to releases of PFOS during the course of the service life of the articles. The possible emissions from these articles are estimated in this Section. An example calculation for the treatment of fabrics is included in Section A4.2.8.

The substances used in treating fabrics were for the most part polymeric materials, i.e. PFOS-polymers. They also contained a small amount of residual PFOS-substances. For these calculations, it is assumed that the level of residual material is 1% (based on the information in Section 2 and on other confidential information provided).

The relevant quantities of substances for these calculations are assumed to be those which were used annually on fabric treatment up until 2000. Annex 3 contains approximate information on the quantities used in these sectors. The overall usage figure for PFOS related substances in the UK was around 100 tonnes (Section 2.2.1, this may be a little under-estimated). Therefore the percentage use figures in Annex 3 have been taken as equivalent to the tonnage used. Hence the use is 23 tonnes in carpets, 15 tonnes in apparel/leather and 10 tonnes in fabrics (upholstery).

Carpets

Releases during the service life of carpets may arise from cleaning (vacuum or washing) or through wear. RIKZ (2002) quote 3M as estimating a 95% loss of PFOS from carpets over their working life, with 50% through walking and vacuuming, and 45% through steam cleaning.

Walking and vacuuming losses may be considered to go to land or to water. The use of vacuum cleaners would probably be expected to lead to removal to solid waste and disposal with household refuse and consequently landfill or incineration. However there is no information to apportion losses to walking (wear) and to vacuuming, so it will be assumed that releases are to the environment as a worst case. In ESR assessments the loss of particulates as wear from plastics has been considered as ‘waste remaining in the environment’ and distributed as 75% to soil and 25% to water. Assuming a similar distribution for these releases gives 37.5% to soil and 12.5% to water. Releases from steam cleaning are assumed to go to water, hence 45% to water. The overall releases are therefore 57.5% to water and 37.5% to soil. The amount remaining on the carpet at the end of the lifetime is assumed to be disposed of with the carpet, to landfill or to incineration.

The loss factors are estimated over the whole working life. As such they can be applied to the annual use level (this assumes a constant level of use). For a tonnage of 23 tonnes, the UK emissions would therefore be 13.2 tonnes to water and 8.6 tonnes to soil. As before, it is assumed that the UK accounts for one fifth of the EU emissions, so the overall totals are 66 tonnes to water and 43 tonnes to soil. The regional emissions are 6.6 tonnes (water) and 4.3 tonnes (soil), the continental emissions are 59.4 tonnes (water) and 38.7 tonnes (soil). The above are emissions of polymeric material, and would be expected to be mostly associated with particulate material worn from the fabric.

The polymers are considered to contain 1% of PFOS-substances, so the releases of these are: regional 66 kg/year (water), 43 kg/year (soil); continental 0.59 tonnes/year (water), 0.39 tonnes/year (soil).

Upholstery and Furnishing Fabrics

There is no specific information on losses of PFOS related substances from these materials so the information on carpets will be used as the basis for the assumptions. These materials will be cleaned, although probably not frequently, and so the loss through washing is taken as the same as that for steam cleaning of carpets, i.e. 45% to water. The degree of wear is assumed to be less than that for carpets, and is taken as half of that figures, i.e. 25%. As for carpets this is split between water and soil in the ratio 25:75, although some would be to solid waste. The overall emission factors are therefore 51.25% to water and 18.75% to soil. The amount remaining on the fabrics at the end of the lifetime is assumed to be disposed of with the fabric to landfill or to incineration.

From a tonnage of 10 tonnes per year, the UK emissions would be 5.1 tonnes to water and 1.9 tonnes to soil. Assuming UK emissions are 20% of the EU emissions, the total emissions would be 25.5 tonnes to water and 9.5 tonnes to soil. The regional emissions are 2.6 tonnes (water) and 0.95 tonnes (soil), the continental emissions are 23 tonnes (water) and 8.6 tonnes (soil). These are emissions of polymeric substances, probably in association with particulate material. As before, taking the content of PFOS-substances as 1% the emissions of these substances are: regional 26 kg/year (water), 9.5 kg/year (soil); continental 0.23 tonnes/year (water), 0.09 tonnes/year (soil).

