

Project Title:

Analysis of the risks arising from the industrial use of Perfluorooctanoic acid (PFOA) and Ammonium Perfluorooctanoate (APFO) and from their use in consumer articles. Evaluation of the risk reduction measures for potential restrictions on the manufacture, placing on the market and use of PFOA and APFO.

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FINAL REPORT (20.12.2008 – 20.10.2009)

European Commission

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PREFACE

RPS Advies (Delft, The Netherlands) has been commissioned by the European Commission by letter of 18 December 2008 to conduct an analysis of the risks arising from the industrial use of Perfluorooctanoic acid (PFOA) and Ammonium Perfluorooctanoate (APFO) and from their use in consumer articles. Succeeded by an evaluation of the risk reduction measures for potential restrictions on the manufacture, placing on the market and use of PFOA and APFO.

Project co-ordinators for the present project for EC are Mrs. G. Luvarà and Dr. S. Pickering. The project team includes Dr. I. van der Putte, Mr. M. Murin, Mr. M.A.J. van Velthoven and Mrs. F. Affourtit. Project team leader is Dr. I. van der Putte.

A kick-off meeting with the Commission involving the set-up of the project was held on 9 January 2009.

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EXECUTIVE SUMMARY AND RECOMMENDATION

Concise summary of the main issues arising from the project

Objectives:

- To continue the work conducted by the OECD using the information under the Screening Information Data Set (SIDS);
- To assess the risks arising from the use of PFOA and APFO in industry as well as from their use in consumer articles.

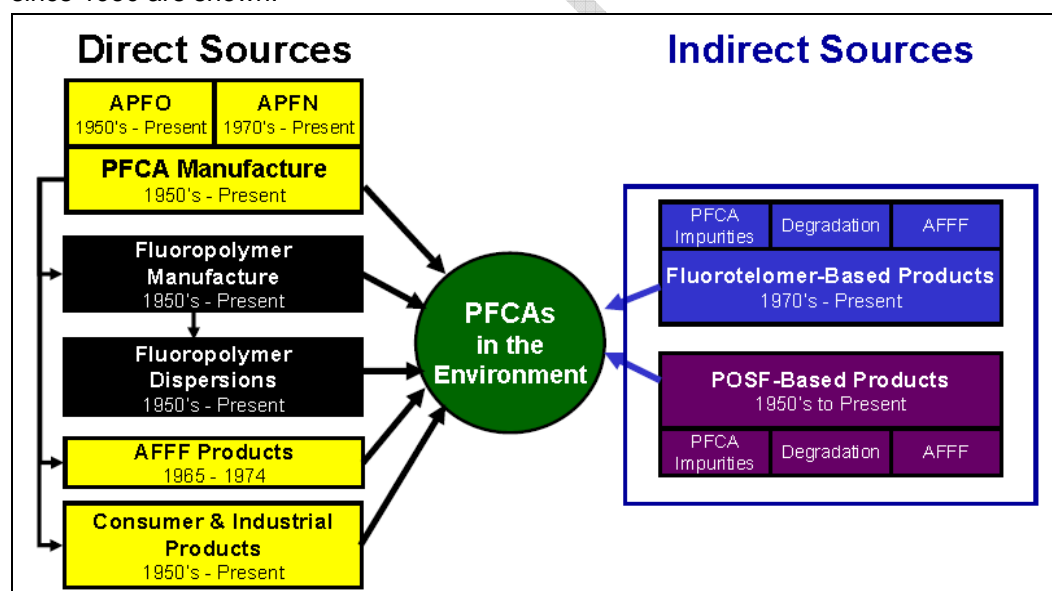
The project proceeded from the kick off meeting on 9 January 2009 with the market analysis and the hazard assessment of PFOA and APFO.

The main conclusions resulting from the outcomes of the various tasks within the project can be summarised as follows:

Task 1: Market analysis

The market volume of production and import of PFOA and related substances has a decreasing trend from 2002 onwards in the EU-27 Member States. For the period 2004-2008 the average market volume is estimated to be maximal 100 tonnes per annum, including direct and indirect sources. The trend in the use of PFOA and related compounds is further decreasing and the market volume outlook for 2010 will most probably be less than 50 tonnes per annum, including direct and indirect sources.

In the following figure (after Prevedouros et al, 2006) the various direct and indirect sources of PFCAs since 1950 are shown.



Historical overview of potential sources of PFCAs in the environment (Prevedouros et al, 2006)

Uncertainties of the Market Analysis

The largest uncertainty in the market analysis lies in the levels of PFOA as an unintended by-product in imported fluorotelomer based products used in consumer products and in the residual levels of PFOA in

imported consumer articles. More research needs to be done on the levels of PFOA in consumer articles, especially those consumer articles that are not produced in the EU-27.

Furthermore it should be noted that the information presented in this report is based on the questionnaires received from the industrial stakeholders and that due to the confidential business information (CBI) nature of this information only a range or a rounded figure could be presented in this report.

Task 2: General assessment and analysis

Using a strict interpretation of the results of the PFOA risk assessment in this report leads to the conclusion that there seems to be no risk for human health in the EU-27 Member States. However, due to uncertainties with regard to carcinogenic and developmental effects firm conclusions on health risks are not possible. Furthermore, PFOA and APFO at the present level of understanding do not meet the criteria as given in Annex XIII of the REACH regulation EC/1907/2006 for PBT or vPvB substances.

Regarding the risk for the environment, it can be concluded that there seems to be no risk for the aquatic, terrestrial and atmospheric compartment. No risk could be identified for the microbial activity in sewage treatment systems.

However, these outcomes may be challenged due to various uncertainties which can be summarised as follows.

Uncertainties in the human health risk assessment

First of all there is evidence that PFOA shows developmental toxicity in experimental animals. From general human health studies there is a suggestion of a negative association between estimates of maternal exposure to PFOA and fetal growth or fertility in humans. However, a number of concerns have been raised about these data including the possibility that they may not be the result of a true causal relationship.

From epidemiological occupational exposure and general human health studies there is only an association between PFOA and prostate cancer, the evidence is not conclusive. Some increases in prostate cancer have been seen, but the cause is not certain.

From Canadian sources a final report on the possible carcinogenic properties is expected by the end of 2009. Furthermore, other epidemiological results from the US C8 research project are expected to be published by the end of 2009 as well.

From the above information it seems to be clear that PFOA and related compounds will most probably be classified as a Category 2 Reprotoxicant. This classification of PFOA as Reprotoxicant 2 is also foreseen in the Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009). The classification of PFOA and its salts as Reprotoxicity Category 2 was agreed in the former TC C&L group in exECB 2006 after the closure of the 31ATP to Directive 67/548/EEC, and was therefore not included in the 1ATP to the CLP Regulation 1272/2008/EC. The Norwegian rapporteur will update their Annex XV C&L dossier on PFOA and send it to ECHA in December 2009. This updated dossier might serve as a basis for possible restrictions for the direct and/or indirect use of PFOA.

Uncertainties regarding the PBT-criteria

Although in the strict sense PFOA is not bioaccumulative according to the REACH Annex XIII criteria, another bioaccumulation mechanism seems to take place due to the fact that PFOA is found in the blood of the general public with a half-life of approximately 4 years. This effect might be judged as of equivalent concern although blood levels of PFOA seem to be decreasing. The decrease might be a result of the decreasing trend in the direct use of PFOA from 2002 onwards.

Uncertainties regarding the environmental risk assessment

From the information in the Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009) there seems to be no risk for the environment. No new data were found which could be used for the revision of risk assessment for the environment.

Task 3: Alternatives evaluation*Alternatives for the direct uses of PFOA in fluoropolymer production*

It is clear that given the commitment of industry to the US EPA PFOA Stewardship Programme it is important that alternatives must perform technically and meet HSE conditions as a first priority and that the cost of the alternative although important is a secondary issue. It should be recognised that there are different processes and different process conditions which are needed to be met. It is highly unlikely that there will be only one single alternative of APFO that can be applied for all the different processes and different process conditions in which PFOA is presently being used. Only experience gained on the longer term will allow to determine the optimum replacements.

At this moment accurate information on the economic feasibility of alternatives could not be given as most alternatives are still under development for the different processes and different process conditions. One alternative is already being produced. However, the pricing information of this alternative could not be provided as the manufacturer does not sell it on the open market and considers this information as confidential business information (CBI). This manufacturer pointed out that the use of the alternative is not a major cost/pricing component in the fluoropolymer production.

The fluoropolymer production is the major direct user of PFOA as processing aid. In this production sector alternatives of PFOA are being developed. Other direct uses include that in the semiconductor industry and in the photographic industry. In these industries no suitable alternative for PFOA for some critical applications are available yet. See task 4.

Alternatives of other indirect sources of PFOA

The direct uses of PFOA in the fluoropolymer production, the semiconductor industry and the photographic industry are considered as direct sources of PFOA in the environment.

Indirect sources of PFOA in the environment are related to fluorotelomer production as unintended by-product, use of resins and dispersions contaminated with PFOA and the use of alternatives to PFOS which may contain trace levels of PFOA in fluoropolymer industry. The development of short-chain fluorotelomer products without PFOA as unintended by-product and the development of alternatives to PFOS without trace levels of PFOA are already available or will become available before 2015.

Task 4: Identification & definition of specific uses without alternatives

In photographic industry as well as semiconductor industry certain critical uses of PFOA are identified.

In the semiconductor industry non-PFOA based alternatives appear to be available for some non-critical applications like the uses as a surfactant. However, there still remain critical uses in the semiconductor industry. These mainly concern uses of PFOA related substances as a constituent material in process chemical formulations for very specialized application steps, such as for the photolithographic applications.

In the photographic industry PFOS and PFOA have comparable critical photographic applications but can not be substitutes by each other. Some individual companies use PFOS for their critical photographic application while others use PFOA for comparable photographic applications. For those companies which use PFOA within their critical photographic applications the same derogations based on the same argumentation as for PFOS will be necessary to continue their production.

In both other derogated uses of PFOS that is in the hydraulic fluids and in the electroplating process, no PFOA is presently being used and therefore no derogations for PFOA will be required for these specific applications.

Task 5: Conclusions and recommendations

Based on the information gathered and processed during this study there seems to be no foundation to impose further restrictions on the use of PFOA/APFO. However, due to the uncertainty in PFOA levels in imported consumer articles it is recommended that detailed research is done on the levels of PFOA in consumer articles, especially those consumer articles that are not produced in the EU-27. From discussions with competent authorities in the various EU Member States it has become clear that a legal framework is lacking to further investigate these levels of PFOA in consumer articles. In case a legal framework is to be developed for this purpose the nomenclature for perfluorinated compounds need to be made more uniform. Industry and its associations are currently working on this aspect. Furthermore, a normalised analytical standard needs to be developed to enable comparison of the results from the various EU Member States.

Further, uncertainty appears to be unclarity as to whether and to which extent PFOA may be formed from precursor substances, and which are the most relevant precursor substances. It is recommended that more research will have to be done on the precursors of PFOA and more efforts have to be made to gather information on international level using the available information of the various international bodies to come to a internationally/globally recognised list of precursor substances. The OECD could be the platform best used for bringing together all this international information. However, the OECD has already put up a list of possible precursor substances that is used by international bodies as well as industry.

When new information on the risks for human health and environment will become available and when based on that information further restrictions on the use of PFOA will be imposed, a number of derogations might be considered. These derogations are to be time-limited based on the expectations that the PFOA Stewardship Programme when executed by the OECD will have a more global coverage. Time limited derogations might include a number of critical uses:

- The direct uses of APFO and APFN in the fluoropolymer industry as a direct source in the environment;

- The process applications as indirect sources of PFOA in fluorotelomer production as unintended by-product, use of resins and dispersions contaminated with PFOA and the use of alternatives to PFOS which may contain trace levels of PFOA in fluoropolymer industry.
- Certain critical **uses** of PFOA and related substances in photographic and semiconductor industry.

It is required that these industries further define these critical uses and that PFOA and related substances are only used under strictly controlled conditions.

Given the goal of the PFOA Stewardship Programme the ultimate phase-out deadline for the direct use of PFOA and related compounds of 2015 might be considered as a starting point.

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1. INTRODUCTION

1.1 Basic project data

Project title

Analysis of the risks arising from the industrial use of Perfluorooctanoic acid (PFOA) and Ammonium Perfluorooctanoate (APFO) and from their use in consumer articles. Evaluation of the risk reduction measures for potential restrictions on the manufacture, placing on the market and use of PFOA and APFO”.

Contract no:

Specific Contract 30-CE-0230115/00-70 implementing Framework Contract 30-CE-0220929/00-38.

Country:

the 27 European Member States (EU-27).

Stakeholders:

The main stakeholders identified that will be requested for assistance to provide information on the production, import, export and use of PFOA and APFO in the EU-27 are:

- Trade associations (e.g. CEFIC);
- Industrial and professional users;
- Labour organisations (including Trade Unions);
- Consumers’ organisations and other stakeholders..

Project start date:

18 December 2008.

Project duration:

10 months.

1.2 Background and objectives

This Request for Service was set out due to additional information that has become available due to the OECD PFOA Hazard Assessment. As mentioned in the restriction on PFOS under the Directive (2006/122/EC), further study is necessary if new information on PFOA has become available.

PFOS was included due to adverse environmental properties. Discussions in environmental committee of the EP showed that PFOA and APFO (as sources of the PFO-anion) may be of concern as well because of these substances are Persistent and Toxic but not Bioaccumulative in the strict sense of Annex XIII of EC Regulation 1907/2006 “REACH” as mentioned in the draft report on the proposal for a directive relating to restrictions on the marketing and use of perfluorooctane sulfonates (http://www.europarl.europa.eu/meetdocs/2004_2009/documents/pr/612/612786/612786en.pdf).

The OECD finished their hazard assessment on the APFO (further details can be found on <http://www.oecd.org/dataoecd/63/49/42565413.zip>). Canada conducted and reported the human health assessment while the German OECD rapporteur was responsible for the environmental part and implementation of both parts.

Furthermore the current PFOS restrictions contain various derogations for applications without any alternatives. These applications may have alternatives available at this point in time. This will also be checked in this study.

Data may still be lacking on the use of PFOA and related substances, especially in SME-industries (mainly electroplating). Also data on the use in new Member States (after EU-15) is hardly available. On the other hand, textile industry is known to have a lot of information on the use of PFO-substances.

The objectives of the service request are:

- to continue the work conducted by the OECD using the information under the Screening Information Data Set (SIDS);
- to assess the risks arising from the use of PFOA and APFO in industry as well as from their use in consumer articles.

1.3 Study approach

Based on the Terms of Reference, the project team has adopted a project structure that is based on sound project management and five main tasks, as follows:

- **Project management:** understanding the needs of beneficiary, budget control, timely completion of deliverables, management of contract experts;

- **Task 1:** Market analysis

The study will make a detailed quantification of the EU market in tonnes of production, use, export and import. Any particular case where use is local or regional rather than EU-wide should be included.

Key output will include:

- Tonnage of PFOA and APFO currently produced in the EU;
- Tonnage of PFOA and APFO currently used in the EU;
- Tonnage of imports of PFOA and APFO from outside the Member States.

- **Task 2:** General assessment and analysis

This stage includes hazard assessment, exposure assessment and risk characterisation of PFOA and APFO for all the industrial applications and uses that are identified. As PFOA can also be a degradation product of some (mainly with a perfluorinated chain of 8 carbon atoms or more) fluorotelomer-based products, an investigation on these potential precursors of PFOA will be included in this study.

Within this task a list of consumer articles available on the market possibly containing PFOA and/or APFO will be included. This list will include consumer products containing fluorotelomer-based substances that potentially degrade to PFOA and related substances (as an unintended by-product) as well as consumer products that might contain PFOA or APFO residues in finished articles due to the manufacturing process itself.

The use of PFOA in fire fighting foams will be evaluated. A detailed evaluation should be conducted on possible fluorotelomer-based substances used in fire fighting foams that can degrade to PFOA and related substances.

Key outputs will include:

- Exposure Scenarios and risk assessment related to identified uses of PFOA and APFO, including:
 - the manufacturing process, placing on the market (via import) or use(s) which pose a risk
 - in what life-cycle stage(s) of the substance is the exposure causing a risk
 - which human populations and/or environmental compartments are (specifically) at risk.
 - List of potential precursors of PFOA and APFO (presented in Annex I)
 - List of either consumer articles containing PFOA and/or APFO and/or fluorotelomer-based substances that may potentially degrade to PFOA and related substance or consumer articles that can contain PFOA or APFO in finished articles due to the manufacturing process itself (presented in Annex II)
 - Special risk evaluation on PFOA and possible fluorotelomer-based substances used in fire fighting foams
 - List of all Stakeholders consulted (presented in Annex IV)
- **Task 3:** Alternatives evaluation
- For those applications and uses, where risks to human health and the environment are identified in task 2, the impact of potential marketing and use restrictions will be quantified as far as possible.
- Our analysis will take into account the availability and the performance and the costs/benefits of the alternatives available as well as the potential risks that such alternatives can cause to the population and the environment.
- A special analysis will be conducted for those substances or technologies which would potentially replace PFOS in those applications currently exempted from the restrictions under Directive 2006/122/EC.
- Key output will include:
- a list of alternatives for PFOA and APFO
- **Task 4:** Identification & definition specific uses without alternatives
- From the outcome of the evaluation of task 3, identify and define specific uses of PFOA and related substances for which there are no suitable alternatives that pose lower risks to human health and environment. The main reasons for including derogations into a restriction proposal are related to the availability and the performance and the costs/benefits of the alternatives available as well as the potential risks that such alternatives can cause to the population and the environment in relation all these aspects related to PFOA and APFO. Also, regulatory and contractual considerations will be taken into account.
- Key output will include:
- proposal to exempt specific uses from the restrictions due to the absence of suitable substitutes posing lower risks
- **Task 5:** Conclusions and recommendations
- General conclusion and recommendations on specific uses of PFOA and APFO, with appropriate justifications. The conclusions and recommendations will be transparent based on sound information, open to review and reflective of the uncertainties.

Key output will largely include recommendations on:

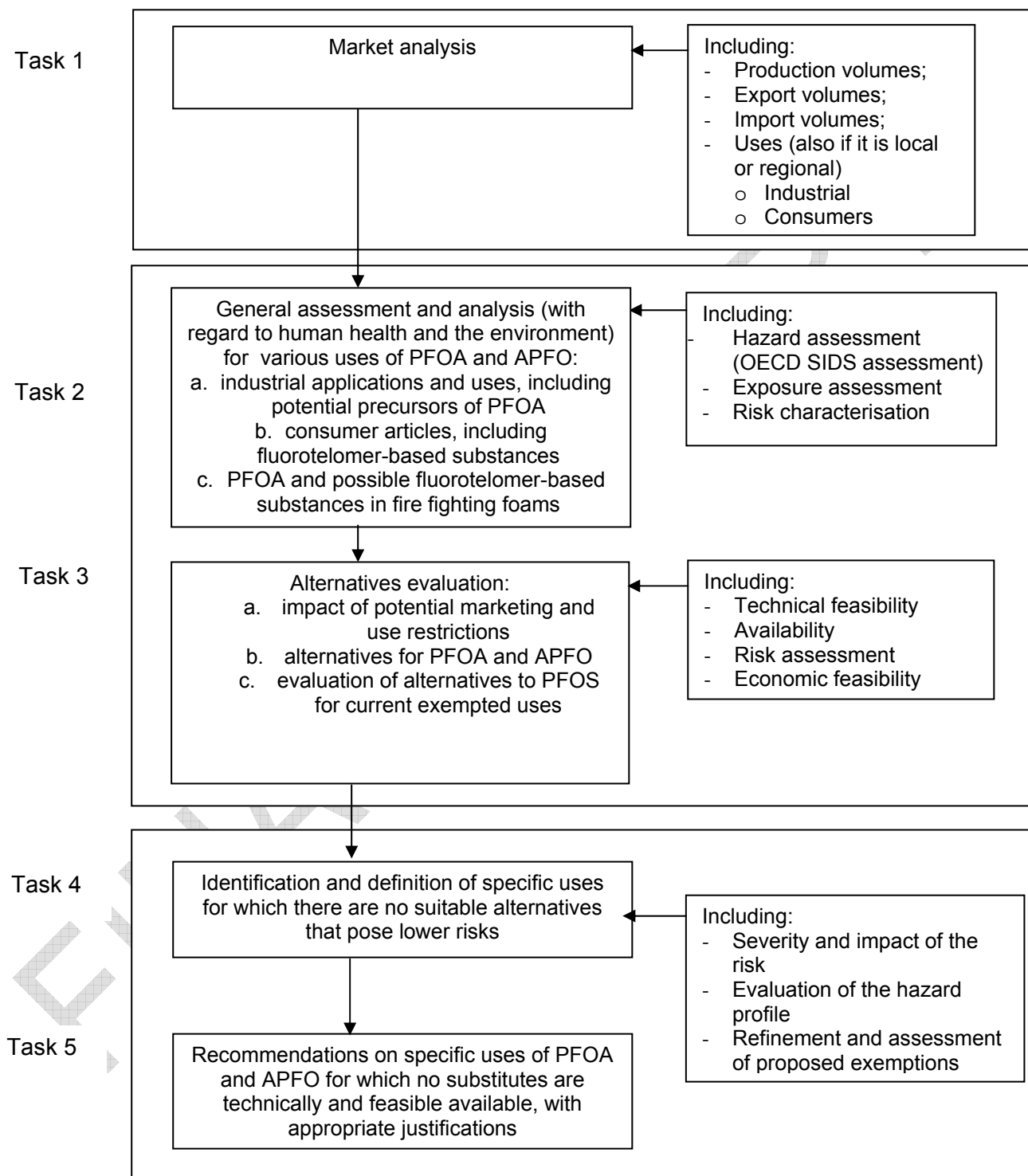
- determine for which specific uses of PFOA and APFO exemptions from a proposed ban should be allowed due to the absence of suitable substitutes posing lower risks.