Apparel and Leather

These two areas are treated together as use in treating clothing. There is no specific information about the loss of PFOS related substances from clothes, so the information on carpets has again been used as the basis for the assumptions. Clothing will be washed more frequently than carpets or upholstery, although the purpose of the treatment is to reduce the staining of fabrics. Against this, the lifetime of most clothing is much shorter than that of the two categories above. Washing losses are therefore taken as half of those above, i.e. 22.5%. Wear is expected to be less than for carpets, and is taken as the same as for fabrics above, i.e. 25%. This is again split as 75% to soil, 25% to water, or 18.75% to soil and 6.25% to water. The overall emission factors are therefore 28.75% to water and 18.75% to soil. From a tonnage of 15 tonnes per year, the UK emissions would be 4.3 tonnes to water and 2.8 tonnes to soil. Assuming UK emissions are 20% of the EU emissions, the total emissions would be 21.5 tonnes to water and 14 tonnes to soil. The regional emissions are 2.15 tonnes (water) and 1.4 tonnes (soil), the continental emissions are 19.4 tonnes (water) and 12.6 tonnes (soil). These are emissions of polymeric substances, probably in association with particulate material. As before, taking the content of PFOS-substances as 1% the emissions of these substances are: regional 22 kg/year (water), 14 kg/year (soil); continental 0.19 tonnes/year (water), 0.13 tonnes/year (soil).

Table A4.10 below provides a summary of emissions from treatment of fabrics (carpets, upholstery and leather) while Table A4.11 provides an overall summary of the emissions from the three classes of substances (PFOS-acids, PFOS-substances and PFOS-polymers). Table A4.11 also includes estimated emissions for the historic sources from Section A4.2.8.

A4.2.8 Historic Sources

There are a number of other activities involving PFOS related substances which are considered to have taken place in the EU in the past but are no longer considered relevant. Default estimates of emissions from some of these have been made to allow comparisons with the calculations above.

Table A4.10: Summary of Emissions from Treatment of Fabrics

	PFOS-polymers		**PFOS-substances**	
Area	**Regional (tonnes/year)**	**Continental (tonnes/year)**	**Regional (kg/year)**	**Continental (kg/year)**
Carpets	6.6 (w) 4.3 (s)	59.4 (w) 38.7 (s)	66 (w) 43 (s)	594 (w) 387 (s)
Upholstery & Furnishing Fabrics	2.6 (w) 0.95 (s)	23 (w) 8.6 (s)	26 (w) 9.5 (s)	230 (w) 86 (s)
Apparel & Leather	2.15 (w) 1.4 (s)	19.4 (w) 12.6 (s)	22 (w) 14 (s)	194 (w) 126 (s)
Total	11.35 (w) 6.65 (s)	101.8 (w) 59.9 (s)	114 (w) 66.5 (s)	1018 (w) 599 (s)

w - water
s- soil

Table A4.11: Summary of Emissions from PFOS-acids, PFOS-substances and PFOS-polymers

Use area	**Compartment**	**Local (per day)**	**Regional (per year)**	**Continental (per year)**
PFOS-acids				
Metal Plating	air	0.33 mg		
	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 - formulation	air	0.13 kg		
	waste water	1.07 kg		
Fire fighting foams – use (alternative local)	surface water	0.57 kg	28.5 kg	257 kg
	soil	0.57 kg	28.5 kg	257 kg
	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

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.

Textiles

The possible continuing emissions from textiles in use have been estimated above. Previously, the treatment of textiles with PFOS related substances took place in the EU. To estimate emissions from this treatment step, information from the risk assessment of decabromodiphenyl ether (EC, 2002) and a draft Emission Scenario Document on textile processing produced by the Umweltbundesamt in Germany were used. This latter document has been reviewed by the OECD Task Force on Environmental Exposure Assessment, and is intended for publication in the OECD Environmental Health and Safety Publications series on Emission Scenario Documents. As in the calculations for service life releases, the substances used here are considered to be PFOS-polymers, with a residual 1% content of PFOS-substances.

The assessment of decabromodiphenyl ether considers losses from the backcoating of textiles, and this will be taken as being similar to the treatment of textiles with PFOS related substances. The loss estimated was of 1 kg of formulation per batch used. This was lost to waste water from the setting up and washing down of the coating equipment. It was also assumed that a representative site would process five batches per day, hence the daily loss would be 5 kg of formulation. From data on products imported to the UK, the average content of PFOS related substances in formulations for apparel, carpets and fabrics was ~27%. Hence the daily emissions to waste water from the site would be 1.35 kg/day.

From above, the amount of PFOS related substances used in the apparel, carpet and fabric areas was 48 tonnes. At an average content of 27% this equates to ~180 tonnes of formulation. RIKZ (2002) indicated that a content of 2-3% by weight of perfluoro product was required in the fabric, which indicates that ~1900 tonnes of fabric could be treated.

From the ESD on textiles, the suggested realistic worst case amount of fabric treated at a site per day is 13 tonnes, with 225 days production giving 2,925 tonnes of fabric treated per year. As it is unlikely that all of a site's production each day will be of only one finish on one fabric type, a factor of 0.3 is used to adjust these figures. The result is 3.9 tonnes of fabric treated with a specific finish per day, and 878 tonnes per year. This yearly figure is just under half of the total estimated above for the whole of the UK, which may indicate that the substances are used over a smaller number of days, or that the amount used on a site is less than estimated.