The proposed system for providing technical support to the Commission to permit specific uses of PFOA and APFO with a sound scientific basis.

The proposed system for providing technical support is shown in Figure 1.

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Figure 1 Proposed system for providing technical support to the Commission to permit specific uses of PFOA and APFO



1.4 Kick-off meeting of the project

During the kick-off meeting of 9 January, 2009 RPS presented the approach to DG Enterprise. The general approach was confirmed. Two remarks were made in addition to the general approach:

- at this point in time there is no clear view on use of PFOA and related substances (PFOA/APFO) in imported articles. Therefore consumer goods authorities might be addressed for more information;
- the uses of PFOA and related substances in medical devices are out of the scope of this study.

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2. DEFINITIONS

Considering the name, identification and definition of PFOA and related compounds, work has to be done as there seems to be great differences in the communication on the various perfluorinated carboxylic acids, on the fluorinated telomer alcohols and on the abbreviations used by both industry and other stakeholders which lead to miscommunication and identification problems. The definitions regarding per- or polyfluorinated compounds will be based on the OECDs Preliminary 2006-list. The list contains about thousands per- or polyfluorinated compounds with an alkyl chain typically between 4 and 12 carbon atoms and where all or most of the hydrogen have been replaced by fluorine. These substances may also contain a more reactive functional group, which may be an alcohol, a carboxylic acid, a phosphoric acid or their derivatives. Below some definitions, abbreviations and structural formulas are given. The structural formulas of substances may contain linear, branched or cyclic carbon chains.

PFOA itself is mainly produced and used as ammonium perfluorooctanoate (APFO). The difference between in branched or linear APFO depends on the manufacturing process perfluorooctyl iodide oxidation (telomerisation) and electro-chemical fluorination (ECF). By the perfluorooctyl iodide oxidation the produced APFO will be 100% linear and by the ECF the produced APFO will be <30% branched.

The relative importance of particular biological targets may well vary for that have different chain lengths and for perfluoroalkyl acids with carboxylate versus sulfonate functional groups (Anderson et al, 2008). Sciali et al. (2007) investigated the possibility if exposure levels of multiple perfluoroalkane acids can be combined for risk assessment purposes by a scaling system analogous to the Toxic Equivalency Factor (TEF). They evaluated pairs of studies performed with different perfluoroalkane acids in the same species using the same design and found that endpoints for perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorobutanesulfonate (PFBS), and perfluorodecanoic acid (PFDA) could be discordant. They evaluated pairs of rat studies of PFOS, PFOA, and PFBS performed with the same design for which dose-response curves could be modelled for the concordant endpoints, but they were unable to identify a scaling system that gave values consistently within an order of magnitude for the same compounds.

Qualitatively it is known that PFOS and PFOS derivatives seem to be more toxic than PFO and its derivatives. Furthermore, the persistence and toxicity of perfluorinated acids increases in general with the chain length and substances with branched chain are less toxic than linear substances. There seems presently to be insufficient background data to make quantitative structure-activity relationships (QSAR) for these homologues.

Currently available data do not support the combining of exposure levels of perfluoroalkane acids for risk assessment. Therefore, within this study the focus was on data related to the exposure of PFOA/APFO and not on data of mixtures of various perfluoroalkane acids or on data of single perfluoroalkane acids, like PFOS.

List of abbreviations used within this report

Fluorochemical (FC): a term used to describe broadly all chemicals containing the element fluorine; Specifically, the term is used most commonly to describe small (1-8 carbon length) fluorinated molecules which are most used for refrigeration, fire suppression and as specialty solvents

Fluorinated chemical (FC): a term used synonymously with "fluorochemical"

- Fluorotelomer (FT):** a term used to describe an oligomer created by reaction of tetrafluoroethylene (TFE) with perfluoroethyl iodide $\text{CF}_3\text{CF}_2\text{I}$ to produce $\text{F}(\text{CF}_2\text{CF}_2)_n\text{I}$ [$n = 3-6$, avg. 4], the term “*telomer*” is often used synonymously with *fluorotelomer*.
- Fluorotelomer-based substance:** a term used for a chemical substance that has the fluoroalkyl portion of the molecule derived from telomerisation of tetrafluoroethylene.
- Perfluorochemical product:** is a term used for perfluorinated or polyfluorinated chemical product that may contain PFOA, Long chain PFCA's, precursors, or mixtures of these substances. Perfluorochemical products are fluoropolymers, fluoropolymer dispersions, and fluorotelomer-based substances.
- Fluoropolymer (FP):** a term used to describe a polymer which has fluorine attached to the majority of carbon atoms which comprise the polymer chain backbone. Common fluoropolymers are: polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), fluorinated ethylenepropylene (FEP), etc. Fluoropolymers are typically high molecular weight polymers.
- Fluoropolymer dispersion:** a term used for a mixture composed of small solid fluoropolymer particles dispersed in an aqueous medium.
- Fluorinated organic polymer:** a term used to describe a polymer which has a hydrocarbon backbone (polyamide, polyester, polyurethane, etc.) to which is appended a fluorinate carbon chain.
- Perfluoro- /Perfluorinated:** describes a substance where *all* hydrogen atoms attached to carbon atoms are replaced with fluorine atoms – CF_n - where $n = 1 - 4$.
- Perfluoroalkylated substance:** a substance which bears a perfluorocarbon, also known as a perfluoroalkyl, functional group. $\text{F}(\text{CF}_2)_n\text{-X}$ where n is an integer and X is not a halogen, or hydrogen.

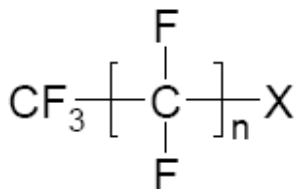


Figure 2: General structure of perfluorinated alkylated substances

- Polyfluoro- /Polyfluorinated:** describes a substance where *many but not all* hydrogen atoms attached to carbon atoms are replaced with fluorine atoms.

Fluorinated organic surfactant: a term to describe a surface active, low molecular weight, substance which contains fluorinated carbons; the term fluorosurfactant is used synonymously.

Perfluorinated surfactant: a term used to describe a surface active, low molecular weight, substance where all carbons bear fluorine in place of hydrogen; the term fluorosurfactant is used synonymously.

Perfluoroalkyl Sulfonate (PFAS) a generic term used to describe any fully fluorinated carbon chain length sulfonate compound, including higher and lower homologues as well as PFOS. PFAS-related substances may be salts of PFAS, or polymers that contain PFAS as a portion of the entire structure.

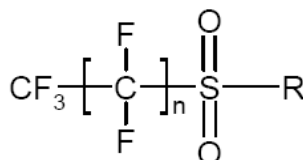


Figure 3: General structure of perfluoroalkyl sulfonates

Perfluorocarboxylic acid (PFCA) a generic term used to describe any carboxylic acid containing a fully fluorinated carbon chain, including perfluorooctanoic acid (PFOA). PFCA-related substances may be salts of PFCA, or polymers that contain PFCA as a portion of the entire structure. The general structure is $\text{CF}_3(\text{CF}_2)_n\text{COO}^-$ (linear or branched).

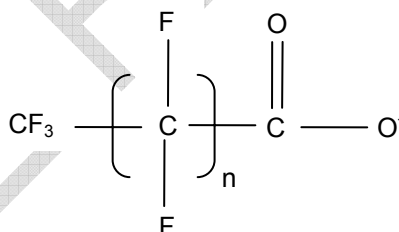


Figure 4: General structure of perfluorocarboxylic acids (anionic)

Perfluorooctane sulfonate (PFOS) a fully fluorinated (eight-carbon chain length) sulfonate containing substances. The term PFOS related substance is used in this study to represent any substance containing the PFOS moiety ($\text{C}_8\text{F}_{17}\text{SO}_2$) with the potential to degrade to PFOS in the environment. The majority of PFOS related substances are polymers of high molecular weight in which PFOS is only a fraction of the polymer.

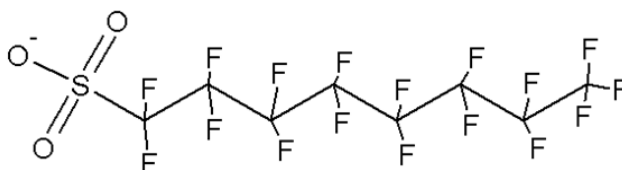


Figure 5: structure of perfluorooctane sulfonate (linear)

Perfluorooctanoic Acid (PFOA)
CAS number: 335-67-1

a fully fluorinated eight-carbon carboxylic acid. PFOA-related substances may be salts of PFOA, or polymers that contain PFOA as a portion of the entire structure. PFOA is primarily a reactive intermediate, while its salts are used as processing aids in the production of fluoropolymers and fluoroelastomers and in other surfactant uses.

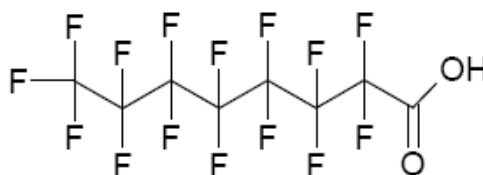


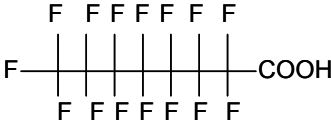
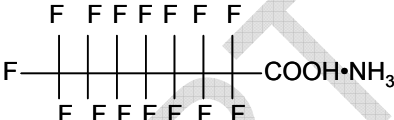
Figure 6: General structure of perfluorooctanoic acid (linear)

PFOA is used as a group name for perfluorooctanoic acid (PFOA) and its salts. However, the perfluorooctanoate anion is of primary interest. Therefore the ammonium, sodium, potassium and silver salts of PFOA are included in this study.

In this study PFOA will be used to describe the PFOA and related ammonium, sodium, potassium and silver salts that dissociate to the PFO-anion. The ammonium salt, APFO (CAS number 3825-26-1), is especially of interest due to its direct use in fluoropolymer industry.

3. INFORMATION ON PFOA RELATED SUBSTANCES¹

3.1 Identification of the Substance

CAS Number:	335-67-1	3825-26-1
IUPAC Name:	Pentadecafluorooctanoic Acid (PFOA)	Ammonium Pentadecafluorooctanoate (APFO)
Molecular Formula:	C ₇ F ₁₅ COOH	C ₇ F ₁₅ COO ⁻ NH ⁺
Structural Formula (linear):		
Molecular Weight:	414.07 g/mol	431.10 g/mol
Synonyms:	Perfluorooctanoic Acid; PFOA; Pentadecafluoro-1-octanoic acid; Perfluorocaprylic acid; Perfluoroheptanecarboxylic acid; Perfluoro-n-octanoic acid; Pentadecafluoro-n-octanoic acid; Pentadecafluorooctanoic acid; n-Perfluorooctanoic acid 1-Octanoic acid, 2,2,3,3,4,4,5,5,6,6, 7,7,8,8,8-pentadecafluoro	Ammonium Perfluorooctanoate; APFO; C-8; Ammonium pentadecafluorooctanoate; Ammonium perfluorocaprylate; DS 101; FC 1015; FC 143; FX 1006; Fluorad [®] FC 143; Perfluorooctanoic acid ammonium salt; Unidyne [®] DS 101-20

There are a number of perfluorooctanoate salts in commercial use, which are used in very small quantities (est. < 1 metric ton·yr⁻¹):

- Potassium perfluorooctanoate CAS # 2395-00-08
- Sodium perfluorooctanoate CAS # 335-95-5
- Silver perfluorooctanoate CAS # 335-93-3

Physical and chemical properties of the salts different from APFO are not subject of this assessment report.

For the purposes of this document, the anion of PFOA (perfluorooctanoate or anionic PFO) is frequently referenced as PFOA or APFO. APFO and PFOA are sometimes used interchangeably as both PFO-anion and PFOA (neutral species) exist in solution.

¹ Source: SIDS Initial Assessment Report (OECD, 2006); details can be found on: <http://www.oecd.org/dataoecd/63/49/42565413.zip>

3.2 Purity/Impurities/Additives

PFOA itself is mainly produced and used as its ammonium salt, ammonium perfluorooctanoate (APFO). The purity and impurity of APFO depends on the manufacturing process perfluorooctyl iodide oxidation and electro-chemical fluorination.

Industrial processes for the synthesis of PFOA

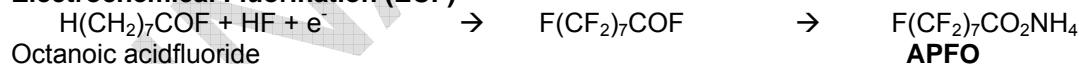
The PFOA acid and its salts can be commercially manufactured by two major alternative processes: The Simons Electro-Chemical Fluorination (ECF) process, and a telomerisation process. These processes will be described below in more details. Releases from manufacturing processes are one source of PFOA in the environment. Historically, most production was by 3M using the ECF process. 3M discontinued its manufacture of PFOA between 2000 and 2002, and most other global producers are using the telomerisation process.

In the ECF process, an electric current is passed through a solution of anhydrous hydrogen fluoride and an organic feedstock of octanoic acid or a derivative. The ECF process replaces the carbon-hydrogen bonds on molecules of the organic feedstock with carbon-fluorine bonds. Perfluorination occurs when all the carbon-hydrogen bonds are replaced with carbon-fluorine ones. The ECF process yields between 30-45% straight chain (normal) perfluorooctanonyl fluoride (PFOF), along with a variable mixture of by-products and impurities. The output of the ECF process consists of a complex combination of chemical substances with varying molecular weights, including higher and lower straight-chain homologues; branched-chain perfluoroalkyl fluorides of various chain lengths; straight-chain, branched, and cyclic perfluoroalkanes and ethers; and other by-products. After disposal or recovery of some of the by-products and impurities, the acid fluoride is base hydrolyzed in batch reactors to yield PFOA.

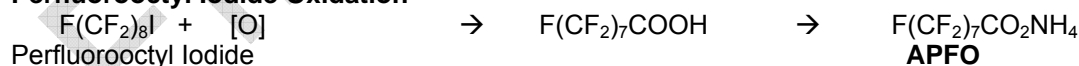
The PFOA salts are synthesized by base neutralization of the acid to the salt in a separate reactor.

In the telomerisation process, tetrafluoroethylene is reacted with other fluorine-bearing chemicals to yield fluorinated intermediates which are readily converted into PFOA. This process yields predominantly straight-chain acids with an even number of carbon atoms. Distillation can be used to obtain pure components. Commercial products manufactured through the telomerisation process, sometimes known as fluorotelomers, are generally mixtures of perfluorinated compounds with even carbon numbers, although the process can also produce compounds with odd carbon numbers.

Electrochemical Fluorination (ECF)



Perfluorooctyl Iodide Oxidation



Process	Perfluorooctyl Iodide Oxidation	Electrochemical Fluorination
Purity of the commercial product :	> 99% (after purification)	99% (after purification)
Impurities:	<ul style="list-style-type: none"> • \leq limit of quantification ($\leq 0.01\%$) of each of the following acids PFNA, PFDA, PFUA, PFDDA, PFTDA 	<ul style="list-style-type: none"> • C-5 through C-7 isomers • 0.2 % PFNA • \leq limit of quantification ($\leq 0.01\%$) of each of the following acids PFDA, PFUA, PFDDA, PFTDA
Linear / Branched	100% linear (after distillation)	< 30% branched (Simons, 1949; Kissa, 2001)

PFNA: perfluorononanoic acid, PFDA: perfluorodecanoic acid, PFUA: perfluoroundecanoic acid, PFDDA: perfluorododecanoic acid, PFTDA: perfluorotridecanoic acid

3.3 US EPA PFOA Stewardship Programme²

In 2006 the eight major fluoropolymer and fluorotelomer manufacturers (3M/Dyneon, Arkema, Asahi, Ciba, Clariant, Daikin, DuPont and Solvay Solexis) were invited to join in a voluntary global program of the US EPA with a commitment to achieve reduction in both facility emissions to all media and product content of PFOA, its precursors and PFOA related higher homologue chemicals, measured from a year 2000 baseline. The eight companies committed to a 95 percent reduction by 2010 and committed to working toward total elimination of PFOA, its precursors, and related higher homologue chemicals from emissions and products by 2015.

These commitments include reductions to be achieved not only in the United States of America, but also through companies' global operations. The programme does not specify how reductions should be achieved so companies have the flexibility to meet goals through a variety of strategies (including treatment and control technologies, process changes, product reformulation and new chemical/product development). At this point in time, many companies are meeting initial targets ahead of schedule. Noteworthy measurable progress has been achieved to date, as evidenced by reduction in the geometric mean for PFOA (and PFOS) in blood which was reduced by 25% (and 32%, respectively), from 1999/2000 to 2003/2004 in a representative sample of the US population.

All eight companies committed to the USA EPA Stewardship Programme have submitted their progress reports by October 30, 2009. The submissions are presented on the US EPA PFOA Stewardship Programme webpage. See Annex III for EPA's summary tables for 2009 Company Progress Reports. Reported percent reductions in emissions and product content of PFOA, Precursors, and Higher Homologues from US and Non-US operations varies from cumulative 51 up to 100% reductions from baseline year through end of 2008.

This programme is the major driver for companies to reduce PFOA residuals in products and to switch from products that may contain (parts of) substances that might break down to (trace levels of) PFOA to safer alternatives.

² Sources: Information on US EPA PFOA Stewardship Programme webpage (<http://www.epa.gov/oppt/pfoa/pubs/stewardship/index.html>) and PlasticsEurope personal communication, 2009

The OECD is expected to take over the US EPA PFOA Stewardship Programme and is considering how best to develop, facilitate and promote national and international product stewardship programmes and regulatory approaches for perfluorinated chemicals based on their existing work programmes and in association with other participating organizations of the IOMC.

Industry has worked with OECD to agree a comprehensive global PFC survey that has started in June 2009.

3.4 Physico-Chemical properties

Table 1 Summary: Perfluorooctanoic Acid (PFOA): Physico-Chemical Properties

Property	Value	Reference	IUCLID
Substance type	Organic compound		1.1.1
Physical state	Solid		1.1.1
UV absorption in water	no absorption < 290 nm	Hori et al., 2005	
Melting point (°C)	54.3 44 - 56.5 (6 references)	Lide, 2003 Beilstein, 2005	2.1
Boiling point (°C)	188 (1013.25 hPa) 189 (981 hPa)	Lide, 2003 Kauck and Diesslin, 1951	2.2
Density	1.792 g/cm ³ (20° C)	HSDB, 2005	2.3
Vapour pressure (Pa)	4.2 (25° C) extrapolated from measured data 2.3 (20° C) extrapolated from measured data 128 (59.3° C) measured	Kaiser et al., 2005; Washburn et al., 2005 Washburn et al., 2005 Washburn et al., 2005	2.4
Partition coefficient n-octanol/water (log value)	For the surface active PFOA K _{ow} is not measurable (USEPA, 2005).		
Henry's law constant	Henry's law constant cannot be calculated from vapour pressure and solubility (dissociating substance).		
Water solubility (g·L ⁻¹)	9.5 (25° C)	Kauck and Diesslin, 1951	2.6.1
Solubility in organic solvents	-		
pH value	2.6, 1 g/l (20° C)	Merck, 2005 (reliability not assignable)	2.6.1
pKa	2.5 2.8 1.5-2.8	Gilliland, 1992, Ylinen et al., 1990 (reliability not assignable) Brace, 1962 Kissa, 2001	2.12
Critical Micelle Concentration (g·L ⁻¹)	3.6 - 3.7	Kissa, 1994	
Conversion factor for the vapour phase	1 ppm = 17.21 mg/m ³		

Table 2 Summary: Ammonium Perfluorooctanoate (APFO): Physico-Chemical Properties

Property	Value	Reference	IUCLID
Substance type	Organic compound		1.1.1
Physical state	Solid		1.1.1
UV absorption in water	no absorption < 290 nm (acid)	Hori et al., 2005	1.1.2
Melting point (°C)	130 (decomposition) 157 - 165 (decomposition starts above 105° C)	3M, 1987 (reliability not assignable) Lines and Sutcliffe, 1984	2.1
Boiling point (°C)	Decomposition	Lines and Sutcliffe, 1984	2.2
Density	0.6-0.7 g/cm ³ (20° C)	Griffith and Long, 1980	2.3
Vapour pressure (Pa)	0.0081 (20° C) calculated from measured data 3.7 (90.1° C) measured	Washburn et al., 2005 Washburn et al., 2005	2.4
Partition coefficient n-octanol/water (log value)	K _{ow} is not measurable for the surface active APFO (US EPA, 2005)		2.5
Henry's law constant	Henry's law constant cannot be calculated from vapour pressure and solubility (dissociating substance).		3.3.2
Water solubility (g·L ⁻¹) at 20 °C	> 500	Shinoda, Hato, and Hayashi', 1972 3M, 1987 (reliability not assignable)	2.6.1
Solubility in organic solvents (g·L ⁻¹)	Heptane, Toluene : 0 Methanol, Acetone : >500	3M, 1987 (reliability not assignable)	2.6.1
pH value in water at 23 °C	approx. 5	3M, 1987 (reliability not assignable)	
Begin of thermal decomposition (°C)	130 Above 105	3M, 1987 (reliability not assignable) Lines and Sutcliffe, 1984	
Critical Micelle Concentration ((g·L ⁻¹))	(see table 1)		
Conversion factor for the vapour phase	1 ppm = 17.92 mg/m ³		

4. MARKET ANALYSIS (TASK 1)

Information in this chapter is based on the questionnaires on manufacturing and use as send back by industry, trade associations and national competent authorities stakeholders as well as on information received in various meetings and/or as received by the project team in other consultations with the afore mentioned stakeholders. An overview of the consulted stakeholders can be found in Annex IV. The percentages that respond to our questionnaire are given in table 3. The reported volumes by manufacturers and downstream users represent 80-100% of the directly used PFOA. Also the information from the OECD reports and US EPA PFOA Stewardship Programme has been taken into account. All figures mentioned in this section are rounded to the nearest 10 tonnes as much as possible.

Table 3 *Percentage of responses on questionnaires*

Consulted stakeholders	% response
EU Member State Competent Authorities	66%
EU Trade Associations	44%
EU NGO & Trade Unions	20%
National Trade Associations	11%
Manufactures, Importers and Downstream Users	48%

PFOA is used primarily to produce its salts, which are used as essential polymerisation aids due to their surfactant properties in the production of fluoropolymers and fluoroelastomers. Although they are made using mainly APFO, finished fluoropolymer and fluoroelastomer products are in general not expected to contain PFOA. With regard to APFO used as a polymerisation aid to manufacture certain fluoropolymers, the telomerisation process produces a range with different alkyl chain lengths. However the starting product perfluorooctyl iodide is refined and distilled to a high purity prior to production of APFO. High purity APFO is necessary to produce PTFE.

The major fluoropolymers manufactured using PFOA salts are polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF). PTFE has hundreds of uses in many industrial and consumer products, including soil, stain, grease, and water resistant coatings on textiles and carpet; uses in the automotive, mechanical, aerospace, chemical, electrical, medical, and building/construction industries; personal care products; and non-stick coatings on cookware. As regards the use of APFO in non-stick coatings in cookware, APFO restricted to be used in repeated use articles, sintered at high temperatures according to the Directive 2002/72/EC. PVDF-based fluoropolymers are high molecular weight polymers with many unique properties, including exceptional weathering resistance, low flame and smoke characteristics, good resistance to most chemicals and solvents as well as to nuclear radiation, and high thermal stability. As a result, PVDF products are used in such critical industrial applications as chemical handling systems, electrical cable insulation and jacketing, architectural finishes and coatings, high purity piping, semiconductor piping and high performance films, such as photovoltaic film.

The most important industrial processes for the synthesis of PFOA (as APFO) are described in the previous chapter. Please be aware that our market analysis only covers APFO and PFOA and not

perfluorocarboxylic acids as a group. The study team will however include the use of possible precursors of PFOA and related substances (presented in Annex I).

PFOA can be placed on the EU market via two distinct ways, either directly or indirectly. The direct sources concern mainly the manufacturing and use of the ammonium salt of PFOA (APFO) while the manufacturing and use of other PFOA salts (potassium, sodium and silver salts) only contribute minimally.

Indirectly, PFOA is present, mainly at residual levels or as an unintended by-product, in imported industrial and consumer products. These products can be best described as products containing fluoropolymer and/or fluorotelomer-based parts.

In figure 7 (after Prevedouros et al, 2006) the various direct and indirect sources of PFCAs since 1950 are shown.

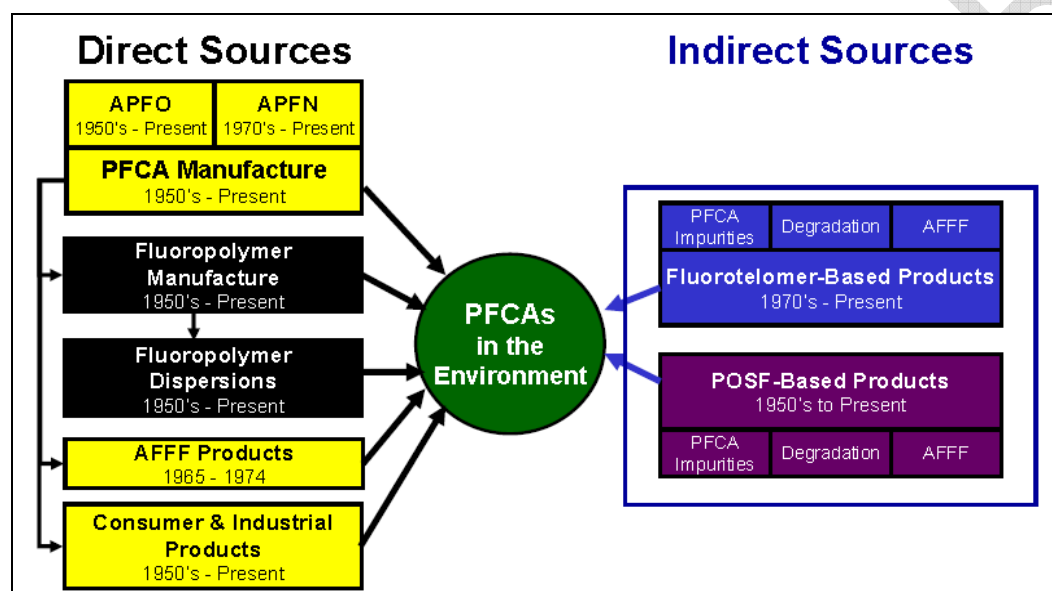


Figure 7 Historical overview of potential sources of PFCAs in the environment (Prevedouros et al, 2006)

The market analysis of the direct sources of PFOA is fairly easy compared to the complexity of assumptions that will have to be made for the indirect sources.

Direct sources- Manufacturing and import in the EU-27 Member States

According the 2006 OECD report the global (EU, US & Japan combined) PFOA and its ammonium salt (APFO) production was estimated to be 200-300 tonne per annum (1995-2002 figures). The 2001 estimated APFO consumption in Western Europe is estimated at 50-80 tonne per annum. The estimated virgin (non-recycled) APFO production in the EU at the Company 1 site is estimated at 40 tonnes per annum (2003-2004 figures). The production of APFO at the Company 4 site has ceased as from 2004.

Manufacturing

According to the information of the study team only one manufacturer of APFO and related substances, Company 1, is currently active in the European Union (EU-27). Company 1 is part of the International Chemical Investors Group (ICIG) who bought Company 1 in February 2009 from Mitsubishi Corp of Japan. The total annual average virgin APFO production of Company 1 (using the ECF process) is 40

tonnes per year and Company 1 upgrades 20 tonnes per year. The annual average EU supply volume from the reporting years 2004-2008 of Company 1 is reported to be round off to 30 tonnes per year. The residual amount is partly exported and partly put on stock.

Company 1 estimates the European market for PFOA/APFO virgin and upgraded to be maximal 90 tonnes in 2008 (divided in 50 tonnes of virgin APFO (including imports) and 40 tonnes of upgraded APFO). Company 1 estimates the European market demand for PFOA/APFO in 2009 to be maximum 60 tonnes of which 50% is virgin material this decrease is due to the strong decreasing trend in the EU-27 market demand.

As mentioned above the demand for APFO has a strong decreasing trend. This has lead to the decision of Company 1 to cease production as per April 2010 and to cease commercialisation as per November 2010. Company 1 already reported in April that they "expect that PFOA will be fully phased out in Europe by the end of 2012-2013".

The strong decreasing trend in APFO demand (from 2002 on) is due to the implementation of the capture and recycling technologies by the main users, within the framework of the US EPA PFOA Stewardship programme that has the goal to work "toward the elimination of PFOA, PFOA precursors, and related higher homologue chemicals from emissions and products by five years thereafter, or no later than 2015" according the US EPA PFOA Stewardship Programme homepage.

Import

The study team has found that limited volumes of APFO for direct use have been imported in the European Union from China during last few years but these imports were approximately 1 tonne per year on average (period of reporting 2004-2008) and the company involved does not import APFO any longer and does not plan to do it in the future. However, this information was received before the Company 1 announcement to cease the production of APFO. The decision of Company 1 to cease APFO production and commercialisation will most probably lead to increased import of APFO from outside the EU Member States as per July 2009. It is estimated that the import of APFO will most probably remain stable at <50 tonnes per annum in the next 5 years because of the efforts of the involved downstream user (fluoropolymer producing) companies all have committed themselves to the US EPA PFOA Stewardship Programme that will have the ultimate goal to phase out the use of PFOA and related substances by 2015.

Company 3 reported that it does not manufacture or use PFOA, but uses a different fluorosurfactant which serves as a processing aid to produce polyvinylidene fluoride (PVDF) based polymers by emulsion polymerization. The fluorosurfactant used is carboxylic acids, C7-13, perfluoro, ammonium salts, (CAS n° 72968-38-8) composed primarily of ammonium perfluorononanoate (APFN) (70-80% by weight), ammonium C-11 perfluoroundecanoate (15-20% by weight), ammonium C-13 perfluorotridecanoate (5% by weight, and less than 1% ammonium perfluorooctanoate. This fluorosurfactant is used and treated in the same way as APFO in other fluoropolymer manufacturing industries.

This substance is imported in quantities of < 5 tonnes per year an average (period of reporting 2004-2008). However, this information was received before the Company 1 announcement to cease production of APFO.

The study team also tried to gain access to import figures for PFOA related substances through EUROSTAT but there seems to be no separate statistical code present for perfluorinated substances in general and PFOA related substances more specifically.

From Company 2 the study team has received the following information “Company 2 has had a policy only to sell APFO to fluoropolymer manufacturers. It is Company 2's intention not to export from the US into Europe any APFO other than for its own uses until phase-out, which will be completed no later than 2015. Therefore our import should equal their consumption (20-25 tonnes annually)”.

All stakeholders that have reported to the study team for the period of 2004-2008 the average annual imported quantity of PFOA and related substances is <5 tonnes.

Direct Uses - Fluoropolymer manufacturing

The information below is based on information received primarily from the PlasticsEurope Fluoropolymer Committee, representing 100% of the fluoropolymer manufacturing industries in the EU-27.

The main direct use of PFOA is as a surfactant (mainly as its ammonium salt, APFO) used in very small quantities (<1%) as an essential processing aid to manufacture some but not all fluoropolymers and fluoroelastomers. Fluoropolymers are high-performance plastic materials, fluoroelastomers are high performance synthetic rubber materials. Nearly all fluoroelastomers are not perfluorinated, while most fluoropolymers are.

Fluoropolymers are used in harsh-chemical and high-temperature environments, primarily in performance critical applications in defence-related industries and in chemical manufacturing, automotives, aerospace, electronics and telecommunications. Typical applications would be wire insulation for computer networks, semiconductor manufacturing equipment, corrosion prevention in environmentally sensitive chemical plant and automotive fuel hoses. About 95 percent of fluoropolymers are used in these types of industrial applications. The other 5 percent are used to make consumer products such as non-stick cookware.

Used APFO which stems from off gas is converted during the production process to the PFOA potassium salt (KPFO) and sent for recycling. Other sources of PFOA in the fluoropolymer production process are captured from process water and recycled, respectively sent for incineration in controlled condition, as much as possible. However PFOA may be present at residual levels in the fluoropolymer products that are placed on the market as resins or as dispersions.

Direct Uses – Photographic and imaging industry

The information below is based on information received from the European Photographic & Imaging Association, (EPIA). EPIA represents 20 photo and imaging companies. Member companies include the major manufacturers of photographic products. All of them were invited to submit data to the notary if they use a substance mentioned in the questionnaire. Four companies replied to use at least one of the substances mentioned in the questionnaire. One of these four companies could only contribute figures for the year 2008.

The photographic industry does not use PFOS or PFOA as such, but PFOS- or PFOA-related substances and APFO play an essential role in manufacturing and performance of certain imaging products because these chemicals provide critical antistatic, surfactant, friction control, and dirt repellent qualities. It is important to note that these substances also provide important safety features by controlling the build-up and discharge of static electricity and preventing employee injury, operating equipment and product damage, and fire and explosion hazards.

PFOA and APFO are used in photographic industry in a total average annual volume of 2.6 tonnes per year. Between the years 2004-2008 the trend has markedly decreased for both PFOA and related substances and for PFOS for the exempted uses in photographic industry. This is a continuation of the decreasing trend that has started globally as from the year 2000 on a voluntary basis.

This can be seen when the 2004 volume being slightly above 3 tonnes is compared with the 2008 volume being slightly below 2 tonnes per year. A more steep decrease is shown when the average use of PFOA and related substances per company is taken into account. Based on these average uses per company the use of PFOA and related substances decreases with more than 50% from 1 tonne per annum per company in 2004 to less than 0.5 tonne per annum per company in 2008.

A similar trend can be seen in the reduction of PFOS for the derogated uses. This average use per company decreased from 147 kg PFOS and related substances per year per company to 28 kg per year per company.

As mentioned, the industry has reduced its total worldwide usage of PFOS- and PFOA-related substances since 2000 through voluntary replacement initiatives. The decreasing use of PFOA/APFO and related substances as well as for PFOS-related substances for the derogated uses is a trend that will most probably continue in the following years. However if restrictions are to be recommended for PFOA/APFO and related substances, it is the position of the photographic industry that comparable derogations as are now in place for PFOS and related substances for certain critical uses are necessary as well because for these critical uses no alternatives exist at this point in time.

Direct Uses - Semiconductor industry

The semiconductor industry is a very minor user of PFOA and related substances estimated at less than 50 kg/year across the entire European industry. PFOA related substances would typically appear as a constituent material of a process chemical formulation, which the industry uses in very specialized sensitive technical manufacturing application steps in very low quantities. Where the industry uses these materials as part of a process formulation, such as in photolithographic applications, these are critical applications of PFOA (i.e. where no alternatives exist, or where PFOA might in some cases be a substitute for some individual previous applications of PFOS). The industry and its supply chain are aware of the concerns regarding these chemicals, and efforts are underway to reduce, and where technically feasible, eliminate the current uses of the relatively minor nature of such uses.

Non-critical applications (i.e. where non-PFOA based alternatives exist, or may become available) include:

- the uses as a surfactant. Like PFOS, PFOA may be used as a wetting agent to enhance adhesion properties in various chemistries across different industry sectors. The trend in the semiconductor industry is to phase out PFOA for non critical uses as happened with the phase out on non critical uses of PFOS over the past decade. It is important to consider that the semiconductor industry has taken proactive steps to move away from PFOS usage where possible in the non critical applications in the past decade. This does not refer to the necessary continued use which the semiconductor industry exemptions/derogation of PFOS for critical photolithography uses in photoresist and antireflective coatings (these are in derogation to EC Marketing and use directive (2006/122/EC) and also exempted in the recent Stockhol Convention POP amendment).

- Uses outside of semiconductor production chemicals. There may be trace amounts of PFOA in materials such as glues, foils, tapes, where PFOA could be a very minor below ppm constituent.

With respect to the unique and specific application, the semiconductor component is only a small part of the final electronic product. The trace amounts of PFOA-related substance used in a unique and specific product line are fully enclosed in the semiconductor component and there is no potential for release or exposure to the work place employee or the end user of the final electronic product.

Other direct uses of PFOA

The study team received no information that PFOA related substances were used directly in household or industrial cleaning products, with water, oil, grease and dirt resistance/protection and/or anti-static properties, formulations and received information that PFOA and related substances were not used directly in paints.

Further, there is no direct consumer use of PFOA related substances reported from consumer goods authorities. In general, most national consumer goods authorities in the EU-27 member states have only little funding available for making a proper study and analysis in consumer goods for substances that are not (yet) included in EU legal framework.

Conclusions direct sources and uses of PFOA

From the above information it can be concluded that the total direct source of APFO/PFOA in the EU-27 will be 50-100 tonnes per annum (including the upgraded APFO). This direct use is industrial only.

Indirect sources of PFOA

Residual levels of PFOA in fluoropolymer products

PFOA might be present at residual levels in the fluoropolymer products that are placed on the market as resins or as dispersions. If such fluoropolymer products are imported from outside the EU it is possible that PFOA is imported as a by product. As mentioned before it was not possible to extract specific fluorochemical imports from the EUROSTAT statistical information.

As can be seen from the US EPA PFOA Stewardship Programme 2008 progress reports (January 2007-December 2007) residual values of PFOA and related substances in fluoropolymer resin products are ranging between 0-150 mg/kg and 5-3000 mg/kg in the fluoropolymer dispersion products of the non-US based (EU & Japan combined) production locations. Reductions of PFOA, PFOA salts and higher homologues and precursors of PFOA in fluoropolymer dispersion products are reported between 54% and 100% in the EPA's summary tables for 2009 company progress reports (See Annex III EPA summary report of 2009 Company Progress Report).

Fluorotelomer products manufactured in the EU-27

PFOA is not used to make a different family of compounds, called fluorotelomers. However, it is found at very low trace levels in some fluorotelomer products as an unintended by-product of their synthesis.

Fluorotelomer based products are used widely in a range of commercial products, including some that are directly released into the environment, such as fire fighting foams, as well as soil, stain, and grease resistant coatings on carpets, textiles, paper, and leather.

The extent to which these fluorotelomer-containing products might degrade to release PFOA is unknown. Preliminary data suggest that only higher perfluorinated homologues (chemicals with carbon chain lengths of eight and higher) would be converted into PFOA via normal environmental pathways.

The total amount of PFOA as unintended by-product in fluorotelomer products from non-US based production locations (EU and Japan combined) is <50 kg and if the precursors and higher homologues of PFOA are taken into account an annual value of 1 tonne might be reached.

The EPA's summary tables for 2009 company progress reports gives reductions of PFOA, PFOA salts and higher homologues and precursors of PFOA in fluorotelomer based products (See Annex III EPA summary report of 2009 Company Progress Report).

Fluorotelomer products used in Aqueous Fire Fighting Foams (AFFF) in the EU-27

PFOA was used in AFFF until around 1975. Further PFOA is an unintended by-product of manufacture of POSF-based products (based on Electrochemical Fluorination—ECF) and may therefore have been found in PFOS-based AFFF up to levels of 0.16%. As these PFOS based AFFF products are to be banned in the European Union a replacement of PFOS based surfactants is now ongoing. The major alternative product used is a telomersulphonate where 6 of the total of 8 carbon atoms are perfluorinated (generally referred to as a 6:2 fluorotelomer sulphonate) and therefore the residual levels of PFOA will already be taken into account with the US EPA PFOA Stewardship data as mentioned above.

Imported fluorotelomer based products from outside the EU-27 Member States

Information from the Scandinavian Product Registers (SPIN³ of Denmark (Danish EPA, 2006 and 2008), Sweden (Swedish Chemicals Agency, 2006) and Norway (Norwegian Pollution Control Authority, 2007)) only refers to products and preparations that are used in these Scandinavian countries. This does also not reveal the possible content of PFOA in products and preparations imported from outside the EU-27 as there is no distinguish made between imported from EU-27 into Denmark, Sweden and Norway or from outside EU-27. PFOA may be present at residual level in imported finished fluoropolymer products.

The main indirect use is via the use of fluorotelomer substances in consumer products. These fluorotelomer based products may contain PFOA as an unintended by-product.

In Norway the total annual emission of PFOA from a range of consumer products in Norway is estimated at 15 kg (Norwegian Pollution Control Authority, 2007). The long range annual transport estimate from this survey of PFOA into Norway from direct and indirect sources mainly from oceans and airborne particles is estimated at 130 to 380 kg. These emissions are considered to be an indirect source of PFOA in the EU-27.

In Sweden, PFOA and PFOA related substances only accounted for 25 kg (Swedish Chemicals Agency, 2006). In total 22 tons of fluorotelomers were reported as well as 2 tons of fluorophosphonates but it was not made clear what quantity of (residual) PFOA might be present in these fluorotelomer and – phosphonates.

In two Danish surveys a maximum amount of 35 kg APFO is reported as used annually in Denmark and a maximum amount of fluorinated substances in consumer products of 38 tonnes is estimated but again no reference is made to any quantity of (residual) PFOA might be present in these fluorinated substances (Danish EPA, 2006 and 2008).

³ Substances in Preparations in Nordic Countries - www.spin2000.net.

It was mentioned that approximately half of the registered fluorinated substances has a carbon chain length of 8 or higher and it was also mentioned that a typical PFOA content of fluorinated products would be 0.1-1.0%.

Table 4 *When using this numbers as a measure for the total EU-27 the following can be estimated:*

Country	Number of inhabitants	Used fluorinated substances (tpa)	Total indirect PFOA from imported consumer products (kg/y)
Norway (Norwegian Pollution Control Authority, 2007)	4.8 million	Not reported	15
Denmark (Danish EPA, 2006 and 2008)	5.5 million	38	155
Sweden (Swedish Chemicals Agency, 2006)	9.3 million	24	215
EU-27 estimate	500 million	--	Approximately 10 tpa

In conclusion when the total amounts of the three mentioned Nordic countries is taken as a worst case assumption of indirect import of PFOA from outside EU-27 this will lead to an additional 10 tonnes of PFOA that enters the EU-27 every year.