Taking the value of 3.9 tonnes per day, at a content of 2.5% PFOS related substance the amount of PFOS related substance used per day would be 97.5 kg. The estimated release per day was 1.35 kg, giving an emission factor of 1.4%. Applying this to the UK use level of 48 tonnes gives an annual emission of 672 kg. Taking the UK emissions are 20% of the EU emissions, the total EU emissions would be 3,360 kg. The regional emission would be 336 kg/year, and the continental emission 3,024 kg/year. These values relate to the PFOS-polymers. Assuming a 1% content of PFOS-substances, the releases of PFOS-substances would be 3.4 kg/year (regional) and 30 kg/year (continental).

Paper and Packaging

PFOS related substances have been used to treat a range of paper types and products. The major type of substance used appears to be phosphate derivatives of N-EtFOSE, and these will be considered here as PFOS-substances. They are considered to be applied mostly during the paper making process, rather than as a coating in subsequent operations.

A level of use of 1–1.5% by weight of paper is indicated (RIKZ, 2002). The approximate usage in the UK was 32 tonnes, so that 2,100-3,200 tonnes of paper could be treated. For the EU, assuming that the UK accounted for 20% of use, the figures would be 160 tonnes of substances, and 10,700-16,000 tonnes of paper.

The Appendices in the Technical Guidance Document have been used to estimate the emissions from paper. The substances are intended to remain in the paper, so the main category is 2, use resulting in inclusion into a matrix. The use category is 31 (impregnating agent). The resulting emission factors are zero to air and 0.05 to waste water.

The information in Section 2.7 suggests there were only a few users for this type of treatment. ‘Large companies’ is chosen as the category for the B table, which results in a fraction of main source of 0.333 and 300 days production. The fraction of main source is applied to the UK tonnage in this case, as this gives a result in keeping with the information available. This results in the use of 10.7 tonnes of PFOS-substances at the site per year, or 35.7 kg/day. The estimated release to waste water is 1.8 kg/day.

From above, the total use in the EU was estimated as 160 tonnes per year. The release is therefore estimated as 8 tonnes per year, with 800 kg to the region and 7.2 tonnes for the continent. These are releases of PFOS-substances to waste water.

The possibility of emissions from paper in use could be considered. However, the lifetime of such papers is not expected to be very long. On disposal, such papers for example food wrappings might be expected to be disposed of with household waste rather than entering the paper recycling streams. Hence most of the substances used are likely to be disposed of to landfill or incineration.

Coatings

A range of possible uses in coatings of various kinds is described in Section 2.10. In some cases there appears to be some overlap with areas which have already been addressed. In order to obtain some indication of the possible emissions from this sector, it has been assumed that the default emission factors for paints, lacquers and coatings in the Technical Guidance Document can be applied.

A use of ~18 tonnes for the UK is assumed for these calculations. The content of PFOS related substances in coatings is indicated to be 0.1-1.0%; taking an average of 0.55% gives a quantity of coating containing PFOS related substances of 3,270 tonnes per year.

The substances are treated as PFOS-substances for simplicity, and are considered to be surface active agents, use category 50. Assuming the paints are water based, the emission factors are zero to air and 0.005 to waste water. Considering the UK emissions as 20% of the EU emissions, the amount of paints containing PFOS-substances in the EU would be 16,364 tonnes. From the B tables this indicates a fraction of main source of 0.1, or use of 1,636 tonnes per year at the representative site. This would be over 300 days, and equates to the use of 9 tonnes of PFOS-substances at the site. Using the factor of 0.005, the emission to waste water would be 45 kg/year, or 0.15 kg/day. The total emissions for the EU would be 450 kg/year, with 45 kg to the region and 405 kg to the continent. These are emissions of PFOS-substances to waste water.

There would also be the possibility of emissions of the PFOS-substances from the coatings during the course of their service life. No information on these possible releases is available, and so no estimates are possible at this time.

A4.2.9 PNEC Values

The data for the aquatic compartment are included in Section 3.3.4. For this evaluation, the freshwater and salt water data are considered together. For freshwater, there are long term tests for three species, with the lowest NOEC being that for fathead minnow at 0.3 mg/l. For saltwater, the combined fresh and saltwater data set is considered. There are still only three trophic levels represented, but the lowest NOEC (and the lowest overall) is that for Mysid shrimp at 0.25 µg/l. An assessment factor of 10 is appropriate for the freshwater environment, and gives a PNEC of 25 µg/l. The appropriate factor for salt water is 100, giving a PNEC of 2.5 µg/l.