However, these figures should be used with much caution because 1) it is not clear how the registered fluorinated products were grouped (e.g. uncertainties on the perfluorinated carbon chain lengths); 2) if these figures from the Nordic countries related to perfluorinated substances or per- and polyfluorinated substances; 3) the uncertainty in possible PFOA content in a range of various fluorinated products; 4) the Scandinavian countries aim to reduce PFOA discharges, and claim PFOA problem since years..

In conclusion, the Key Outputs of this task are shown in the table 5.

Table 5 *Key Outputs of task 1*

Key outputs Task 1	Direct source (tonne per annum)	Indirect source (tonne per annum)
Tonnage of PFOA and APFO currently produced in the EU	50-100	< 1
Tonnage of imports of PFOA and APFO from outside the Member States	< 5	< 10
Tonnage of PFOA and APFO currently used in the EU	50-100	< 1

5. GENERAL ASSESSMENT AND ANALYSIS – HAZARD ASSESSMENT (TASK 2)

5.1 Introduction

The 2006 SIDS report was used as a starting point for the hazard assessment for this study. The objective of the hazard assessment is to identify Predicted No Effect Concentration (PNEC) for the environment and Derived No Effect Level (DNEL), No Observed Adverse Effect Level (NOAEL) or Acceptable Daily Intake (ADI) for humans, or to determine values with other appropriate methodologies in the case of non-threshold effects, for use in the risk characterisation.

In addition to the SIDS report also results from more recently conducted research (either via publicly available scientific peer reviewed literature, via industry contribution or via any other international sources and bodies) regarding new or refined findings on human health and/or environmental hazards and/or exposure are included in this report.

For this the focus has been on data gathering from literature and from stakeholders, including international bodies (e.g. IARC, US EPA, FDA and OSHA) in order to prepare a detailed overview of the existing hazard and exposure information.

Furthermore, the information from the Chemical Safety Report on PFOA as conducted in collaboration between the German Authorities and industry (and delivered to the Commission in April) contains information which is taken into account in this study. However, other EU Member States were not involved in this process and therefore the information from this Chemical Safety Report should only serve as a basis for further risk assessment.

5.2 Update Hazard assessment human health

Many studies have been performed and published after the publication of the OECD SIDS report. In this chapter summaries of several publications are given.

In conclusion from these publications it is clear that PFOA can induce liver effects and tumors in liver, pancreas and testis in rats exposed to PFOA (Anderson, 2008). In utero exposure to PFOA in mice alters mammary gland development (White et al., 2007) and has effects at low dose on body weight and serum parameters such as circulating levels of insulin and leptin when measured in animals during mid-life (Hines et al., 2009).

PFOA is also considered immunotoxicant in wild-type mice as well as in PPAR α -null mice treated with PFOA (DeWitt et al., 2009). Moreover, PFOA cause deficits in neonatal growth and viability in both rats and mice (Lau et al., 2007). However, the relevancy of those effects in humans needs to be further evaluated as most of the effects are not found in cohort studies of workers or general public. More epidemiological studies to explore potential human health effects are ongoing (Fletcher et al. 2007).

The most sensitive endpoint from animal studies is related to the developmental effects of PFOA on the PPAR-system in the liver. This system does not seem to be too relevant for the human situation.

Further, only limited epidemiological data is available at this point in time. The outcomes of the first part of the US C8 study are expected before the end of this year.

More work is needed to further understand the modes of action related to other toxicities observed in laboratory animals and to establish relative human risk. These studies should contain the following points:

- Understanding the biological processes that are time and dose dependent, and in accounting for any interaction in kinetics between PFOA and endogenous fatty acids that may compete for binding proteins or transporters;
- In differences in pharmacokinetics between species and genders, this may account for differences in pharmacodynamic responses to PFOA especially the large species differences in half-lives. Therefore, the effective doses that cause specific responses across gender and species should be compared on basis of achieved concentration in target tissues.
- Rats, dogs and monkeys excrete PFOA within few days. In humans few years. It can therefore presently be assumed that the human body is exposed to these substances for a considerable longer period. Some evidence suggests that its persistence in humans is likely to be the result of a highly efficient reabsorption of PFOA by the kidneys compared with less efficient processes in other species.
- Determine if peripubertal PFOA exposure increases or decreases susceptibility to mammary gland cancer in experimental animals, this may have implications about breast cancer risk in PFOA-exposed girls (Yang et al., 2009).

Animal studies

Carcinogenicity

In sub-acute and chronic studies, PFOA affected primarily the liver. The characteristics liver effects seem to be shared by most PFAAs are (Andersen et al. 2008):

- 1) lack of direct genotoxicity;
- 2) an ability to cause hepatomegaly and, in some cases, hepatotoxicity, in rodents and primates, including an increased incidence of hepatocellular adenoma in rats.

Rats fed dietary levels of PFOA showed decreased levels of serum cholesterol and triacylglycerol (Andersen et al. 2008). Such changes in serum cholesterol and triglycerides are consistent with the effects seen with hypolipemic drugs that are also PPAR α agonist.

The PPARs consists of a group of three isotypes called PPAR α , PPAR β and PPAR γ . The PPARs are nuclear receptors that control many cellular and metabolic processes. Endogenous fatty acids are natural ligands of PPAR α . PFOA is a PPAR α agonist. Continued studies of PFAAs specificity in inhibiting transporter-mediated uptake, and specificity in interacting with fatty acid binding proteins and with PPAR proteins.

PFOA induce liver, pancreas (both at same doses) and testicular tumors (lower dose) in rats. Based on the weight of evidence at present, the carcinogenic effects in rats appear to be due to indirect/non-genotoxic modes of action, but by PPAR α . Even though PPAR α is activated in human liver, there is no evidence that this activation leads to anything but the therapeutic hypolipidemic effects of PPC exposure (Ren et al. 2009). Liver tumor induced by PPAR α is unlikely to occur in humans. This is point of view that the rodent PPAR α mode of action associated with tumor induction is not operational in human hepatocytes is supported from studies with humanized and nullizygous mouse, as well as studies in human primary hepatocytes (Rosen et al, 2009). However, PPAR α -independent pathways alter by PFOA could contribute to liver effects and liver tumors observed in PPAR α -null mice.

Other modes of actions are for example activation of the constitutive androstane receptor (CAR) and pregnenolone X receptor (PXR). There is very little evidence that CAR/PXR-like responses are induced in human tissues by PFAA. Ren et al (2009) concluded:

1. PFAAs, including PFOA, vary in their ability to activate PPAR α in vivo based on microarray analysis and convectional RT-PCR data in rats and mice.
2. There is some evidence that CAR and PXR are activated after PFAA, including PFOA, exposure in rodent liver.
3. Although there is some evidence that PFAA exposure leads to XME changes in the livers of chickens and fish exposed to PFAAs, including PFOA, further work is needed to determine whether xenobiotic-sensing nuclear receptors are involved.
4. There is an inverse correlation between the mRNA expression levels of CAR and regulated genes and levels of PFAAs in the blood of human populations indicating partial dependence of PFAA levels on the expression of CAR-regulated genes may be involved in transport PFAAs.
5. Results suggest that PFFAs could potentially act as hepatocarcinogens at the level of gap junctions in addition to or instead of through peroxisome proliferation. (Upham BL et al, 1998)

Further within this study Ren et al (2009) found that CAR- and possibly PXR-dependent transport genes expressed in the liver and possibly the intestine may be playing a role in eliminating PFAAs (Ren et al, 2009).

Development of pancreatic acinar-cell hypertrophy, hyperplasia, and adenomas in the rat by PFOA have been suggested to be related to modification of steroid hormones, growth factors such as cholecystokinin (CCK) and expression of these factors, and to diet, particular fat intake (Anderson et al., 2008). The mechanism of action is poorly understood. There is evidence that the mode of action involves stimulation of PPAR α leading to bile stasis and/or bile acid compositional changes, ultimately resulting in an increased CCK, which stimulates pancreatic acinar cell proliferation and eventual production of tumors.

It is premature to conclude that the mode of action for pancreatic acinar cell tumor is understood well enough to extrapolate the rat findings directly to humans.

The existing data demonstrate that the induction of Leydig cell tumors in rats by PFOA may be attributed to some extent to a hormonal mechanism whereby PFOA either inhibits testosterone biosynthesis and/or increases serum estradiol levels via induction of hepatic aromatase activity. Both mechanisms appear to be mediated by PPAR α . Again, the hormonal effects on rat Leydig cells appear to be species specific.

For all 3 tumor types it is unlikely to be relevant for humans (Anderson et al, 2008). However, more details are needed for the modes of actions to be certain. Epidemiological studies indicate a lack of carcinogenic activity by PFOA, PFOS, or other PPAR α agonists in humans.

Reprotoxic and developmental effects

PFOA affected primarily the liver and can cause developmental and reproductive toxic effects at relatively low dose levels in experimental animals. In rats a variety of developmental endpoints were evaluated throughout different life stages in a two-generation reproductive toxicity study (Butenhoff et al., 2004). Butenhoff et al. (2004) found a reduction in weight gain of the F1 pups during lactation and an increase in mortality during the first week following weaning 30 mg/kg/day. There was a significant delay in the timing of sexual maturation for F1 male and female pup in the high-dose group. However, when these developmental delays were co-varied with body weight at weaning, no significant differences were found. This outcome is consistent with the observation that decreased body weights can result in non-specific delays in puberty (Stoker et al., 2000a,b). Adult systemic toxicity considered of reductions in body weight in both the F0 and F1 animals. Other studies in rats and rabbits showed that maternal exposure to PFOA (0-

150 mg/kg) during organogenesis (gestation day 6-17) does not result in embryo-fetal toxicity or developmental abnormalities in the off-spring (Kennedy Jr et al 2004).

Further, PFOA had no effect on fertility at 30 mg/kg by rats (Butenhoff, 2004b). However, taking in consideration the pharmacokinetics in which the female rat clears PFOA quickly, some uncertainties on the possible impact on female fertility still remains, because studies using other species which shows a more protected elimination are not available.

As rats pronounce a gender difference in elimination of PFOA, tests were extended to mice, which do not exhibit the gender difference in elimination (Lau et al., 2004). When pregnant mice were exposed to PFOA throughout pregnancy and allowed to give birth, there was neonatal mortality (time and dose dependent). More recently Lau et al. (2006) reported on the maternal and developmental toxicity of PFOA in CD-1 mice. They found dose-dependent full-litter resorption and decreased weight gain in dams that carried pregnancy to term. Increased mortality and growth deficits were observed in PFO-treated litters. In addition, significant delay in eye opening was noted at 5 mg/kg and higher dosages, and accelerated sexual maturation was observed in male off-spring.

Since PFOA exposure causes decreased neonatal body weights and survival, its effects on maternal lactation was studied by White et al. (2007). They looked at the impact of prenatal PFOA exposure on mammary gland development in the nursing mouse dams and in the female mouse pups. They found that gestational exposure of the mouse to PFOA clearly alters normal differentiation of the lactating gland in the dam, and the early branching and migration in the female offspring. As PPAR is not a critical element of mammary gland development in the neonate, the effects of gestational PFOA exposure on neonatal mammary tissue are not thought to be mediated through this pathway.

To corroborate the mammary gland differentiation data, White et al. (2009) performed three concurrent experiments: late-life cross-fostering study, early-life cross-fostering, and a restricted exposure study. These studies confirm a window of mammary gland sensitivity in late fetal and early neonatal life, and demonstrate developmental PFOA exposure results in early and persistent mammary gland effects, suggesting permanent consequences. Further, the results suggest that the threshold for effect may be lower for mammary gland development delays as compared to that for body growth defects, and that mechanisms responsible for these effects may differ.

Furthermore, this is the first work to the knowledge of White et al. (2009) that reports effects of developmental PFOA exposure occurring as late as the postnatal period – via the presumed lower transmission route of nursing – that persist into adulthood and late-life. An important finding was also illuminated in the dosimetry data, specifically that offspring with intrauterine PFOA exposure exhibited higher serum concentrations on postnatal day 1 than did the treated dams they nursed on. They observed that lactation-only exposure in CD-1 mice also delays mammary gland development.

White et al (2009) found that early prenatal loss in CD-1 mice did not appear to be requiring PPAR α expression. Other effects including impaired postnatal body weight gain, delayed eye opening among pups, and postnatal mortality – were found to be dependent upon PPAR α expression. However, mammary gland development is not considered in this study (results are underway). It is noteworthy that mammary gland effects have been observed to occur in the absence of growth defects, which have been identified as PPAR α -dependent effects. Furthermore, because these delays in body weight gain and developmental indices were shown not to result from lactational exposure only, while mammary gland effects were, there

is evidence that mammary gland developmental effects may not be mediated by a similar mechanism and may represent a more sensitive endpoint. They suggested in previous paper (White et al., 2006) that delayed development of these glands could be attributed to poor suckling behaviours of PFO-exposed pups.

However, caution should be taken when drawing conclusions about the effects of PFOA based on one single mouse strain (Yang et al., 2009). They found the peripubertal period (21 through 50 days of age) as an important window of mammary gland susceptibility to environmental exposures that may affect breast cancer risk later in life. They reported significant effects on mammary gland development. Importantly, the effects differ significantly between the C57Bl/6 and Balb/c mouse strains.

Further, peripubertal PFOA treatment caused similar hepatocellular hypertrophy and delayed vaginal opening in both mouse strains. For these effects there were no differences between the two mouse strains.

Wolf et al (2007) found that CD-1 mouse exposed to 5 mg/kg-day PFOA in utero was sufficient to produce the postnatal effects on liver weights, survival, eye opening, and defects in weight gain and that lactational exposure was not a major contributor to these effects. Indeed exposure earlier in gestation generates stronger effects. However, in utero exposure alone appeared not to be sufficient for neonatal lethality.

Some of polyfluorinated chemicals, like PFOA, are potential developmental toxicants and are suspected endocrine disruptors with effects on sex hormone levels resulting in lower testosterone levels and higher oestradiol level (Jensen et al, 2008). However, Yang et al. (2009) suggest that PFOA may not possess direct estrogenic activity as PFOA does not possess estrogen-dependent proliferation capacity in human breast cancer cell line (MCF-7) and in yeast two-hybrid assay that employs the interaction between the human ER α or ER β ligand binding domain and coactivator TIF2 (transcription intermediary factor 2). However, a recent study performed in rare minnows (*Gobiocypris rarus*) revealed estrogen-like properties of PFOA. It was found that PFOA can disturb the activity of estrogen in mature male rare minnows by inducing the expression of the hepatic estrogen-responsive genes, vitellogenin and ER β , and inhibiting female reproduction. It is not clear if these findings are due to a direct or indirect effect of PFOA, or are relevant to the effects of PFOA in mammals.

PFAA, including PFOA, do indeed have direct, developmental neurotoxicant actions and they target specific events in neural cell differentiation. All perfluorinated chemicals are not the same in their impact on neurodevelopment and it is unlikely that there is one simple, shared mechanism by which they all produce their effects (Slotkin et al., 2008).

In utero exposure to PFOA in mice has effects at low dose on body weight and serum parameters such as circulating levels of insulin and leptin when measured in animals during mid-life (Hines et al, 2009). This study demonstrates an important window of exposure for low-dose effects of PFOA on body weight gain, as well as leptin and insulin concentrations in mid-life, at a lowest observed effect level of 0.01 mg PFO/kg BW. The mode of action of these effects and its relevance to human health remain to be explored.

For PFOA and possibly for other PFAAs, PPAR α activation plays a seminal role in the developmental effects or the fetal effects occur at doses, which are toxic to maternal animal. (The developmental toxicity of PFOA is reviewed by Lau et al. (2004)).

Microarray expression analysis of fetal lung and liver from litters of PFO-treated mice suggested that genes related to fatty acid catabolism were altered in their expression (Rosen et al., 2007). Implicating PPAR α signalling as a potential mode of action.

A review by Abbott et al. (2009a) shows that PPAR α , β , and γ are expressed in the rodent and human embryo at early stages. The patterns of expression differ with developmental stage and tissue. In many organs, PPAR α , β , and γ have overlapping patterns of expression. Information on the expression of PPARs during human development was only available for the GI tract, and all three isoforms were detected as early as 7 weeks of gestation. With the exception of the disruptions in development that were discovered using genetically altered mice, little is known about the roles of the PPARs during development, however the expression patterns of PPARs during development suggest that PPAR α , β , and γ have important functions throughout development in many cell types and organs.

The mode of action responsible for the general growth defects and neonatal death resulting from gestational/prenatal exposure of PFOA in CD-1 mice depends on the expression of PPAR α (Abbott et al., 2007). Interestingly, early prenatal loss did not appear to require PPAR α expression.

Two studies found that neonatal mortality observed for PFOS may reflect functional defects related to the physical properties of the chemical rather than to transcript alterations (Rosen et al., 2009; Abbott et al., 2009b). Also PFOA was shown to interact with the main components of lung surfactant.

Immunotoxicity

In the SIAR it is stated that PFOA is not immunotoxic in rats. PFOA appears to be immunotoxic, at least in mice – dietary exposure of PFOA resulting in adverse effects on the thymus and spleen and suppressed immune responses (US EPA, 2005). Therefore the US EPA identified immunosuppression as an end point of concern.

In recent study PFOA is considered immunotoxicant in wild-type mice as well as in PPAR α -null mice treated with PFOA by DeWitt et al. (2009). However, these data suggest that adaptive immune functions may be sensitive to PFOA at concentrations which are approximately 50- to 100-fold greater than the concentration of PFOA reported in sera of humans living near a PFOA production plant. It should also be noted that some indication ought to be provided regarding the relationship between immunotoxic effects in mice and other produced marked systemic toxic effects.

However, these data and the data reported by Yang et al. (2000, 2002) suggest that the immune system is a target of PFOA. Also the variety of effects and mechanisms investigated in the posters presented at the Society of Toxicology Contemporary Concepts in Toxicology Symposium underscored the interest that has been generated in the potential immunological effects of PFFAs (Anderson et al., 2008).

Human health - epidemiological data

In the OECD SIDS report it is stated that the PFOA possess properties indicating a hazard for human health (eye irritation; sub-chronic toxicity; potential carcinogenicity; developmental toxicity). Epidemiological studies have not shown a conclusive association of PFOA exposure and adverse health outcomes. Mainly male workers were included in these studies.

Recent epidemiological data suggest a negative association between estimates of maternal exposure to PFAAs and fetal growth or fertility in humans. However, a number of concerns have been raised about

these data including the possibility that they may not be the result of a true causal relationship. An epidemiological study carried out in a non-occupational population in 2005-2006 in the Mid-Ohio Valley, Savitz et al (2009) found little support for PFOA being related to pregnancy outcome (miscarraging, low birth weight, preterm birth, with some uncertainty regarding preeclampsia and aggregated birth defects. However, the relative risks were only modestly elevated and none showed clear increasing risk with higher exposure.

In Baltimore, Maryland, Apelberg et al (2007) examined the relationship between concentrations of PFOA in cord serum (surrogates for *in utero* exposures) and gestational age, birth weight, and birth size among offspring of humans. They reported small negative associations between relatively low cord serum concentration of PFOA and birth weight (after adjusting for gestational age), ponderal index, and head circumference. However, Apelberg et al. only found a statistically significant decrease in head circumference among vaginal deliveries (not C-sections). Whereas Fei et al. (2008a) reported no statistically significant associations except for those associated with nulliparous births or obesity in the mother (BMI ≥ 30). In both instances, ponderal index was positively, not negatively associated with PFOA concentrations.

Fei et al (2008a) found that maternal blood PFOA levels in early pregnancy were associated with small decreases in birth length and abdominal circumference. In further examination of the Denmark cohort, Fei et al. (2007) found statistically significant negative association with birth weight and PFOA. However, no association was found with other fetal growth indicators. Fei et al. (2008b) found no convincing association between developmental milestones in early childhood and levels of PFOA as measured in maternal plasma early in pregnancy. Fei et al. (2009) asked women from the cohort how many months it took to get pregnant before they succeeded (time-to-pregnancy) and concluded that their data suggested exposure to PFOA at concentrations found in the general population may reduce fecundity. However, in the review of Olsen et al. (2009) limitation in the epidemiological causal model are discussed which may lead to a more ambiguous interpretation of their findings.

In an additional Danish cohort, semen quality was assessed in men from the general population, and while statistically significant effect was reported with reduced numbers of normal spermatozoa when data from PFOA and other perfluoroalkyls were combined, no significant association was found when PFOA was analysed separately (Joensen et al., 2009). In addition no significant association was found between the combined perfluoroalkylic acids (PFAA) levels and sperm concentration, total sperm count and sperm motility. Jensen et al. (2009) speculated that men and women living together may have similar exposure to PFAAs and that decreased semen quality caused by high PFAA levels may contribute to the longer waiting time to pregnancy found by Fei et al. (2009).

But no peer-reviewed scientific evidence that may confirm these speculations has been published so far.