There are no data for sediment organisms. The usual method in this case would be to use the equilibrium partition method. The measured Kd values for soil and sediment can be used in this method, hence the extrapolation is not affected by the lack of a log Kow value. However, the results should be considered tentative as the pathways for uptake and effects may be different between aquatic and terrestrial organisms, especially for this type of substance. As both the PEC and PNEC for sediment are estimated using the partitioning approach, the results are the same as those for the aquatic compartment and are not considered separately.

From the acute toxicity result for earthworms, a PNEC of 373 µg/kg dwt is derived. This is lower than the value obtained using the equilibrium partition method on the aquatic PNEC and so is used in the evaluation.

For the assessment of secondary poisoning, the most sensitive endpoint is effects on the liver in rats. The OECD assessment concluded that the NOAEL for these effects in a two year feeding study was 0.5 ppm in male rats. This converts to a PNEC of 0.0167 mg/kg.

A4.3 Model calculations

A4.3.1 Approach and Scenarios

A number of different degradation scenarios have been considered for the groups of PFOS related substances. Some of these do not relate to actual situations either now or in the future, but have been used to examine the dependence of the outcomes on various factors.

The simplest scenario is to have only those inputs of PFOS-acids which are currently relevant (i.e. only the emissions from the PFOS-acids as summarised in Table A4.11)). This effectively assumes there is no contribution from the PFOS-substances and PFOS-polymers, but does include continuing emissions from fire fighting foams.

To include the contribution from PFOS-substances, the release and property data for the substances are used to model the distribution of the substances. The resulting steady state concentrations are then used to estimate a ‘production rate’ for PFOS in each compartment, based on the degradation rate of the substances in the compartment, which can be added to the direct emissions. This requires values for the degradation rate of the PFOS-substances in the compartments. There are limited rate data for the degradation of these substances, and so values have been selected to represent different possibilities. The simplest is that the degradation occurs rapidly on release to the environment. For this, the releases of PFOS-substances are converted directly to releases of PFOS-acids and combined with the PFOS-acids emissions. To examine the effect of slower degradation processes, half lives in water and soil of 20.5 days and 1 year will be used. It is assumed that the degradation proceeds to PFOS with no by-products, so that the yield is 100%. The relative molecular weight for the chosen representative substance means the yield is 0.94 kg for 1 kg of PFOS-substances.

For the PFOS-polymers, a similar approach to that for PFOS-substances can be taken. Again there are no data on degradation rates or on the extent to which PFOS may be produced, so again values have been selected to represent possible outcomes. The half lives for PFOS-polymers are expected to be longer than those for PFOS-substances, so a half life of 30 years has been used. The yield of PFOS from the polymer has been taken as 30%, based on the composition of examples.

The above scenarios include all of the use areas in Table A4.11, including those considered to be historic. A ‘current’ scenario is also included, which assumes that the use in paper treatment and coatings has ceased, that fabrics are no longer treated, and that fire fighting foams containing PFOS are no longer produced. Continuing use of stocks of fire fighting foams and releases from treated fabrics in service are included.

To look at a realistic near future situation, a combination of the PFOS-acids and PFOS-substance emissions from the four continuing uses (so excluding fire fighting foams and textiles as having ceased emissions) is considered.

There are a number of limitations in the data and in the approach taken which have already been mentioned, but there are two others which should be kept in mind when examining the results of the modelling. The scenarios involving the PFOS-substances and the PFOS-polymers use the steady state concentrations of these components. Such a steady state may take many years to reach, while the releases from two of the sectors (fire fighting foams and textiles) are expected to cease within the next ten or so years. Therefore these scenarios may well over-estimate the contribution from these sources.

Against the above limitation, it is not possible with the model to include an existing burden together with the current emissions. As PFOS is not degradable, there has been an opportunity for accumulation in the environment. These two aspects may to some extent cancel each other out, but there is no way to investigate this.

Table A4.12 below outlines a summary of the scenarios used in the model calculations.

Table A4.12: Summary of Scenarios Used

Scenario	**Substances included**	**Comments**
1	PFOS-acids	All uses from Table A4.11
2	PFOS-acids + PFOS-substances	All uses, assumes instant conversion of substances to PFOS
3	PFOS-acids + PFOS-substances	All uses, assumes conversion of substances to PFOS with half life of 20 days in water, sediment and soil
4	PFOS-acids + PFOS-substances	All uses, assumes conversion of substances to PFOS with half life of 1 year in water, sediment and soil
5	PFOS-acids + PFOS-substances + PFOS-polymers	All uses, same as for 3, plus conversion of polymers to PFOS with 30 year half life in water, sediment and soil
6	PFOS-acids + PFOS-substances + PFOS-polymers	Chrome plating, photolithography, photography and aviation uses with use of foams and textile service life emissions (20 day half life for substances, 30 year half life for polymers)
7	PFOS-acids + PFOS-substances	Chrome plating, photolithography, photography and aviation uses only

A4.3.2 Scenario Outcomes

It is emphasised that the model calculations necessarily involve a large number of assumptions, and as such the results should be considered to be indicative. The results for each scenario can be found in greater detail in the Draft RER (RPA & BRE, 2004) with an overview of the results given here (for the most part in a qualitative form).