In a cross-sectional drinking water study in Washington County, Ohio, (Nolan et al., 2009) and a nested analysis in Canada (Monroy et al., 2008), no associations were found between maternal exposure to PFOA and birth weight or gestational age.

In Sapporo, Japan, Washino et al. (2009) conducted a hospital-based prospective cohort study between July 2002 and October 2005. They found a negative trend between birth weight and PFOA (Washino et al, 2009).

Many of these developmental studies are discussed in more detail in the review article by Olsen et al. (2009), which includes an examination of the methodological strengths and weaknesses, coherence with toxicological results, consistency, and biological plausibility for each study. The conclusions are that caution is needed in interpreting the results of these studies and that more attention should be given to the alternative explanation for developmental findings, including maternal plasma volume expansion and physiology of the pregnancy. Also, interindividual metabolic differences may be related to exposure as well as to developmental events such as the weight or ponderal index of a newborn.

Under the C8 Science Panel Studies few are completed but not all are published yet. Briefly, higher PFOA was linked to higher cholesterol and to less dramatically to high uric acid (Steenland et al., 2009). However, these reports do not provide conclusive evidence regarding whether there is a probable link between PFOA and disease because 1) one cannot determine whether PFOA exposure preceded or followed the outcome of interest, and 2) in many cases the outcome is a biomarker and not a disease itself. Nonetheless they provide useful evidence that adds to the overall picture (Steenland et al. 2009).

Either, type II diabetes nor high fasting glucose level did not seem to be related to higher PFOA concentrations (Steenland et al, 2008). However, these data are limited by their cross-sectional nature, because we cannot be sure the serum level of PFOA in 2005-2006 correctly reflects the exposure level preceding the onset of diabetes. Therefore they concluded that based on these data the possibility of a true relationship between PFOA and the occurrence of diabetes can not be excluded.

Results suggested that there may be a relation between immune function and PFOA exposure in exposed persons. However as noted in the report, these results cannot be directly interpreted as indicating an increase in immunological disease risk in this population, but they warrant further investigation which is underway.

5.3 Safe levels of PFOA humans

The objective of the hazard assessment is to identify No Observed Adverse Effect Level (NOAEL) combined with assessment factors to address potential uncertainties to established Derived No Effect Level (DNEL) or Acceptable Daily Intake (ADI) for humans for use in the risk characterisation. There is no evidence to suggest that non-threshold modes of action are operative for any of the effects observed in experimental studies; PPAR α and CAR activation. Therefore a threshold approach is used for PFOA, although PFOA is considered to be an animal carcinogen by US EPA.

The UK government's expert advisory Committee on Toxicology (COT) has agreed to cut its provisional tolerable daily intake (TDI) for exposure to PFOA. The new limit of 1.5 $\mu\text{g/kg bw/day}$ is 50% less than before, aligning the Committee on Toxicology with European Food Safety Authority guidelines (CoT, 2009; EFSA, 2008). This was not due to the toxicological endpoints used to derive the TDI, but in the uncertainty factors applied and their derivation. The toxicological endpoint was based on liver effects in mice and rats. The critical difference between the assessments made by the US EPA, EFSA and COT was the uncertainty factor used for interspecies toxicokinetics, in view of the large difference in half-life and clearance of PFOA between humans and mice.

The lowest NOAEL identified of 0.06 mg/kg bw/day for increased liver weight in subchronic study in male rats was not used by EFSA, as results from long-term studies indicated higher NOAELs for effects on the liver (EFSA, 2008). EFSA noted that the 95% lower confidence limit of the benchmark dose for a 10% increase in effects on the liver (BMDL10) values from a number of studies in mice and male rats were in

the region of 0.3 - 0.7 mg/kg bw per day. Therefore, they concluded that the lowest BMDL10 of 0.3 mg/kg b.w. per day was an appropriate point of departure for deriving a TDI.

However, the US EPA use a BMDL₁₀ of 0.46 mg/kg/day calculated from a developmental study in mice performed by Lau et al. (2006), which lies in the middle of the range as departure for the derivation of Provisional Health Advisory value for PFOA. This BMDL10 was calculated by EFSA on the basis of raw data provided by the principal author Lau (ESFA, 2009).

EFSA (2008), US EPA (2009) and CoT (2009) have a different approach than the industries within the Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009) as the TDI established by EFSA, US EPA and COT is based on external dose and DNEL established in Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009) is based on internal dose. This is done by the German industries because the internal dose seems to be the determinant of response, not the exposure route.

Within the Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009) the biological DNEL based on clinical/epidemiological indications of disease, >0.8 µg PFO/ml serum/plasma, was chosen as the critical biological DNEL because it is based on extensive human-data, which is most relevant for humans. They make a conversion of the biological DNEL to a daily intake rate of 0.08 µg/kg-day.

The New Jersey Department of Environment has developed health-based guidance for PFOA in drinking water of 0.04 µg/L (New Jersey Department of Environmental Protection, 2007). This limit of safe level of exposure to PFOA in tap water is 10 times lower than the provisional health advisory value given by US EPA (US EPA, 2009). Also, here the difference is due to use of external doses of PFOA which result in adverse effects in experimental animals and the blood levels of PFOA associated with these external doses and the use of given human blood levels of PFOA as a result of exposure from environmental media such as water, food, or air. Their reason for the use of blood levels rather than external dose is that the kinetics of PFOA is very different in humans and experimental animals because the half life of PFOA in humans is much longer than in animals.

US EPA (2009) used the following the general equation for the calculation of a Provisional Health Advisory:
(NOAEL or BMDL10) x BW x RSC

UF x Extrapolation Factor x Water intake

Where BW = body weight; RSC = relative source contribution; UF = uncertainty factors.

The following input values were used:

BMDL10 = 0.46 mg/kg/day

BW = 10-kg child, (this population subgroup was used because children, who consume more drinking water on a body weight basis than adults, have a higher exposure on a body weight basis than adults. The selection of children's exposure parameters will help to ensure that the Provisional Health Advisory is protective of sensitive populations potentially exposed.)

RCS = 0.2 (A default RSC of 20% was used to allow for exposure from other sources such as food, dust and soil)

UF = 10x intraspecies

Extrapolation factors = 3 x for toxicodynamics and 81x for toxicokinetic

Water intake = 1 L/day consumed by a 10-kg child

This leads to a provisional health advisory of 0.4 µg/L.

The New Jersey Department of Environment has used the NOAEL for female rats as identified by US EPA (2005), from a chronic (2 year) dietary exposure study (Sibinski, 1987), which was 1.6 mg/kg/day (30 ppm in diet). At 16.1 mg/kg/day, decreased body weight gain and decreased erythrocytes, haemoglobin concentration, and hematocrit occurred.

In the study of Sibinski (1987), blood levels were not measured, and the blood levels and daily area under the curve (AUC) in the female rats receiving 1.6 mg/kg/day are estimated by US EPA (2005) from a pharmacokinetic model. This model is based on pharmacokinetic parameters obtained from two other studies in adult female rats administered a single dose of PFOA. The half-life of PFOA in female rats is very short, measured at approximately 3-16 hours depending on the dose, and in the USEPA pharmacokinetic model, 3.2 hours is used as the half-life (USEPA, 2005). Because of the very short half-life of PFOA in female rats, steady-state is not reached if PFOA is given as a bolus dose, and blood levels will thus fluctuate throughout the day. As stated above, the rats in the Sibinski (1987) study were exposed through the diet, so that exposure was more constant than if dosing was by gavage, although daily fluctuations in blood level almost certainly occurred. The predicted daily AUC for female rats dosed chronically at 1.6 mg/kg/day is 44 ug x hr/ml, which is equivalent to a mean daily blood concentration of about 1800 ppb. Standard uncertainty factors for a NOAEL from a chronic study of 100, including 10 for interspecies extrapolation and 10 for intraspecies extrapolation, were applied to the blood concentration at the NOAEL of 1800 ppb, resulting in a target blood level in humans of 18 ppb.

Using the 100-fold concentration factor between drinking water and blood discussed above, the drinking water concentration estimated to result in an increase in PFOA blood level of 18 ppb (ug/L) is 0.18 ppb, assuming drinking water is the only source of exposure. Application of the Relative Source Contribution factor of 20% discussed above gives a drinking water concentration of 0.04 ppb.

A recent review by ATSDR (2009) on the toxicological profile for perfluoroalkyls is concluded that it is difficult to define points of departure for minimal risk levels derivation with any degree of confidence based on the human data available at this time. Furthermore, there is currently not enough information regarding the pharmacokinetics of PFOA in humans to facilitate estimations of exposure levels resulting in measurable body burdens of perfluoroalkyls.

Table 6 and 7 gives an overview of the safety limits established by authorities of like EFSA (2008), US EPA (2009) and Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009).

Table 6 Standards derived from external doses of PFOA for human health

Human Hazard	NOAEL	AF	ADI	Reference
Systemic toxicology	0.3 mg/kg b.w./day (BMCL ₁₀)	200	1.5 µg/kg bw	EFSA (2008); long-term rats and mice, liver effects
Systemic toxicology	0.3 mg/kg b.w./day (BMCL ₁₀)	200	1.5 µg/kg bw/day	Committee on Toxicology (2009); aligning with EFSA (2009)
Systemic toxicology	0.46 mg/kg/day (BMDL ₁₀)	0.82	0.4 µg/L (provisional health advisory value)	US EPA (2009); mice, maternal liver weight at term
Systemic toxicology	1.6 mg/kg/day resulting in target blood level in humans of 18 µg/L	0.002	0.04 µg/L	New Jersey Department of Environmental Protection, 2007

Table 7 Standards derived from internal doses of PFOA for human health

Human Hazard	Steady state serum concentration	AF	DNEL	Reference
Epidemiologically based health parameters	> 5 µg/ml	6.4	≥0.8 µg PFO/ml serum/plasma	Risk assessment of perflourooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009); Human
Carcinogenicity	125 µg/ml (BMCL ₁₀)	24	5.2 µg PFO/ml serum/plasma	Risk assessment of perflourooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009); Rat 2 years; Leydig cell tumors
Reproductive Toxicology – Fertility Impairment	>39 µg/ml	8	≥4.9 µg PFO/ml serum/plasma	Risk assessment of perflourooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009), Rat
Reproductive toxicology – Developmental	16 µg/ml (BMCL ₅)	8	2.0 µg PFO/ml serum/plasma	Risk assessment of perflourooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009); Mouse pup; decreased postnatal body weight
Repeated dose toxicology	60 µg/ml (BMCL ₁₀)	8	7.5 µg PFO/ml serum/plasma	Risk assessment of perflourooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009); Monkey; 6 months; based on bodyweight change

The safety exposure limit or biological DNEL set for workers are given in table 8. When the biological DNEL based on clinical/epidemiological indications of disease, ≥1.7 µg PFO/ml serum/plasma can be converted into a daily intake rate of 0.2 µg/kg-day.

The OEL of 5 µg/m³ can be converted into a daily intake rate of 0.7 µg/kg-day (assuming 10m³ air inhaled per working day and a person of 75kg).

Table 8 Standards derived from external doses of PFOA for workers

Human Hazard	NOEL	AF	OEL/DNEL	Reference
Systemic toxicology			5 µg/m ³	German MAK
Systemic toxicology			10 µg/m ³	ACGIH (1999)

Table 9 Standards derived from internal doses of PFOA for workers

Epidemiologically based health parameters	> 5 µg/ml	3	≥1.7 µg PFO/ml serum/plasma	Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009); Human
Carcinogenicity	125 µg/ml (BMCL ₁₀)	7.5	≥5.2 µg PFO/ml serum/plasma	Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009); Rat 2 years; Leydig cell tumors
Reproductive Toxicology – Fertility Impairment	>39 µg/ml	7.5	2.1 µg PFO/ml serum/plasma	Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009), Rat
Reproductive toxicology – Developmental	16 µg/ml (BMCL ₅)	7.5	8.0 µg PFO/ml serum/plasma	Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009); Mouse pup; decreased postnatal body weight
Repeated dose toxicology	60 µg/ml (BMCL ₁₀)	22.5	5.6 µg PFO/ml serum/plasma	Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009); Monkey; 6 months; based on bodyweight change

5.4 Update Hazard assessment environment

5.4.1 Environmental Fate Properties

Physico-chemical determinants

Most perfluoroalkyl substances (PFAS) are very stable compounds, which have low vapour pressures, surface energies, and special surface-active properties. There are similarities to persistent organic pollutants (POPs) in being stable and hydrophobic but differ with PFAS having both oleophobic properties in one end of the molecule and sometimes polar/hydrophilic properties in the other functional end, where POPs are lipophilic and nonpolar. Hence, PFAS will not accumulate in fatty tissues and will often occur dissociated as anions and interacts with polar sites in membranes and in sediments. For PFOA a reported octanol-water partition coefficient (Log P_{ow}) is 5 (3M, 2000), but the special solubility profiles of PFOS and PFOA make environmental fate predictions based on octanol-water partition coefficients irrelevant for these chemicals (Danish EPA, 2006).

Fluorinated chemicals can be used to provide water repellency, stain resistance and soil release or repellency properties to a treated surface which is related to the physico-chemical properties of these fluorinated materials. The critical surface tension is the determining physico-chemical parameter why fluorinated chemicals can repel both water and oil substances. There is a relationship of the chain length of the perfluorinated chains that is related to the critical surface energy of the surface (J.F. Colbert et al., 1983; J. M. Corpart et al., 1997).

PFOA forms multiple layers in octanol/water mixtures, making determination of the octanol-water partition coefficient (K_{ow}) extremely difficult (Prevedouros et al., 2006); it is also believed that the K_{ow} in this case does not allow to estimate the environmental partitioning of these compounds (Norwegian Pollution Control Authority, 2008).

To our current state of knowledge there are, at this point in time, no reliable values for the K_{ow} of PFOA mainly because of the high surface activity of PFO(A). The abbreviation PFO(A) is used here because both PFO-anion and PFOA (neutral species) exist in solution causing another complication in deriving K_{ow} .

The neutral (PFOA) and its conjugate base (PFO) have very different physical and chemical properties. It is therefore important to understand the properties of both species in order to predict their activity in natural waters. This speciation (is it the anion (PFO) or the acid (PFOA) in solution or a mixture of both?) plays an important role. The controversy over the pK_a has to be resolved to sort this out.

Further, K_{ow} measurements are very questionable because of surface activity of PFOA and its anion PFO. PFOA tends to accumulate at the interface between octanol and water and sorbs to the glass. Because of measurement problems K_{ow} of each species has to be estimated using various models and estimation methods may be flawed. A method sometimes used is to avoid using K_{ow} and use K_{oc} directly in models

Regarding the pK_a value of PFOA the following has to be mentioned. If the pK_a is 3.5 then a sorption will be more dependent on the neutral species. When pK_a is estimated at 2 or lower it simplifies matters because then it can be assumed that sorption is dominated by the anion and use experimental K_{oc} directly in a model without worrying about the neutral species. However, there is no scientific consensus on this important topic yet and therefore any EUSES results can only be used with some caution.

Other multicompartiment models might be more suitable to estimate the environmental risks of the use of PFOA but these models are only of limited use if there is no scientific consensus on the physical-chemical parameters that will have to be used in these models.

The Henry's law constant cannot be calculated from vapour pressure and solubility because both PFO-anion and PFOA exist in solution. The respective values of the vapour pressure and solubility for PFOA and APFO can be found in the tables 1 (PFOA) and 2 (APFO) on the pages 21 and 22 respectively.

Degradation

Based the OECD SIAR report (rev18032007) and on the studies in the available literature, PFOA is persistent based on test results and expected half-lives of PFOA via biodegradation, hydrolysis, and photolysis under environmentally relevant conditions.

However, there are still uncertainties concerning the potential for biotransformation in soil and sediments under varying environmental conditions and anaerobic sludges.

Environmental distribution

PFOA due to its physico-chemical properties is not a simple chemical to assess with regard to the environmental distribution and behaviour. Different authors used variety of models and their modifications and work to derive relevant partition coefficients. This work is still on-going.

Preferred models in the literature for the general environmental fate and transport are SPARC (Hilal et al 2004) and COSMOtherm (Eckert et al, 2005).

Based on the physico-chemical properties - relatively high water solubility, low vapour pressure and moderate affinity to sediment sorption – predominant compartment for PFOA is water.

Long Range Transport

PFOA has been found widespread in the environment including the Arctic. The different chemical-physical properties of PFOA versus volatile precursors will result in differences in the transport pattern of the two compound groups. Directly emitted PFOA is expected to dissociate in the environment almost entirely to the anionic PFO. With negligible vapour pressure, high water solubility and moderate sorption to solids, accumulation in surface waters and to particulate matter is likely. The predominant compartment for PFOA is water (Mabury, 2004).

Based on transport models, several distribution pathways to the Arctic have been postulated, including those that suggest a role for precursor materials. It is unlikely that there is only one pathway contributing, however, the relative contributions of each of these postulated pathways still remains to be understood and clarified. In a Norwegian report the following processes are mentioned be predominant for the occurrence of PFOA in Norway from distant locations (Norwegian Pollution Control Authority, 2007):

- i) Long range transported dissolved in ocean waters
- ii) Resolving from ocean surface waters (foam etc.)
- iii) Long range transported via air currents adsorbed to particles
- iv) Atmospheric degradation of 8:2 Fluorotelomer alcohols

Water

Among others, it has been suggested that PFOA in the water phase is transported to the Arctic via marine water currents. Yamashita *et al.* (2005) detected PFOA as the major perfluorinated compound in oceanic waters. Wania (2007) and Armitage *et al.* (2006) have confirmed by ocean transport modelling that oceanic currents are a global transport vehicle for PFOA and likely the major pathway for PFOA transport to Arctic waters.

It is anticipated that PFOA will exist predominantly in the water compartment. Partitioning to sludges, soils, and sediments will likely be limited and any PFOA associated with these environmental matrices will likely be found in the water phase of sludges, soils, and sediments. Partitioning to air from water will not occur for dissociated APFO or PFOA, but for the protonated form of PFOA, volatilization may be possible depending on the pH.

Air

PFOA may also be transported in the gaseous phase via air. Also formation of, and PFOA transport via, marine aerosols has been mentioned. Precursors may also contribute to the occurrence of PFOA in the Arctic. For instance, they may be transported to (via air), and then deposited in the Arctic, taken up (as the precursor molecule) by local biota, and subsequently biotransformed into PFOA. Alternatively, these

precursors may be transported via air, degraded to the PFOA in the atmosphere, with subsequent deposition in the Arctic, followed by uptake by biota.

The whole problem of precursors seems to be not satisfactorily understood. The study "PFOA in Norway" (2007) worked with a list of 362 substances that are either PFOA related compounds or compounds that potentially may degrade to PFOA because of their chain length.

The protonated acid has a very high vapour pressure lending it capable of atmospheric transport (Kaiser, 2005). Experiments have shown that PFOA can be measured in the air above an aqueous solution containing PFOA (Norwegian Pollution Control Authority, 2008).

An available study investigating emissions from an industrial facility showed that indeed air transport over long distances of particle-bound PFOA directly emitted from a fluoropolymer manufacturing site is possible (Norwegian Pollution Control Authority, 2008).

Unlike PFOA, volatile and semi volatile precursors, such as the fluorotelomer substance with a perfluorinated 8 carbon chain (more commonly referred to as 8:2 FTOH), will be distributed in the atmosphere available for long-range transport prior to degradation and deposition as the final product PFOA (Young *et al.* 2007). Both photodegradation, radical initiated oxidation as well as biotransformation of suitable precursor compounds can lead to the formation of PFOA far away from the original emission (Norwegian Pollution Control Authority, 2008).

Research to better understand the long-range transport processes is on-going and new data concerning measured concentrations are available for the models development for better prediction of the regional and global processes related to PFOA fate in the environment.

However, like stated in the CSR (Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry 2009), there are still uncertainties concerning the environmental fate of PFOA including:

- 1) sources of PFOA in the environment;
- 2) transport / distribution mechanisms;
- 3) ultimate sinks and
- 4) role of aerosols in transport and distribution of PFOA in the environment.

5.4.2 Bioaccumulation

The OECD SIAR report (rev18032007) provides information on bioaccumulation in the section on bioaccumulation (2.2.6). The Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009) provides further updates from the published literature or company reports.

In tests with the rainbow trout *Oncorhynchus mykiss* a BAF of 0.038 and BCFs for organs of 27 (blood), 8.0 (liver) and 4.0 (carcass) were obtained. The results indicate a low potential for bioaccumulation of PFOA in fish.

The average soil-to-earthworm ratio (BAF) was for PFOA was 1. These data provide support for the lack of bioaccumulation of PFOA by earthworms from soil.

In some marine and Canadian Arctic mammalian food web studies, a potential for biomagnification has been suggested. However, the existing field data provide highly variable evaluations of the extent of bioaccumulation and biomagnification. When whole body concentration data are used for bioaccumulation

and biomagnification calculations, the field results reported in most of the published papers are inconclusive due to differences in temporal and spatial comparability of samples (i.e., samples were not collected at the same times and locations) and uncertainty in actual exposure concentrations. However, data from one source (Houde 2006b) demonstrate sporadic biomagnification for some species in the food chain- although the Trophical Magnification Factor indicates that PFOA does not biomagnify at the top of the trophic chain.

5.4.3 Secondary Poisoning

The OECD SIAR report (rev18032007) provides information on secondary poisoning in the section on bioaccumulation (2.2.6).