The local emissions to freshwater for the most part do not give rise to indications of risk. The main exceptions relate to the fire fighting foams. The calculations for the formulation of foams give rise to a risk in all of the scenarios which include this use. The emission estimates are based on default values and what appears to be a large volume of use. The use of fire fighting foams gives rise to a risk in the scenario where the used foam is discharged to a waste water treatment plant (Use B). One other ratio above one is found, for paper treatment in Scenario 2, where the PFOS-substances release is assumed to break down instantly to PFOS.

The uses indicating potential risks for the terrestrial compartment are the same as those for water.

Calculations are also performed to assess the risk of secondary poisoning, through the consumption of food which has taken up the substance. These calculations assume a combination of food from local and regional sources. There are four endpoints for secondary poisoning:

- freshwater food chain;
- marine predator feeding on fish;
- marine top predator; and
- terrestrial food chain.

For the freshwater food chain, all the use areas indicate a possible risk in all scenarios for which they are relevant. The regional concentrations in water calculated for each of the scenarios are higher than the level which would give rise to a risk without a local contribution from the specific use. However, the specific uses in most cases make a contribution to this exposure route which is greater than that from the region, the only exception being the processing life stage for photography. In addition, all use patterns in all scenarios indicate potential risks for marine predators and marine top predators.

Most use patterns indicate a risk in one or more of the scenarios for the terrestrial food chain. Exceptions are chromium plating, and the fire fighting foams use pattern (Use A).

The different scenarios produce very similar results in terms of the risk characterisation ratios, certainly for the freshwater and terrestrial environments. For these environments, the regional concentrations are much lower than the PNEC values, and so the risk characterisation depends only on the local emissions, which do not change between scenarios. The background concentrations for water vary only by a factor of three in the different scenarios. Those for the terrestrial environment vary much more, over two orders of magnitude, but are still low. This lack of significant variation between the background concentrations is in spite of significant differences between the degradation rates of PFOS-substances in the scenarios, including the instant degradation of Scenario 2. This might suggest that the rates at which the substances break down do not need to be known with great accuracy (although the secondary poisoning results are more variable, see below). Information on the yield of PFOS from the breakdown of the PFOS-substances (and PFOS-polymers) may have more influence (for this evaluation PFOS was considered to be the only product).

The secondary poisoning ratios are more variable. Here the background concentration is high enough to indicate a potential risk without a local contribution for the freshwater and marine food chains.

Scenario 7 looking at releases only from the areas identified as of continuing interest (chromium plating, photolithography, photography and aviation) led to potential risks from secondary poisoning. This calculation assumed a half life of 20 days for the PFOS-substances. As with other scenarios, the regional background concentration is sufficient to indicate a possible risk for secondary poisoning. So although there are only local calculations for three of the use areas, all of them contribute to the possible risk. The use making the smallest contribution locally to the possible risk is chromium plating, where the local contributions to the concentration are very small. However, this use area leads to a larger contribution to the overall emissions.

For each of the scenarios, the releases from each use area can be used to give some indication of the relative contributions of each use to the background concentration. To do this a combined release value (i.e. the sum of releases to all compartments) has been calculated for each use. For the indirect sources of PFOS through the breakdown of the PFOS-substances, the contribution from the breakdown has been included and apportioned between the different uses in the ratio of the substance releases from those uses. A similar approach has been used for the polymer releases.

Table A4.13 summarises the emissions under the various scenarios for regional releases only.

The largest source in over half of the scenarios is chromium plating. As was noted earlier in the estimation of emissions from this use, there is some inconsistency between the amount calculated as released based on scaling up from a local site, and the amount used in the industry each year. Better information on the fate of PFOS in the process would help to resolve this and could lead to a change in the emissions.

In the scenarios considering all of the areas where PFOS related substance have been used, Scenarios 2 to 5, the releases from the breakdown of PFOS-substances make a moderate contribution to the PFOS in the regional environment. Considering Scenarios 2 to 4 (so excluding the contributions from polymer breakdown), the contribution from PFOS-substances breakdown ranges from 29 – 48% of the total. Where the polymer-related emissions are included (Scenario 5), these contribute 61% and the PFOS-substances contribution is 14%.