There is no information available on the occurrence of secondary poisoning effects.

5.4.4 Toxicity to aquatic organisms

This chapter is using data summarized in the CSR (Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry 2009).

The toxicity of PFOA has been studied in different aquatic organisms (algae, invertebrates and fish). Most of these data are from tests using APFO.

Generally, PFOA is not toxic at the normal environmental concentrations in water. However, effects have been observed for specific cellular functions, such as mechanisms involving the uptake of xenobiotics. Other biological endpoints affected by PFOA are survival, growth, and emergence. Some intermediate degradation products of fluorotelomer acids have been found to be more toxic by a factor 10,000 than their end products (PFCAs) (Danish EPA, 2008).

The available ecotoxicological studies using APFO (OECD SIDS) indicate a low acute toxicity for aquatic organisms. In the short term tests using fish, invertebrates, and algae, effective concentrations were as follows:

<i>Oncorhynchus mykiss</i> LC ₅₀ (96 h)	= 707 mg/l	(nominal)
<i>Daphnia magna</i> EC ₅₀ (48 h)	= 480 mg/l	(measured)
<i>Pseudokirchneriella subcapitata</i> EC ₅₀ growth rate/biomass (72 h)	> 400 mg/l	(nominal)

Effective concentrations in the critical studies of the long term tests (using fish, invertebrates, algae, and midge) were as follows:

<i>Oncorhynchus mykiss</i> , NOEC, 85 d	= 40 mg/l	(measured)
<i>Daphnia magna</i> , NOEC, 21 d	= 20 mg/l	(measured).
<i>Pseudokirchneriella subcapitata</i> , NOEC _{growth rate/biomass} (72 h)	= 12.5 mg/l	(nominal)

In a 10 day study using *Chironomus tentans* no effects were observed up to a nominal concentration of 100 mg/l.

In addition to that, the following information about effects on community level (indoor and outdoor microcosm studies) is available:

Zooplankton community 35 d-LOEC _{species richness}	= 10 mg/l	(nominal)
<i>Myriophyllum spicatum</i> 35 d-EC ₁₀	= 5.7 mg/l	(measured)
<i>Myriophyllum</i> spp. 35 d-NOEC	= 23.9 mg/l	(measured)

In several tests on effects using activated sludge, no inhibition of microbial activity was measured up to a nominal concentration of 1000 mg/l.

PNEC derivation for the aquatic organisms

The predicted no effect concentration (PNEC) is calculated by dividing the relevant toxicity value (L(E)C50 or NOEC) by an appropriate assessment factor.

In this case three trophic levels can be taken into consideration; the chronic NOEC values measured for fish (40 mg/l), invertebrates (20 mg/l) and algae (12.5 mg/l). Applying a standard assessment factor of 10X to the lowest reported chronic endpoint would result in a PNEC value of 1.25 mg/l, as also proposed by Colombo et al (2008).

Further information is available from the community level microcosm studies where an EC10 of 5.7 mg/L is reported for an aquatic macrophyte (*Myriophyllum spicatum*). It can be assumed that the EC10 value corresponds effectively to a NOEC. A reduction of the assessment factor below 10 is not used in this case, since information on the representativeness of the tested microcosm community for the field situation is not available. Hence, application of a standard assessment factor of 10 to this EC10-value would result in a PNEC 0.57 mg/L.

The PNEC_{aquatic} of 0.57 mg/L is therefore considered as a worst case approach.

5.4.5 Toxicity to terrestrial organisms

A chronic toxicity study with reproduction of earthworm in the soil environment performed according to OECD222 is available. The lowest NOEC observed in this study was for juvenile weight with a measured value of 16 mg/kg soil (ww).

A reproduction study in earthworms (*Eisenia fetida*) was performed in agreement with OECD guideline 222 (SFT, 2006). Exposure concentrations were 0, 10, 20, 40, 80, 150, 250 and 500 mg/kg. Some soil chemical analyses were performed for calculations of bioconcentration factor (BCF) at nominal concentrations of 10, 20 and 40 mg/kg ww. Results indicated there was no adult mortality in any of the concentrations tested, and that PFOA was harmful to earthworm reproduction when the soil concentration levels exceeded 16 mg/kg (e.g. NOEC based on measured value = 16 mg/kg ww). Effects observed were a reduced number of cocoons, reduced hatchability, and reduced number and weight of juveniles with a nominal NOEC of 150, 80, 10 and 10 mg/kg, respectively. The lowest nominal EC50 (with 95% confidence interval) was for weight of juveniles with a value of 50 (40-61) mg/kg soil.

In the Norwegian Pollution Control Authority Study focused on evaluation of risks to soil and soil living organisms on four fire fighting training sites in Norway posed by PFCs, PFOA was evaluated taking into account measured levels in soil, water streams and earthworms (Norwegian Pollution Control Authority, 2008).

PNEC derivation for the terrestrial organisms

The predicted no effect concentration (PNEC) is proposed in the CSR (Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry 2009) to be derived from the available study PNEC_{soil} = 0.16 mg/kg ww. The same value is used by the Norwegian study (Norwegian Pollution Control Authority, 2008).

5.4.6 Atmospheric Compartment

The OECD SIAR report (rev18032007) provides the available information on toxicity in the atmospheric compartment in the section on other environmental effects (4.3). There is currently no information reported, nor are there updates in the published literature or company reports.

5.4.7 Microbiological Activity in Sewage Treatment Systems

The OECD SIAR report (rev18032007) provides information on microbiological activity in sewage treatment systems in the section on other environmental effects (4.3). There are currently no updates in the published literature or company reports.

In several tests on effects using activated sludge, no inhibition of microbial activity was measured up to a nominal concentration of 1000 mg/l, thus NOEC > 1000 mg/L

PNEC derivation

As stated in the Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009) report, the predicted no effect concentration (PNEC) is calculated by dividing the relevant toxicity value (EC50 or NOEC) by an appropriate assessment factor. The largest standard assessment factors that are applied to the test results from systems measuring the effect of chemicals on microbial activity are 10 and 100 for NOEC and EC50 values, respectively. (See Table 17, Part 2 of the EU Technical Guidance Document, 2003)

In order to derive a PNEC the absence of inhibition of microbial activity at the limit concentration of 1000 mg/L (NOEC > 1000 mg/L) was taken into consideration. A standard assessment factor of 10X is applied to this endpoint.

The $PNEC_{\text{microorganisms}} > 100 \text{ mg/l}$.

5.5 PBT AND vPvB ASSESSMENT

Persistence

Based on studies in the available literature, PFOA meets the international criteria for persistence (including the criteria as mentioned in Annex XIII of EC Regulation 1907/2006, REACH) based on expected half-lives of PFOA via biodegradation, hydrolysis, and photolysis under environmentally relevant conditions. It is anticipated that PFOA will exist predominantly in the water compartment. Partitioning to sludges, soils, and sediments will likely be limited and any PFOA associated with these environmental matrices will likely be found in the water phase of sludges, soils, and sediments. Partitioning to air from water will not occur for dissociated APFO or PFOA, but for the protonated form of PFOA, volatilization may be possible depending on the pH. However, there are still significant uncertainties concerning the environmental fate of PFOA including: 1) sources of PFOA in the environment; 2) potential for biotransformation in soil and sediments under varying environmental conditions and anaerobic sludges; 3) transport / distribution mechanisms; 4) ultimate sinks and 5) role of aerosols in transport and distribution of PFOA in the environment.

Bioaccumulation

Based on studies in the available literature, PFOA does not meet international regulatory criteria (including the criteria as mentioned in Annex XIII of EC Regulation 1907/2006, REACH) for bioaccumulation. In tests

with the rainbow trout *Oncorhynchus mykiss* a BAF of 0.038 and BCFs for organs of 27 (blood), 8.0 (liver) and 4.0 (carcass) were obtained. The results indicate a low potential for bioaccumulation of PFOA in fish.

The average soil-to-earthworm ratio (BAF) was for PFOA was 1. These data provide support for the lack of bioaccumulation of PFOA by earthworms from soil.

In some marine and Canadian Arctic mammalian food web studies, a potential for biomagnification has been suggested. However, the existing field data provide highly variable evaluations of the extent of bioaccumulation and biomagnification. When whole body concentration data are used for bioaccumulation and biomagnification calculations, the field results reported in published papers are inconclusive due to differences in temporal and spatial comparability of samples (i.e., samples were not collected at the same times and locations). In one monitoring study sporadic biomagnification was demonstrated for some species although the Trophic Magnification Factor indicates that PFOA does not biomagnify at the top of the food chain. Data from a wide range of species, e.g., dolphins, panda bears, polar bears, guillemots, and turtles suggest that food chain transfer is not significant, based on a weight of evidence approach, especially when PFCAs with eight carbons or less are compared to well-established POPs.

Toxicity

Based on the available studies, PFOA does not meet the criteria for T-categorisation based on environmental toxicity. However, also human health related criteria are included in this categorisation, and the outcome of the classification and labelling according to 67/548/EEC for human health endpoints is used in this context. Based on the available information, PFOA does meet the criteria as mentioned in Annex XIII of EC Regulation 1907/2006, REACH for T-categorisation.

Conclusion

PFOA can be considered as very persistent (vP) and toxic (T), but not bioaccumulative (B) as defined in the EU legislation.

Despite to the strict REACH Annex XIII definition of PBT, due to long-range transport characteristics and occurrences in biota and wildlife, it might be advocated to evaluate PFOA from the position of the chemical of the equivalent concern to PBT.

6. GENERAL ASSESSMENT AND ANALYSIS – EXPOSURE ASSESSMENT (TASK 2)

6.1 Update human exposure assessment

General public

PFOA has been detected in human blood, plasma, liver, seminal fluid, breast milk, and umbilical cord blood of a wide array of individuals, most prominently among those working with the compound as well as individuals residing in the vicinity of facilities that manufacture PFOA (Fromme et al. 2009). The consumption of highly contaminated fish food may also cause an increased in body burden (Fromme et al, 2009). See Lau et al. (2007) for recent review of the monitoring and toxicity of these compounds. The exposure of the general public is based on the internal exposure of 4-5 ng PFO/mL serum (Steenland et al, 2009). In a recent PhD thesis the total average internal exposure to PFOA in humans were assessed by using a Scenario-Based Risk Assessment (SceBRA) (Horowitz 2007). The modelled internal exposure to PFOA is in the range of 1 ng/kg bw/day (adults) to 4 ng/kg bw/day (infants)

Humans can be exposed to PFOA via multiple routes including drinking water, food, and air. The average (and upper) daily exposure including all potential routes amounts to 2.9 ng/kg bw (12.6 ng/kg bw) for PFOA in adults in the general population (Fromme et al, 2009; Tardiff et al. 2009). Dietary exposure is the dominant intake pathway of the total intake of the general population using mean intake data (Fromme et al, 2009; Tardiff et al. 2009; Horowitz 2007). The EFSA noted the indicative human average and high level dietary exposure for PFOA of 2 and 6 ng/kg bw per day respectively (EFSA, 2008). However, for children of the 1.5-4.5 year age group the highest estimated daily intakes were reported by UK FSA, being in the order of 4–200 and 10–300 ng/kg b.w. for average and high consumers respectively (EFSA, 2008).

Fish seem to be an important source of human exposure to PFOA in the dietary as fish might be affected by PFOA levels present in the environment (Tardiff et al, 2009; Danish EPA, 2008). In relatively polluted areas this might lead to an overestimation of exposure of the general population from commonly consumed fish (EFSA, 2008). Trudel et al. (2008) found a range between the lowest and highest doses is approximately two orders of magnitude in all consumer groups.

Table 10 shows the estimated adult daily intake of PFOA for the general population reported by Fromme et al. (2009). A simple one compartment toxicokinetic model showed that the dietary intake corresponds well with the plasma level of the same population (Fromme et al., 2009).

Table 10 The estimated adult daily intake of PFOA for the general population

Route of exposure	Daily intake ng PFOA/kg bw	
	Mean	High
Indoor air	0.0009	0.0009
Outdoor air	0.0013	0.012
House dust	0.0164	1.0283
Diet	2.8167	11.48
Drinking water	0.0217	0.0867
Overall intake	2.9	12.6

For PFOA, the total contribution from the non-food sources, mainly indoor exposure, could be as high as 50% compared to the estimated average dietary exposure to PFOA (EFSA, 2008). Measurements have confirmed that PFOA and PFOS can be found in vacuum cleaner dust in private households. The most

important human exposure may be through inhalation of air and the dust in private homes. Oral exposure from hand-to-mouth contact with carpets and incidental ingestion of dust contribute to some extent to the exposure of PFOA of infants, toddlers, and children (Horowitz 2007).

Normally, PFOA is not present in the consumer products after production as the direct use of PFOA is mainly limited to be a processing aid for the polymerisation of fluoropolymers (Danish Ministry of the Environment, 2006). Only the ammonium salt of PFOA is found in very small quantities as residue in fluoropolymer products or as unintentionally by-product in fluorotelomer based-products. However, PFOA can also be formed in the environment from abiotic and biotic transformation of commercially synthesized precursors (Fromme et al. 2009). Overall, the contribution of PFOA precursors to the total exposure via all potential routes, indoor and ambient air, house dust, drinking water and food, to the general adult population seems to be limited (Fromme et al, 2009).

Further, PFOA is a significant contaminant in the use of PFOS-related chemicals in products. However, PFOS may only be used for the exempted uses under the directive 2006/122/ EC as repealed by COM Regulation (EC) No 552/2009.

Although, residues of PFOA (typically between 0.1 and 1% of the total content of fluorinated substances) in consumer articles can be detected (Danish EPA, 2006 and 2008, Swedish Chemicals Agency, 2006 and Norwegian Pollution Control Authority, 2007), potential exposure to PFOA from consumer articles is negligible (Washburn et al, 2005). It is estimated that a hypothetical annual average intake reasonable maximum aggregate exposure of an adult resident at approximately 2.2 ng PFO/kg bw from clothing and carpet. For the more typical exposure scenarios intake estimates were generally 1-2 orders of magnitude lower than the corresponding reasonable maximum aggregated exposure intakes. The aggregated exposure estimated corresponds to serum concentrations of 0.05 ng/mL to 0.25 ng/mL (Washburn et al, 2005). These levels should not result in quantifiable levels of PFOA in blood.

This supports the EFSA (2005) conclusion that “consumer exposure [of the PFOA in the production of PTFE for] in repeated use articles, sintered at high temperature, is considered negligible” and the US EPA conclusion that “the routine use of household products [containing fluoropolymers] does not indicate to poses a concern.”.

Conclusion

The average daily intake is in the range of 2 ng/kg bw up to 13 ng/kg bw, with higher intakes possible with contaminated food, mainly fish, or drinking water. Trudel et al. (2008) found a range between the lowest and highest doses is approximately two orders of magnitude in all consumer groups. The highest estimated daily intakes were reported by UK FSA for the 1.5–4.5 year age group, being in the order of 4–200 and 10–300 ng/kg bw for average and high consumers respectively (EFSA, 2008). However, the highest estimates are more representative for consumption of contaminated fish, or drinking water than for the exposure of the general European population.

Children seem to be a high risk group because EFSA estimated that the importance of possible pathways of non-food human exposure to PFOA seems to decrease when moving from childhood into adulthood (EFSA, 2009). Also, Trudel et al. (2008) concluded that children tend to experience higher total uptake doses (on a body weight basis) than teenagers and adults because of higher relative uptake via food consumption and hand-to-mouth transfer of chemical from treated carpets and ingestion of dust. The uptake estimates based on scenarios are within the range of values derived from blood serum data by applying a one-compartment pharmacokinetic model.

Future studies should take into account precursors and their effect on consumer exposure to PFOA. It is likely that fluorotelomer alcohols taken up by humans are metabolically converted to PFOA (Trudel et al., 2008).

Exposure workers (industrial uses)

PFOA is used as surfactant in the production of fluorotelomers and fluoropolymers, which are used in the production of consumer articles. PFOA measured in consumer articles comes from degradation of fluoropolymers and fluorotelomers and as impurity during the production process. However, due to the commitment to the US EPA PFOA Stewardship programme, most companies have reduced impurities and losses of PFOA to a minimum.

In contrast to general population serum concentrations, occupational exposure has produced mean serum concentrations of PFOA and PFOS that are two to three orders of magnitude higher than those reported for the general population (Olsen and Zobel, 2007; Olsen et al., 2003b). These serum concentrations tend to be job and location specific.

Table 11 gives an overview of the scenarios of the direct use of PFOA related products. Other industries do not use PFOA related products directly but use fluoropolymers or fluorotelomers. For data and remarks on the exposure scenarios, reference is made to the second questionnaire and report of Exposure Scenarios as mentioned in Annex III, Annex IV and Annex V of the Risk assessment of perfluorooctanoic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009) report.

Table 11 Overview of exposure scenario's of direct use of PFOA

Industrial use	Scenario available	Alternative available
Production APFO	Yes, from Company 1	Company 1 will cease production in 2010
Production fluorotelomers	Yes	PFOA is an unintended by-product and therefore precursor substances would have to be investigated further
Production fluoropolymers	Yes, from PlasticsEurope and Company 2	No alternatives available yet
Photographic industry	Yes, from EPIA	PFOA is in some cases used as an alternative for PFOS but phased out where possible. However some critical uses without alternatives remain.
Semiconductors	Yes, from ESIA-EECA	PFOA is in some cases used as an alternative for PFOS but phased out where possible. However some critical uses without alternatives remain.

Company 1

APFO, the ammonium salt of PFOA is manufactured by a three-stage production process;

- a) synthesis of the acid fluoride (PFOF) from capryloyl-fluoride via an electrofluorination process to obtain a cell-product intermediate;
- b) hydrolysis and purification of the cell product to obtain the pure PFOA;
- c) reaction of PFOA with ammonia to obtain the final APFO salt, which is then dried before dissolution in water (the form supplied to customers).

Company 1 has one APFO/PFOA manufacturing plant in Italy which will cease their production of APFO as per April 2010 and cease commercialisation as per November 2010.

Company 1 has carried out a health surveillance of their production workers every year since 1978, according to the Italian Legislation concerning health and safety at work. Since 2000, the PFOA biological monitoring began and has been repeated each year since and including 2008.

Both PFOA airborne emission levels measured in work places and PFOA measured serum levels in exposed workers have led to a PFOA worker exposure reduction plan implementation; further technical containment control measures - by a dedicated Company investment plan - and improvement in operational risk management - by training, no-leak awareness and good housekeeping practices - have led to a continual decrease of PFOA serum levels.

Company 1 has reduced environmental PFOA emissions. All gasses from electro-fluorination steps are treated on site by water scrubbing and high temperature incineration. Liquid streams from the PFOA process are collected and treated in a dedicated production section where PFOA is captured and then recycled into the process. Residual wastewaters is treated in an on-site facility (neutralization and GAC treatment) before discharge into a local/regional wastewater treatment plant and subsequent deposition of sludge into controlled landfill sites.

Since 2004, a PFOA/APFO Emission Reduction Program, supported by a dedicated Company Investment Plan is in progress in order to achieve general improvements in Environmental Contamination control and Worker Exposure reduction. In the mentioned Investment plan, different PFOA/APFO recovery processes have been developed to improve the overall site mass balance.

Within the Risk Assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009) Company 1 has developed exposure scenarios for the manufacturing of PFOA/APFO. Although it has been concluded in this risk assessment that there is no risk this could not be verified as a number of the exposure data are based on Confidential Business Information data.

All production workers classified as exposed, ex-exposed and not exposed have been submitted every year since late 70's to physical examination (blood and urine for 40 parameters). Since 2000, the Employees health studies related to PFOA biological monitoring was developed and the Health Surveillance program was repeated every year, including 2008. No clinical evidence of specific disturbances or health disorders has been recorded over 30 years of observation of workers exposed to PFOA in the publication of Costa et al (2009).

Fluoropolymers manufacturing industry (represented by the Fluoropolymers Committee of PlasticsEurope)

It is very unlikely that emissions of PFOA have occurred between 2004 and 2008 as the use of these substances is isolated, rare and undefined. In general any adventitious release is caught and incinerated in a controlled manner. Additionally the fluoropolymer industry recycle PFOA substances in a closed loop system, any unintentional releases are unmeasurably low.

In general all outdoor emissions are collected and incinerated in controlled conditions and in line with individual plant Environmental consents. All releases to the workplace (indoor air) are minimal and are kept well below the TLV/OEL for PFOA in line with local legislation. In 2005, the German MAK commission established an occupational exposure limit of 0.005 mg/m³ for PFOA. In 2006, this limit was also proposed in the Netherlands but was not ultimately adopted because of implementation of REACH. Other European OELs (circa 2004):

- * The Netherlands OEL = 0.01 mg/m³, skin (Ariel, 2004)
- * Belgium OEL = 0.1 mg/m³, skin (RTECS)
- * Denmark OEL = 0.01 mg/m³, skin (Ariel, 2004)
- * Ireland OEL = 0.01 mg/m³, skin (Ariel, 2004)
- * Italy OEL = 0.01 mg/m³, skin (Ariel, 2004)
- * Spain OEL = 0.01 mg/m³, skin (Ariel, 2004)

The fluoropolymers industry has worked and is continuing to work closely with US EPA and other stakeholders to identify and reduce emissions and potential exposures to PFOA. In particular, in 2001, the principal fluoropolymer producers worldwide have each committed to a minimum 50% reduction in total global emissions by 2006 using 2000 as baseline year. However, it is expected that this reduction will be much more than 50% agreed. Furthermore, within the US EPA product Stewardship program the fluoropolymer industry will work towards the elimination of PFOA products by 2015.