In Scenario 2, the PFOS-substances are assumed to break down instantly to PFOS. In this scenario, the contribution from the substances is almost half of the releases. For Scenario 3, where a half life of 20.5 days to break down to PFOS in the environment is assumed, the contribution is reduced to 35%, or 57% of the ‘maximum’ contribution calculated for Scenario 2. These PFOS-substance emissions come mainly from the paper treatment use pattern, with other major contributions from textile service life and coatings. These older uses therefore contribute significantly to the PFOS loading in the modelled environment. In Scenario 6, where only the textile service life of these three is still included, the contribution from PFOS-substances is reduced to 3% of the total, and for the ‘future’ Scenario 7, it is reduced further to 1.4% as the textile service life emissions are not included.

Table A4.13: Summary of Regional Emissions based on Scenarios

Use	Regional release (kg/year)	Percentage
Scenario 1 - PFOS-acids		
Chrome plating	1000	94.4
Photography (film production)	0.71	0.07
Aviation	1.46	0.14
Fire fighting foams	57	5.4
Scenario 2 - PFOS-acids plus instant release of PFOS-substances		
Chrome plating	1000	48.8
Photography (film production)	0.71	0.03
Aviation	1.46	0.05
Fire fighting foams	57	2.8
PFOS-substances (total) of which:	991	48.3
Photolithography	23.5	1.2
Photography (developing)	0.71	0.03
Textile (treatment)	3.2	0.16
Textile (service life)	169.5	8.3
Paper treatment	753	36.7
Coatings	42.5	2.1
Scenario 3 - PFOS-acids plus PFOS-substances with 20.5 day half life		
Chrome plating	1000	61.5
Photography (film production)	0.71	0.04
Aviation	1.46	0.09
Fire fighting foams	57	3.5
PFOS-substances (total) of which:	568	34.9
Photolithography	13.6	0.84
Photography (developing)	0.4	0.02
Textile (treatment)	1.8	0.11
Textile (service life)	97.1	6.0
Paper treatment	431	26.5
Coatings	24.4	1.5
Scenario 4 - PFOS-acids plus PFOS-substances with 1 yr half life		
Chrome plating	1000	67.1
Photography (film production)	0.71	0.05
Aviation	1.46	0.10
Fire fighting foams	57	3.8
PFOS-substances (total) of which:	431	28.9
Photolithography	10.3	0.7
Photography (developing)	0.3	0.02
Textile (treatment)	1.38	0.09
Textile (service life)	73.7	5.0
Paper treatment	327	21.9
Coatings	18.5	1.2

Table A4.13: Summary of Emissions based on Scenarios		
Use	**Regional release (kg/year)**	**Percentage**
Scenario 5 - PFOS-acids plus PFOS-substances with 20.5 day half life plus PFOS-polymers		
Chrome plating	1000	24.1
Photography (film production)	0.71	0.02
Aviation	1.46	0.04
Fire fighting foams	57	1.4
PFOS-substances (total) of which:	568	13.7
Photolithography	13.6	0.33
Photography (developing)	0.4	0.01
Textile (treatment)	1.8	0.04
Textile (service life)	97.1	2.3
Paper treatment	431	10.4
Coatings	24.4	0.6
PFOS-polymer (total) of which:	2517	60.7
Textile (treatment)	46	1.1
Textile (service life)	2471	59.6
Scenario 6 - PFOS-acids plus PFOS-substances with 20.5 day half life plus PFOS-polymers for current uses		
Chrome plating	1000	27.5
Photography (film production)	0.71	0.02
Aviation	1.46	0.04
Fire fighting foams	57	1.6
PFOS-substances (total) of which:	119	3.3
Photolithography	14.5	0.4
Photography (developing)	0.43	0.01
Textile (service life)	104	2.9
PFOS-polymer (textile service life)	2454	67.6
Scenario 7 - PFOS-acids plus PFOS-substances with 20.5 day half life for continuing uses		
Chrome plating	1000	98.4
Photography (film production)	0.71	0.07
Aviation	1.46	0.14
PFOS-substances (total) of which:	14.5	1.4
Photolithography	14.1	1.4
Photography (developing)	0.4	0.04

The two smallest contributions to the emissions are aviation and photography. In Scenario 7, where the combined other sources are the lowest, these account for 0.14% and 0.11% of emissions respectively. In order to consider the possible effects of the continuing uses more closely, the model was run for each use separately so that there were no contributions to the background from other sources. Where PFOS-substances were involved (photography, photolithography), instant conversion to PFOS was assumed for simplicity. For all use patterns except the developing of photographic film, the calculations indicate possible risks from secondary poisoning. The calculation for chromium plating gave a background concentration high enough to indicate a risk for secondary poisoning without a local contribution. The other areas gave background concentrations below this threshold, reflecting their small contribution to the overall emissions. However, these use patterns did give rise to a risk based on their local emissions.

Overall, the lack of risk for direct effects on aquatic and terrestrial organisms for most uses reflects the moderate toxicity of PFOS to these organisms. The potential risks indicated for secondary poisoning result from the low PNEC value derived for this endpoint. As this value is based on the results of a 2-year study with rats, it is unlikely that the PNEC would be changed significantly in the light of further tests. There are uncertainties in the exposure estimates for each use pattern which, if addressed, could result in the revision of the evaluation. 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. It may be noted that in view of the low PNEC for secondary poisoning, only small releases are needed to reach a PEC above this value (for water, 83 mg/day to waste water treatment in the standard TGD calculation).

It should be noted that none of the scenarios make any allowance for the presence of PFOS from other older sources – the calculations effectively assume a clean environment into which the emissions estimated above are released continuously. Hence there may be historical contributions to the back ground level which are not included. However, the results suggest that even without such an historic background, low levels of release as calculated can lead to accumulation in the environment such that secondary poisoning risks are possible. This is in spite of the fact that PFOS and PFOS substances are largely removed from the regional environment through air and water movement.

EUSES 2 includes a further scale of model, at the global scale, outside of the continental model. This scale is made up of moderate, arctic and tropical parts. This can give an idea of the overall fate of a substance, especially when it is not degradable. For the PFOS calculations, the bulk of the substance (>90%) at steady state is found in the water compartments of the global scale model in all scenarios. This reflects the fact that much of the PFOS is removed through water movement from the regional and continental models and suggests the potential accumulation of PFOS in remote waters.

ANNEX 5

LIST OF CONSULTEES

ANNEX 5: LIST OF CONSULTEES

Note that six organisations requested not to be included in the list below. An asterisk indicates organisations that have responded either by providing information or by completing an RPA Questionnaire.

Trade Associations

Alliance for Beverage Cartons & Environment (ACE)
Asociacion de Investigacion de las Industrias del Cvurtido y Anexas, Spain (AIICA)*
Association Internationale de la Savonnerie de la Detergence et des Produits d'Entretien (AISE)*
Association of Plastic Manufacturers in Europe (APME)
Association of Master Upholsterers*
British Adhesives and Sealants Association (BASA)*
British Association for Chemical Specialities (BACS)
British Carpet Technical Centre
British Cleaning Council
British Coatings Federation (BCF)*
British Fire Protection Systems Association (BFPSA)*
British Footwear Association (BFA)*
British Furniture Manufacturers (BFM)
British Interior Textiles Association (BITA)
British Leather Confederation (BLC)
British Leather Technology Centre Ltd.
British Lubricants Federation (BLF)*
British Luggage and Leather Goods Association (BLLA)
British Plastics Federation (BPF)
British Wood Preserving and Damp Proofing Association
Carpet Foundation
CEFIC – European Committee of Surfactants and their Organic Intermediates (CESIO)
CEFIC – European Photographic Chemicals Industry
CEFIC – Fluorocarbon Technical Committee
Centre Technique Cuir, France (CTC)
Centro Technologico das Industrias do Couro, Portugal (CTIC)
Commission on Engineering & Technical Systems (CETS)
Confederation of European Paper Industries (CEPI)
The Confederation of National Associations of Tanners & Dressers of the European Community (COTANCE)*
CIA-Organic Surfactants Group
Construction Products Association

Trade Associations

Crop Protection Association
Dutch Federation of Tanneries (FNL)
European Apparel and Textile Organisation (Euratex)*
European Automobile Manufacturers Association
European Carpets Association*
European Carton Makers Association (ECMA)
European Council of the Paint, Printing Ink & Artists' Colours Industry (CEPE)*
European Crop Protection Association (ECPA)
European Information and Communication Technology Industry Association (EICTA)
European Oilfield Speciality Chemicals Association (EOSCA)
European Semiconductors Industry Association (ESIA)*
European Textile Finishers Association (CRIET)*
Europen
Federation of the Sporting Goods Industry (FESI)
Fire Industry Research Association (FIRA)
Hellenic Leather Centre
Industry Council for Packaging & Environment (INCPEN)
Institute of Packaging
Lederinstitut Reutlingen Gerberschule, Germany (LGR)
Liquid Food Carton Manufacturers Association (LFCMA)
Metal Packaging Manufacturers Association (MPMA)*
Ministry of Defence*
National Carpet Cleaning Association
National Health Service, Purchasing and Supply Agency (PASA)*
Paper Chemicals Association (PCA)*
Paper Federation of Great Britain*
Paper Industry Research Association (PIRA)
Paper Industry Technical Association (PITA)
Photo Imaging Council (PIC)*
Rovesta Environment
Semiconductors Equipment & Materials International (SEMI)*
Society of Motor Manufacturers and Transporters (SMMT)
Society of British Aerospace Companies (SBAC)
Stazione Sperimentale per l'Industria del. Pelli et del. Materie Concianti, Italy (SSIP)
Surface Engineering Association*
Swedish Association of Industrial and Hygiene Products
TEGEWA*