Semiconductor industry (represented by the European Semiconductor Industry Association)

PFOA where it is used is used in small quantities as a constituent of a process material substance. There is no release to the work place due to the use of closed systems processes. Solvent waste is collected at the factories and sent for incineration. Exhaust systems with abatement equipment (scrubber) are used. There is very minimal release to the environment in wastewater. Based on an industry figure of usage per annum of <50kg, overall emissions through wastewater based on expert engineer knowledge of the process technology and waste stream would give rise to an estimated 4kg per annum. This is a conservative estimate than the reality (more likely 2-3kg) for the whole industry for a year. PFOA is very important but the amount used is minimal. The conservative estimate of 4 kg/a is extrapolated from a mass balance approach put together by industry engineers for PFOS. It is an analogy based extrapolation.

Photographic and imaging industry (based on information received from the EPIA, the European Photo and Imaging Association)

The total annual emission of PFOA to air in the photographic industry is estimated to be non-detectable due to the manufacturing in closed systems. Environmental releases from the production plant are directed to an on site waste water treatment facility. As the sludge from this on site facility is incinerated, any emission to soil due to sludge application is eliminated. Environmental emissions are possible in wet film processing, where PFOA chemicals may potentially be released into photoprocessing solutions.

Processing films used for medical applications is considered to represent the worst case situation with regard to environmental emissions. Films used for medical applications are coated on both sides and contain per top coating the maximum amount of PFOA to guarantee the required film quality/sensitivity. In

addition, in the wet processing of medical films a maximum of carry-over is anticipated as the processing involves only two steps (developing and fixing) followed by a rinsing step (water). Developer and fixer waste solutions are collected and disposed off as chemical waste (incineration). Rinsing aqueous solutions (containing PFOA from carry-over) are directed to the sewer.

In order to quantify the amount of PFOA in the rinsing solution, actual concentrations were measured in a typical hospital setting. Analytical data revealed a mean concentration of 0.27 µg PFOA per L rinsing solution (Analytical Report dated 31.10.2007 by the Laboratory NIERSSVERBAND – Am. Niersverband 10, 41474 Viersen, Germany), resulting in a PEC/PNEC value at the emission point of 0.000 000 010.

The exposure to humans is only relevant during the manufacturing of imaging articles such as films, papers, and printing plates in which only workers are exposed. The workers involved are only exposed for a short term (maximum frequency of exposure is twice per month because of the use of the PFOA/APFO in only specific coating applications for which diluted solutions of the substance are prepared a few times per month), but actually much lower if different workers are involved. Dermal exposure is not expected due to use of gloves. The type of gloves used depends on the actual imaging article and on the use of other chemicals in the associated coating solutions chemical-resistant gloves, such as nitrile or butyl rubber gloves are typically used.

For certain critical uses, no PFOA/APFO-free techniques are available. The concentration of PFOA/APFO-related substances in the end product is 0.1-0.8 µg/cm².

Special assessment Aqueous Film Forming Foams (AFFF)

The below is based on information received from the Fire Fighting Foam Coalition and Company 2.

Fluorosurfactants are essential components of AFFF as no other class of surfactants can provide the required low surface tension. Only the combination of fluorinated surfactants and hydrocarbon surfactants provides the positive spreading coefficient and enables film formation on top of lighter fuels.

Only 3-6% of the total global fluorochemicals production is used in AFFF. AFFF are mainly applied as a 1-3% solution. The formed foam solution generally contains up to 0.05% surfactants (fluorosurfactants and hydrocarbonsurfactants combined)

AFFF historically were manufactured using PFOS and contained trace levels of PFOA. The new generation AFFF is based on fluorotelomer-technology and does not contain or degrade to PFOS and contain 30-60% less fluorine than PFOS-based AFFF. Current fluorotelomer-based AFFF products are not made with PFOA or other PFCA's.

Some fluorotelomer (with a carbon backbone of C8 and higher) based AFFF may breakdown to PFOA. However, the majority (>75%) of fluorosurfactants in telomer based AFFF are based on six-carbon (C6) technology. However they may contain trace levels of PFOA and the C6 acid, perfluorohexanoic acid (PFHxA). Some current AFFF formulations contain over 95% C6-based fluorosurfactants while others contain a higher % of C8 (or higher)-based fluorosurfactants

The predominant breakdown product from the six-perfluorinated carbon (C6) based fluorotelomer-surfactants is commonly referred to as the 6:2 fluorotelomersulfonate (6:2 FTS).

A US EPA workgroup already determined in 2003 that PFOA exposure from these telomer based AFFF products are not likely to be a significant. Further, emission of PFOA from fluorotelomer based AFFF

products are included in the US EPA PFOA Stewardship Programme that obliged the committed industrial partners to phase out PFOA emissions by 2015. C6-technology will become dominant in the next few years due to requirements from US EPA PFOA Stewardship programme.

In conclusion, the current basic fluorotelomer surfactants used in concentrations up to 0.5% in AFFF do contain traces of PFOA. These traces are much lower than the 200-1600 ppm of PFOA that might be present in PFOS based AFFF. Current fluorotelomer based AFFF suppliers are in a continuous effort towards lowering the PFOA quantities below 1 ppm (in the fluorotelomers that are present at maximum levels of 0.5% in AFFF). In other words, even if PFOA is present in concentrations <100 mg/kg fluorotelomer, the maximum concentration of PFOA in the final AFFF product will be <1 mg/kg and minimal risks are to be expected.

However, currently non-fluorinated (organohalogen free) AFFF are on the market meeting the toughest amongst the fire fighting standards.

6.2 Update environmental exposure assessment

The information in the OECD SIDS report is used as a basis for this chapter and this information is extended with data from recently published peer reviewed scientific literature. These new data from Europe are in line with previously available information.

APFO is used as a surfactant in the production of fluoropolymers. In 2002, its world-wide production was about 200-300 metric tons. As anticipated, the highest concentrations are measured closed to the production and processing sites in waste waters, ground water and soil. It is believed that contaminated waste water is a primarily source of surface water pollution. Ordinary the STP is not able to treat (degrade) the PFOA and precursors.

Entry into the environment occurs during production and use of PFOA / APFO. Other sources for releases to the environment are residual contents of PFOA in fluoropolymer and fluoroelastomer products, PFOA as a by-product in end products and fire-fighting foams containing perfluorocarboxylates, PFOA contaminations in perfluorooctyl sulfonyl (PFOS) based products, and PFOA contamination in fluorotelomer products. An indirect source for PFOA in the environment is the degradation (biotic and abiotic) of some fluorotelomer-based products.

The global distribution of PFOA was demonstrated by several monitoring studies. Elevated PFOA concentrations were measured near industrialized and urbanized regions. PFOA could be detected in air in concentrations in the range of pg/m³, ng/g dw in soil, in sediment, suspended matter, and sewage sludge.

PFOA concentrations up to 67,000 ng/l and 3,200,000 ng/l were analysed in sewage effluent and landfill effluent. Sporadically, PFOA was determined in ground water samples (up to 3,400,000 ng/l). In fresh water samples (rivers, lakes, rain water) PFOA was regularly measured. The maximum concentration determined was 11,300 ng/l. Elevated concentrations of PFOA were also detected in coastal waters near industrialized and urbanized areas; the maximum concentration was 15,300 ng/l.

In freshwater and salt water fish PFOA was detected occasionally. The maximum concentration (91 ng/g ww) was found in common shiner (liver samples) after a spill of fire retardant foam. The highest PFOA concentration in birds was determined in liver samples of cormorants (450 ng/g ww). However, it should be noted that for this colony of cormorants the highest value (450 µg.kg⁻¹ ww) appeared to be an outlier as the

concentration was 4.5 times greater than the standard deviation of the mean. The occurrence of PFOA even in remote areas was demonstrated by analysis of polar bear liver samples (highest concentration: 55.8 ng/g ww). Liver samples of other mammals (e.g. seals, whales, walrus, dolphin) contained PFOA; concentrations up to 62 ng/g ww.

The PERFORCE report is providing information concerning environmental concentrations in the Europe (de Voogt, 2006). PFOA values for the STP are shown in the table 12.

Table 12 PFOA values for STP

Matrix	Concentration range (ng/l)	Ref. page and table in the PERFORCE Report
STP – Influent	20 – 65	p. 67, figure 6.1
STP – Effluent	20 – 110	p. 68, figure 6.2

Data provided in the OECD SIDS report concerning the 3M and Dyneon manufacturing operations for water which includes both the wastewater treatment effluent as well as non-contact cooling water used in the manufacturing process. PFOA was present at an average of the levels summarized in table 13 (3M, 2003b; Santoro, 2003). However, it should be noted that the situation has changed significantly since these data were recorded.

Table 13 PFOA concentrations in the wastewater treatment effluent as well as non-contact cooling water used in the manufacturing process of 3M and Dyneon

Year	Concentration (ng/l)
1998	602,000
1999	766,000
2000	1,028,000
2001	310,000
2003, January	58,000
2003, May	88,300

The HAZARDOUS project (2009) summarizes the PFOA concentrations in Nordic countries as shown in the table 14.

Table 14 PFOA concentrations in Nordic countries

Matrix	Concentration range	Value	Ref. page and table in the HELCOM Report
STP - Untreated Waste Water	2,0 – 24,0	ng/l	p. 48, table 5.8
STP - Treated Waste Water	2,0 – 24,0	ng/l	p. 48, table 5.8
STP – Sludge	0,8 – 20,0 (1,2 median)	µg/kg dry weight	p. 48, table 5.8
Sea Water (coastal side)	0,58 – 7,7	ng/l	p. 54, table 5.12
Sea Water (open sea)	0,49 – 0,59	ng/l	p. 54, table 5.12
Sediment (coastal)	0,11 – 0,4	µg/kg dry weight	p. 54, table 5.13
Sediment (open sea)	0,06 – 0,2	µg/kg dry weight	p. 54, table 5.13

Just recently published European-wide study focusing on river waters summarized that PFOA is to be found in measured European fresh water streams in the 97% of the samples, with maximum concentration of 174 ng/l, average of 12 ng/l and median concentration of 3 ng/l (Loos et al., 2009).

In this study special focus was given to the analysis of water-soluble perfluorinated carboxylic acids (PFCAs), because of their persistent character in water and the recent interest in the scientific community for them. Perfluorooctanoic acid (PFOA) has been identified before as a major industrial contaminant present in European rivers (Loos et al., 2008a; McLachlan et al., 2007). The Po River in northern Italy was identified as a major PFOA sink from the European Continent; the highest concentration measured was 200 ng/L PFOA found at a median river flow of w1500 m³/s (McLachlan et al., 2007). In this study we could identify other important European PFOA sinks; the chemical was found in the following big rivers: River Danube in Austria (25 ng/L, flow w1500 m³/s), River Scheldt in Belgium and The Netherlands (88 and 73 ng/L; w150 m³/s), River Rhone in France (116 ng/L; w1500 m³/s), and the River Wyre in the UK (100 ng/L). These rivers are likely to be together with the Po River the major PFOA sinks in Europe.

7. GENERAL ASSESSMENT AND ANALYSIS – RISK ASSESSMENT (TASK 2)

7.1 Community wide risk assessment – human health

General public

OECD formulated that APFO is a candidate for further work. Also, the recent ATSDR report (2009) concluded that little research has been done on the general population to answer the question whether perfluoroalkyls may be associated with adverse health effects. The ATSDR did not derive Minimal Risk Levels (MRLs) for perfluoroalkyl compounds based on lack of adequate human data and uncertainties related to the appropriateness of using animal data for human risk assessment. Their conclusions were based on the available and recently published toxicology data in humans and animals. No new evidence is published afterwards to make a different conclusion for the hazard assessment.

Recommendations and regulations are updated periodically as more information becomes available. The latest update is by the US EPA (2009) provisional drinking water advisory for PFOA is 0.4 µg/L (ppm). The Provisional Health Advisory for PFOA, was calculated based on the BMDL₁₀ of 0.46 mg/kg/day in the Lau et al. (2006) study. The derived Provisional Health Advisory is based on external dose. However, some industry or authorities take the internal dose for establishing safety levels as the internal dose seems to be determinant of response, not the exposure route, and also the kinetics of PFOA are very different in humans and experimental animals because the half life of PFOA in humans is much longer than in animals (Risk assessment of perflourooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry, 2009; New Jersey Department of Environment Protection, 2007). However, that the serum levels in rats at the BMDL₁₀ are expected to be in the region of three orders of magnitude higher than in serum levels of PFOA from European citizens who do not have occupational exposure.

The main contributor (99%) of PFOA exposure is via food (Fromme et al, 2009; Tardiff et al. 2009). EFSA (2008) noted that the indicative human average and high level dietary exposure for PFOA of 2 and 6 ng/kg bw per day, respectively, are well below the TDI of 1.5 µg/kg bw per day. However, higher intakes of PFOA are estimated. These higher estimates are substantially influenced by contaminated food, mainly fish, or drinking water from polluted areas rather than for the exposure of the general European population. More information on the exposure of general public to PFOA via food will become available in 2012 within the PERFOOD project commissioned by the European Commission.

Further, children seem to be a highest risk group among the general population because of oral exposure from hand-to-mouth contact with carpets and incidental ingestion of dust which contribute to some extent to the exposure of infant, toddlers, and children (EFSA, 2008; Trudel et al., 2008; Horowitz. 2007).

Workers

The recent ATSDR report (2009) concluded long-term occupational exposure by inhalation or dermal contact to PFOA at work has not been associated with significant adverse health effects, but two studies in workers found changes in sex hormones and cholesterol associated with levels of PFOA in blood. However, these observations could be due to chance, or to factors other than PFOA.

Within the US EPA PFOA Stewardship program need to be by 2010, 95% global reduction in manufacturing emissions and product content of PFOA with as base year 2000. This will lead to a reduction of exposure to workers, consumers and environment.

Company 2 and Company 4 are conducting extensive monitoring and looking for health effects (Costa et al, 2009). Fifty-three males' workers (20 to 63 years) were submitted every year from 1978 to 2007 to medical examination and blood chemical chemistry tests, and serum PFOA dosage. In the latest survey PFOA serum levels ranged from 0.20 to 47.04 µg/mL in currently exposed workers and from 0.53 to 18.66 µg/mL in workers no longer exposed being retired or transferred to other departments in the meantime. A significant decrease in PFOA blood levels (-37% mean level and -45% in peak level) was recorded in the 4 last years after plant renovation and improvement of working conditions. However, in evaluating this trend it is necessary to take into account the long biological half-life of substance, so that the present blood levels largely reflect the exposure conditions of the previous years.

The highest PFOA serum levels found in the study of Costa et al. (2009) are above the DNEL of 1.7 µg PFOA/mL serum of the Risk assessment of perfluorooctanoic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009). However, no clinical evidence of any specific decreased well being or disease in relation to PFOA exposure has been recorded over the 30 years within the study of Costa et al. (2009), and all the biochemical parameters, including liver, kidney and hormonal functions, turned out to be within the reference ranges, but a significant association of total cholesterol and uric acid with PFOA serum level was evidenced. A probable interference of PFOA on intermediate metabolism deserves further investigations.

Further, Exposure Scenarios were developed within the Risk assessment of perfluorooctanoic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009) for the manufacturing of PFOA/APFO by Company 1, for the fluoropolymer industry by Company 2 and for the photographic industry by EPIA. These scenarios illustrate that the exposure to workers, consumers and environment are well controlled and below the DNELs developed within the Risk assessment of perfluorooctanoic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009).

7.2 Community wide risk assessment – environment

Risk characterization was performed according to the guidelines given in the Technical Guidance Document (TGD) of the European Chemicals Bureau⁴. The PEC and PNEC data which were defined in a local and regional scale and used for the risk characterization are discussed in the previous chapters: 5.4 Update Hazard assessment environment and 6.2 Update environmental exposure assessment.

Aquatic Compartment (incl. sediment)

Local scenario fresh water (river)

A PNEC for the surface water of 0.57 mg/L is used.

A local PEC value of 200 ng/L (Po river, McLachlan et al., 2007) = 0.2 µg/L = 0.0002 mg/L.

$$RCR = PEC/PNEC = 0.00035$$

Conclusion: no risk.

Regional scenario fresh water (river)

A PNEC for the surface water of 0.57 mg/L is used.

A regional PEC value of 12 ng/L (EU average, Loos et al., 2009) = 0.012 µg/L = 0.000012 mg/L.

$$RCR = PEC/PNEC = 0.000021$$

⁴ Freely available at: http://ecb.jrc.it/documents/TECHNICAL_GUIDANCE_DOCUMENT/EDITION_2/tgdpart2_2ed.pdf

Conclusion: no risk.

Local scenario marine water (coastal side)

A PNEC for the surface water of 0.57 mg/L is used.

A local PEC value of 7.7 ng/L (HAZARDOUS project, 2009) = 0.0077 µg/L = 0.0000077.

$$RCR = PEC/PNEC = 0.000013$$

Conclusion: no risk.

Regional scenario marine water (open sea)

A PNEC for the surface water of 0.57 mg/L is used.

A local PEC value of 0.59 ng/L (HAZARDOUS project, 2009) = 0.00059 µg/L = 0.00000059.

$$RCR = PEC/PNEC = 0.000001$$

Conclusion: no risk.

Terrestrial Compartment

A PNEC for the soil compartment of 0.16 mg/kg is used.

A local PEC value of 18,097 ng/kg was found (Norwegian Pollution Control Authority, 2008). This equals 18,097 µg/kg, or 0.018 mg/kg.

$$RCR = PEC/PNEC = 0.11$$

Conclusion: no risk.

Atmospheric Compartment

No PNEC for the atmospheric compartment was derived.

Microbial Activity in Sewage Treatment Systems - general

A PNEC for the microorganisms in the STP of >100 mg/L is used.

A local PEC value of 110 ng/L (HAZARDOUS project, 2009) = 0.00011 µg/L = 0.00000011 mg/L.

$$RCR = PEC/PNEC = 0.000000001$$

Conclusion: no risk.

Microbial Activity in Sewage Treatment Systems - maximum

A PNEC for the microorganisms in the STP of >100 mg/L is used.

A local PEC value of 3,200,000 ng/L = 3.2 mg/L (OECD SIDS, 2008).

$$RCR = PEC/PNEC = 0.032$$

Conclusion: no risk.

The concentrations of PFOA analysed in sewage effluent and in landfill effluent ranged from not detected to 3,200,000 ng/l (OECD SIDS, 2008). The risk characterisation ratio PEC/PNEC for the microbial activity in sewage water treatment systems used highest concentrations found in landfill effluent.

8. EVALUATION OF ALTERNATIVES (TASK 3)

8.1 Evaluation of alternatives of PFOA

Much of the information on alternatives has a high level of confidentiality due to the commercial sensitivity of especially detailed information on any possible alternatives. Further, each processing technology is unique and alternatives must be evaluated for properties and performance in use. However, a general overview of alternatives that are already on the market or can be expected to come on the market very soon is given below.

Public available information is presented during a workshop organized by UNEP and the US Government (US EPA) on managing perfluorinated chemicals and transitioning to safer alternatives held in Geneva, Switzerland on 12-13 February, 2009, the alternatives of various companies were discussed (UNEP SAICM Workshop Safer Alternatives, 2009).

With regard to alternatives, US EPA has reviewed over 100 new chemicals by end of 2008, and is taking an integrated approach to testing of chemicals to speed the development of data needed to understand issues and concerns that may be presented (Workshop Safer Alternatives, 2009). Mainly shorter chain-length fluorotelomeric substances have been notified as alternatives. In consistency with the US EPA PFOA Stewardship Program, it is required that alternatives do not contain significant levels longer chain-length perfluorinated substances of concern as unintended by-products.

In general it can be stated that due to the commitment of the major industries to the US EPA PFOA Stewardship Program, alternatives will have to be in place in 2015 or earlier if possible, the price of the various alternatives will not delay transition.

It was not possible to perform an economic analysis of the alternatives of PFOA as most alternatives of PFOA are still under development and not yet on the open market. Only company 4 already produces an alternative of PFOA. This company could, however, not provide the study team with pricing information on their alternative. This company is not selling this alternative on the open market and considers the price as confidential business information. The company stated that the alternative is more expensive than PFOA itself. The cost of the alternative is not a major factor in the cost/price of the fluoropolymers production.

Although it was not possible to get an exact price quantification from industry, in general it can be expected that products produced with the alternatives will be more expensive than the current based on APFO. This is due to the following factors:

1. research costs were made for finding a suitable alternative, and additional costs were made for the development and implementation of a production process of the suitable alternative substance;
2. the alternative substances can be less efficient in the fluoropolymer production process than APFO, so possibly more of the alternative product has to be used per kg polymer produced;
3. the degree of recycling of the alternative is currently uncertain versus that of APFO,
4. current installed abatement systems and techniques may not be as efficient for the alternative substance as for APFO and may need to be upgraded;
5. finally, the fluoropolymer products manufactured with the alternative substance will have to meet specific customer qualifications. This will need additional testing by both fluoropolymer manufacturers and their customers.