Trade Associations

Textile Finishers Association (TFA)*
UK Cleaning Products Industry Association (UKCPI)
UK Fire Service*
UK Offshore Operators Association (UKOOA)
Veersuchsanstallt fur lederindustrie, Austria (VAL)*
Wood Panels Industries Federation

Companies

3M
Akzo Nobel*
Alekos Chemicals*
Angus Fire*
Apollo Scientific*
Aquados (UK) Ltd.
Asahi Glass Fluorochemicals UK*
Asahi Glass Japan
Atofina*
Atotech UK Ltd.*
Axminster Carpets
Basildon Chemical Co*
BASF plc, Agricultural Division
Baker Engineering Ltd.*
Bayer Crop Science plc*
Bayer plc*
Belchim Crop Protection Ltd., Agricultural Products Group
BIP Allchem*
Boeing
Borchers
Breaks
Brunner Mond Ltd.
Catomance Technologies*
Carpets International Ltd.
Carter-Lyne Ltd.
Causeway Carpets
Certis Europe BV
CHT Group*

Companies

Ciba Speciality Chemicals*
Clariant*
Colgate-Palmolive Ltd.
Crompton Europe Ltd.
Cussons
Daikin Chemical Europe *
Delrivados Del Fluor
Delta Fire
Dianippon
Doff Portland Ltd.
Dow AgroSciences Ltd.
Dr Petry UK*
DuPont Belgium*
DuPont (UK) Ltd.
East Lancs Chemicals
Ecolab
Enthone
Fisher Research Ltd.
Fisher Scientific*
Flexalan Products Ltd*
Fluorochem
Fluorine Technology Ltd.
Forsheda
Global Research & Development
GWP Group
Headland Agrochemicals Ltd.*
Hugh Mackay (Carpets)
Huntsman
Gibson*
Ilford Imaging Switzerland GmbH*
Ineos Chlor*
Jeyes*
John Drury & Co. Ltd.
Joseph Metcalf Ltd.
Kemira Chemicals*
Kodak UK*
Lancaster Synthesis*

Companies

Lever Feberge
London Oil Refining Co.
Louis De Poortere
Luxan (UK) Ltd.
Makhteshim-Agan (UK) Ltd.
Mandops (UK) Ltd.*
Mcdermid
Millchem
Miteni S.p.a
Monochrome Plating Co. Ltd.*
Monsanto Agriculture
My Cartons*
N2N Enviro Ltd.*
Nexus Chemicals
Nufarm UK Limited*
Nu Swift Ltd*
P and M
PBI Home & Garden Ltd.
Pelchem
Pownall Carpets
PPG*
Procter and Gamble
Protex International
Reckitt Benckiser
Robert McBride
Rudolf Chemicals Ltd
Ryalux
Sainsbury’s
Sasol*
SB Chemicals Ltd.
SC Johnson*
Senzora
Silvani Fire
Solberg*
Solutia*
Solvay Fluor
South West Metal Finishing Ltd.*

Companies

Stephenson Thompson*
Sthamer
Svanen*
Syngenta Crop Protection UK Ltd.*
Synquest Labs
Texchem*
Ulster Carpets
Unilever
Uniqema
United Phosphorus*
Universal Crop Protection Ltd.
Vitax Ltd.
Westex Carpets
White Peak Fine Chemicals Ltd.*
Wools of New Zealand
Zschimmer

Competent Authorities and Academia

Environment Agency for England and Wales*
Environment Canada*
UK Health and Safety Executive*
Pesticides Safety Directorate (PSD)*
Swedish National Chemicals Inspectorate (KemI)*
University of Michigan*
University of Manchester Institute of Science and Technology (UMIST)*
US Environmental Protection Agency*

Fire Authorities

Northumberland Fire and Rescue Service*
West Midlands Fire Service*
Humberside Fire and Rescue Service*
Leicestershire Fire and Rescue Service*
Tyne & Wear Fire and Rescue Service*
Staffordshire Fire and Rescue Service*
Shropshire Fire and Rescue Service*
Cumbria Fire Service*

Devon Fire and Rescue Service*
London Fire & Emergency Planning Authority*
Dumfries & Galloway Service HQ*
Northamptonshire Service HQ*
North Yorkshire Brigade HQ*
Dorset Fire and Rescue Service*
Buckinghamshire Fire and Rescue Service*
Manchester Fire and Rescue Service*
Hereford and Worcester Fire Brigade*
Durham & Darlington Fire and Rescue Service*
Norfolk Fire Service*
Hampshire Fire and Rescue Service*
Essex County Fire and Rescue Service*
Surrey Fire and Rescue Service*
South Wales Fire Service*
Lancashire Fire and Rescue Service*
Avon Fire Brigade*
Lothian and Borders Fire Brigade*