Any possible price increase of specific fluoropolymers will depend on the market situation and the competitive situation at a certain point in time. However it is certain that all EU-based fluoropolymer manufacturers that will replace APFO will have to invest heavily to have the same products available to meet the customer demand and requirements.

As a benefit the manufacturers which are part of the US EPA PFOA Stewardship Program will comply in time with the replacement of APFO. In conclusion, technology using alternative substances seems economically feasible but the Return on Investment (RoI) will be primarily based on maintaining the business versus the loss of business.

Direct Uses – Fluoropolymer manufacturing

The ammonium salt of PFOA (APFO) is used as a surfactant to produce some but not all fluorinated polymers. Companies committed to the US EPA PFOA Stewardship Program will have to replace APFO by 2015.

Company 4

APFO is no longer used by Company 4 as it has developed an alternative, most probably based on PFBS technology, which replaces APFO in production of fluoropolymers by emulsion polymerization. The performance of the alternative is equal to APFO and has a favourable environmental, health, and safety profile, i.e., low toxicity, rapid elimination, etc. Further, this alternative is suitable for recovery, recycling, & reuses (containment).

Mammalian toxicology of the alternative:

- is rapidly eliminated from the body, does not accumulate in the liver, and does not show dramatic gender or species differences in pharmacokinetics
- is not genotoxic in vivo
- is 10 to 30 times less toxic than APFO in developmental toxicity studies in rodents
- is 5 to 17 times less toxic than APFO in 28-day oral toxicity studies in rats
- its primary target organ is the liver, like APFO, however, the effects are less severe.

Environmental toxicology of the alternative:

- has been assessed to date using Structure Activity Relationship modelling, literature searches, and acute testing
- is not environmentally bioaccumulative; the fish BCF is <1.0
- acute testing shows low aquatic toxicity
- additional environmental studies in progress are intended to validate modelling, support regulatory processes and enable derivation of environmental media standards

Company 2

Company 2's alternatives program is accelerating the development of next generation technologies, including fluoropolymers made without PFOA. Company 2 has an alternative polymerization processing aid to replace APFO in the manufacturing of fluoropolymers. The alternative lies within the range of branched fluoro-ethers that can be applied for all products. This new product line offers the same or improved performance and its manufacturing process will utilize low emission technology. Commercial scale quantities of some fluoropolymers made without APFO are now available. The customer testing is underway.

This alternative is already registered and approved by various authorities and has a rapid bio-elimination/body clearance of 12 -24 hours in various animals' species and a better toxicology profile than APFO.

Company 5

Company 5 will use an alternative for APFO in the manufacturing of PTFE as from early 2009. It is said to have regulatory clearances attained in Japan, US (TSCA) and Europe Union (REACH).

The APFO alternative used as PTFE polymerization aid proved to be much more favourable based on toxicological and pharmacokinetic data. The US TSCA 5(e) Consent Orders state that the APFO alternative is of "different and less toxic" while requiring toxicological & environmental studies and exposure & emission control.

Company 6

Company 6 is a not based in Europe that employs a range of design parameters for alternatives of APFO as the surfactant in polymer production including less biopersistence, less overall toxicity, drop-in replacement and compatibility with the existing emission control technology. The result is that 50% of the polymer product line has already been replaced. Company 4 is on track to cease use of APFO by 2012.

Direct uses - Semiconductor industry and Photographic and imaging industry

For the other direct uses within the Semiconductor industry (based on information received from EECA-ESIA European Semiconductor Industry Association) and the photographic and imaging industry (based on information received from the EPIA, the European Photo and Imaging Association) there are still critical application of PFOA where no alternative exist.

In the semiconductor industry non-PFOA based alternatives appear to be available for some non-critical applications like the uses as a surfactant. However, there still remain critical uses in the semiconductor industry. These mainly concerns uses of PFOA related substances as a constituent material in process chemical formulations for very specialized application steps, such as for the photolithographic applications.

Since 2000 the photographic industry is conducting research, development and testing on possible alternatives. If available PFOA/APFO based products are replaced by alternatives. These alternatives are mostly fluorotelomers and other per- or polyfluorinated substances. The average use per company decreased from 1000 kg PFOA/APFO and related substances per year per company to < 500kg per year per company between 2004 and 2008. The decreasing use for PFOA/APFO-related substances is a trend that will most probably continue in the following years but at this point in time some critical uses remain for the photographic applications.

8.2 Evaluation of alternatives of PFOS which may contain trace levels of PFOA

In this paragraph any alternatives to possible indirect sources of PFOA are discussed. This includes alternatives to PFOS-alternatives because many of these PFOS-alternatives may contain (trace levels of) PFOA as an unintended by-product. Please be aware that where PFOS alternatives are mentioned below, this refers to products that may contain a source of PFOA as an unintended by-product.

Fluorotelomer products manufactured in the EU-27

The focus of alternatives of indirect sources of PFOA should be on fluorotelomer products, fluoropolymer products market as resins or as dispersions and on PFOS and PFOS-related substances (e.g. alternatives to PFOS and related substances) as PFOA may be present in these products as unintended by-product.

Information from the Danish survey (Danish EPA, 2006) demonstrates that PFOS-related substances that are used for impregnation of textiles, leather and carpets as well as impregnation of paper and cardboard seem to be more or less historical as alternatives for PFOS based products are in use from 2006 (Danish EPA, 2006). The Danish survey also demonstrates that substitution of PFOS-related substances for cleaning agents is taking place within the cleaning products for industrial use (Danish EPA, 2006).

They concluded that the most important area with respect to emission of PFOS-related compounds from January 2004 - November 2004 seems to be the use area of waxes and floor polishes (Danish EPA, 2006). However, this are historical figures as PFOS is banned for these uses after 2006.

Non-fluorinated alternatives, such as different hydrocarbon surfactants and silicone products, have been identified and are in use within specific areas as alternatives to PFOS-related compounds, the general picture is that in most cases or at least in larger application areas, other fluorinated compounds are used instead. Generally, the reason for this is that the non-fluorinated alternatives do not work as well, especially in situations, where extreme low surface tension is needed (Danish EPA, 2006).

Table 15 gives an overview of the environmental exposure and effects of non-fluorinated alternatives of PFOS-related compounds identified in the Danish survey (Danish EPA, 2006).

Table 15 *Non-fluorinated alternatives of PFOS-compounds*

Alternatives	Environment	Health
Hydrocarbon surfactants	Readily biodegradable	
Fatty alcohol polyglycoether sulphate	Readily biodegradable	Acutely toxic by ingestion
Sulfosuccinates	Easy biodegradable, but harmful to aquatic organisms.	Irritants to eyes, skin and respiratory system; long term effects dermatitis and CNS depression; mildly harmful to toxic if swallowed
Biphenyls derivatives	Potentially bioaccumulative, acutely toxic to aquatic organisms, biphenyl moiety seems easily biodegradable.	Irritating, may produce skin sensitisation or dermatitis, CNS damage as well as liver and kidney damage
Naphthalene derivatives	Potentially bioaccumulative, no acute toxic effects in investigated fish species, naphthalene moiety seems slowly biodegradable.	Irritating. The parent compound naphthalene is classified as possible carcinogenic in humans. However, no carcinogenicity has been identified for the specific naphthalene derivatives.
Silicone polymers	Classified R51/53; toxic to aquatic organisms and bioaccumulative.	Irritating, harmful by inhalation

The new finding that higher carbon chain fluorotelomer alcohols may break down to PFOA in the environment has as a consequence that the use of fluorotelomer alcohols still may be a source of PFOA in the environment.

Any fluorinated products, used as alternatives for fluorotelomer based products that may break down to PFOA and related substances, are typically fluorinated products using shorter perfluorinated chain lengths (compared PFOA and related substances) such as fluorotelomer alcohols (mainly with a carbon chain length of maximal 6), PFBS (perfluorobutane sulfonate), or perfluorinated polyethers based on a CF₃ or a C₂F₅ structure (Danish EPA, 2006).

Among the polyfluorinated alkyl compounds the bioaccumulation potential and hazard increase by increasing length of the alkylated alkyl group. Polyfluorinated compounds with an alkyl chain length of 5 carbon atoms or less do not seem to be significant bioaccumulative and toxic. They are, however, still substances that will remain present in the environment for decades, and the implications for human health and the environment are unclear, as the toxicity and ecotoxicity of these shorter chained fluorinated compounds are yet to be examined (Danish EPA, 2006).

Table 16 Fluorinated alternatives of PFOS-compounds (Table from Danish EPA, 2006)

Alternative	Company	Used in / used for
Perfluorobutanesulfonate (PFBS) - C4 or based on different C4-perfluorocompounds	Company 4	Paint and coatings industry. As electronic coating. Industrial and commercial cleaning. Cleaner for solder flux residue. Degreasing applications.
Dodecafluoro-2-methylpentan-3-one (CF ₃ -CF ₂ -C(O)-CF(CF ₃) ₂)	Company 4	Fire-fighting fluid
C6 fluorocompounds (predominantly ~ 80%)	Company 2	Fire-fighting fluid
CF ₃ or C ₂ F ₅ pendant fluoroalkyl polyethers	Company 8	Surfactant and flow, level, and wetting additive for coating formulations. Also used in floor polish.

Alternatives to PFOS without possible indirect sources of PFOA

Company 4

The PFOS alternative of Company 1, PFBS, has undergone extensive testing, applications are generally non-dispersive, and PFBS-based products can be used in protective treatments and surfactants.

Table 17 Comparison of hazardous properties of PFBS vs. PFOS

Study	PFOS ¹	PFBS (C4 sulfonate) ¹
28-Day Repeat Oral-Rat (NOEL, mg/kg/day)	<3	100
2-Generation Repro-Rat F2 Generation (NOEL, mg/kg/day)	0.1	1,000
90-Day Chronic-Rat (NOEL, mg/kg/day)	0.6	200(f) 60(m)
Primate (Monkey) PK Study: T ½	200 days	<12 hr
Acute Oral-Rat LD50 (mg/kg)	50-500	> 2,000
Daphnia 21-day NOEC (mg/L)	7	500
Bluegill sunfish 96-hr LC50 (mg/L)	31	6400
Fathead minnow 96-hr LC50 (mg/L)	10	1900

¹ Source: 3M Technical Data Bulletin - PFBS

Company 2

Company 2's alternatives program is accelerating the development of next generation technologies and is not limited to finding alternatives to PFOS without PFOA as an indirect source using short-chain fluorotelomer products but also for the fluoropolymer manufacturing without the direct use of PFOA, but also to finding alternatives. Their alternative products will be registered on global inventories in all countries where they are sold. Their alternative products may potentially degrade to PFHxA which has low biopersistence and is not bioaccumulative.

Alternative product – Example Toxicology Profile:

- Very low acute and repeated-dose oral and dermal toxicity.
- Low acute aquatic toxicity.
- Not a selective developmental or reproductive toxicant.
- Not damaging to DNA, not genotoxic or mutagenic.

- Not biopersistent and not bioaccumulative.

6-2 Fluorotelomer alcohol raw material – Toxicology Profile:

- Low acute oral and dermal toxicity.
- Moderate aquatic toxicity.
- Not damaging to DNA, not genotoxic or mutagenic.
- Low biopersistence and not bioaccumulative.
- Repeated-dose toxicology similar to published results for other fluorotelomer alcohols studied. Benchmark dose analysis.
- Not expected to be harmful to human health or the environment at environmentally relevant concentrations. The results of these studies support no C, M or R classification for 6-2 FTOH for Reach classification and labelling

Potential degradation product is perfluorohexanoate (PFHxA) – Toxicology Profile:

- Low aquatic toxicity.
- Low acute oral toxicity.
- Not damaging to DNA, not genotoxic or mutagenic.
- Not a selective developmental or reproductive toxicant. Benchmark dose analysis.
- Low biopersistence and not bioaccumulative.
- Not expected to be harmful to human health or the environment at environmentally relevant concentrations.

For the surfactants used in AFFF (as an alternative to PFOS) Company 2 now uses the fluorotelomer raw materials with a perfluorinated 6 carbon chain (6-2 fluorotelomer) with potential degradation product being 6-2 fluorotelomer sulfonate (6-2 FTS). 6-2 FTS surfactant is not biopersistent, not bioaccumulative (BCF < 50) and less toxic (chronic fish NOEC of 2.6 mg/L) compared to PFOS and avoiding a possible indirect source of PFOA.

6-2 Fluorotelomer alcohol- raw material:

- Low acute oral and dermal toxicity.
- Moderate aquatic toxicity.
- Not damaging to DNA, not genotoxic or mutagenic.
- Low biopersistence and not bioaccumulative.
- Repeated-dose toxicology similar to published results for other fluorotelomer alcohols studied. Benchmark dose analysis.
- Not expected to be harmful to human health or the environment at environmentally relevant concentrations. The results of these studies support no C, M or R classification for 6-2 FTOH for REACH classification and labelling

Table 18 Overview alternatives for PFOS without a possible source of PFOA presented during the UNEP SAICM Workshop for Safer Alternatives

Company	PFOS-alternatives	Ready for market
Company 4	<p>Electrochemical fluorination (EFC) – PFBS “C4”</p> <p>$\text{H}(\text{CH}_2)_n\text{SH}$ aliphatic mercaptan</p> <p>$\downarrow \text{HF, e}^-$</p> <p>$\text{F}(\text{CF}_2)_n\text{SO}_2\text{F} \longrightarrow \text{F}(\text{CF}_2)_n\text{SO}_3\text{X}$</p> <p>Sulfonyl fluoride</p> <p>\downarrow</p> <p>$\text{F}(\text{CF}_2)_n\text{SO}_2\text{N(R)CH}_2\text{CH}_2\text{OH}$</p> <p>Perfluoroalkyl sulfonamido ethanol</p> <p>PFDS $n = 10$ PFOS $n = 8$ PFH₂S $n = 6$ PFBS $n = 4$</p>	
Company 2	<p>C6-based fluorotelomer</p> <p>$\text{CF}_2=\text{CF}_2$ (TFE)</p> <p>\downarrow</p> <p>$\text{F}(\text{CF}_2)_6\text{I}$ Perfluoroalkyl iodide</p> <p>\downarrow</p> <p>$\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{I}$ Fluorotelomer iodide</p> <p>\downarrow</p> <p>$\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OH}$ Fluorotelomer Alcohol</p>	2008-2010
Company 5	C6-based fluorotelomer	2006
Company 6	<p>C6-based fluorotelomer</p> <p>$\text{CF}_2=\text{CF}_2$ (TFE)</p> <p>\downarrow</p> <p>$\text{F}(\text{CF}_2)_6\text{I}$ Perfluoroalkyl iodide</p> <p>\downarrow</p> <p>$\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{I}$ Fluorotelomer iodide</p> <p>\downarrow</p> <p>$\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OH}$ Fluorotelomer Alcohol</p>	2012

Company 6

Company 6 reports to have designed fluorotelomer products with a perfluorinated carbon backbone of 6 to replace the 8 carbon backbone fluorotelomer products that were used as alternatives to PFOS. However, due to their 8 carbon perfluorinated backbone these first alternative products for PFOS contained a possible indirect source of PFOA.

The result is that 50% of the polymer product line has already been replaced. Company 6 is on track to cease manufacturing, use and sales of PFOA and the 8 carbon backbone fluorotelomer products by 2012.

Company 7 – (based on information from their website)

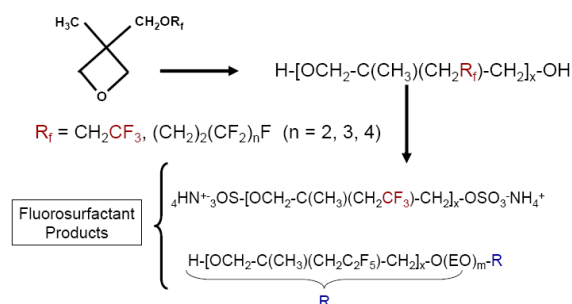
Company 7 has a brand for the portfolio of functional chemicals used as surface treatment in the paper and paperboard industry. All these grades are free of perfluoro-octane sulfonate (PFOS) and are not based on telomer chemistry, nor does it contain PFOA or will degrade into PFOA. PFPE-diol ($\text{HOCH}_2\text{-CF}_2\text{O})_m\text{-(CF}_2\text{CF}_2\text{O})_n\text{-CF}_2\text{CH}_2\text{OH}$) is the raw material of the PFPE.

This can, like the above examples, be considered as an alternative to PFOS without a possible indirect sources of PFOA.

Company 8 - (based on information from their website)

Company 8 has a fluorochemical technology with a full line of environmentally-preferred materials. Regulatory approvals have been obtained from agencies such as the US EPA, the U.K. Health and Safety Executive and Environmental Agency, METI in Japan and Environment Canada.

Their fluorochemicals are manufactures at their facilities in Mogadore, Ohio. Their fluorochemicals are unique hydrocarbon polyether polyols with fluorinated side chains of controlled chain length. They may be manufactured by substituting a fluorinated alcohol onto a halogenated methyl oxetane and undergoing ring opening polymerization. Both the degree of polymerization (molecular weight) and the length of fluorinated side chains can be controlled precisely.



Company 9

Company 9's textile business with chemicals intended for the use in the textile processing industry sells two new fluorocarbon finishing systems for stain repellence and release. These new systems are alternatives to PFOS but do not contain a possible indirect source of PFOA. Both contain the 6 fluorocarbon backbone-based finish and a booster, booster, which has been specially developed to enhance the performance of the 6 fluorocarbon finish. This does not reflect the position towards other markets only the Company 9 Textile chemicals.

With the 6 carbon backbone technology, perfluorooctanoic acid (PFOA) levels are reduced to below the detectable limit using state-of-the-art analytical methods. The 6 fluorocarbon protector do not require a hazard warning label in accordance with EC Directives.

Worst case consumer exposure is calculated based on expert judgment for both the textile treated with typical finish based C6-chemistry and typical finished based on conventional C8-chemistry:

- Typical finish based on conventional the 8 carbon backbone -chemistry
 - < 1000 ppb PFOA in a typical finish based on the 8 carbon backbone -chemistry
 - 100 g/L finish dosage in liquor (absolute worst case)
 - 70% pickup in the textile <then dry, cure>
- Result:** <70 ppb PFOA is expected to be in the finished textile

- Typical finish based on the 6 carbon backbone -chemistry
 < 5 ppb PFOA in a typical finish based on the 6 carbon backbone -chemistry
 100 g/L finish dosage in liquor (absolute worst case)
 70% pickup in the textile <then dry, cure>
 Result: <0.35 ppb PFOA is expected to be in the finished textile

Table 19 Comparison of PFOA levels of textiles treated with C6 and C8 based chemistry

Consumer articles	Amount present (mg/kg product)	Description consumer exposure route	Consumer exposure estimation (mg/kg bw/d)
Textile treated with typical finish based on the 6 carbon backbone -chemistry	< 0.35 ppb PFOA	Skin contact	about 0 mg/ kg bw /d
Textile treated with typical finish based on the conventional 8 carbon backbone -chemistry	< 70 ppb PFOA	Skin contact	about 0 mg/ kg bw /d

8.3 Alternatives for the derogated uses of PFOS

Chromium plating

The study team has been in touch with Company 10 regarding the possible alternatives on the use of PFOS in mist suppressants for chromium plating. Their alternative product, however, contains up to 2,5% of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanesulphonic acid (EC No. 248-580-6; CAS No. 27619-97-2). Polyfluorinated substances claim to have an improved environmental, health and safety profile. This is most probably due to the fact that they are less persistent and better biodegradable because of the lower number of highly stable C-F bonds in these molecules.

However, in the scientific, peer reviewed literature no such claim could be verified because in most cases per- and polyfluorinated substances are grouped together.

Hydraulic fluids

Company 11 informed the study team that after discussions with their hydraulic fluid suppliers it has become clear that up till this point in time no acceptable PFOS-free alternative is available, nor will an alternative be available in the near future. Suppliers indicated that significant resources and time (beyond the next five years) are needed to develop and test alternatives, and that the results of any such efforts are uncertain. Information on the quantity of PFOS contained in hydraulic fluid is said to be < 0.1% weight-by-weight. However, PFOS serves a very critical function as it is the only effective anti-erosion agent known for use in hydraulic fluid that qualifies to some aircraft specifications.

Semiconductor industry

It is important to consider that the semiconductor industry has taken proactive steps to move away from PFOS usage on non critical uses of PFOS over the past decade. However, this does not refer to the necessary continued use of PFOS which the semiconductor industry exemptions/derogation of PFOS for critical photolithography uses in photoresist and antireflective coatings (these are in the derogation to EC Marketing and use directive (2006/122/EC) and also exempted in the recent Stockholm Convention POP amendment.

Photographic Industry

The average use of PFOS per company decreased from 147 kg PFOS and related substances per year per company to 28 kg per year per company between 2004 and 2008. The decreasing use for PFOS-

related substances for the derogated uses is a trend that will most probably continue in the following years but at this point in time some critical uses remain as are defined in the derogation to EC Marketing and use directive (2006/122/EC).

Aqueous Film Forming Foams

New PFOS-based AFFF products are banned at EU level and the replacement of PFOS-based surfactants for AFFF is now ongoing. The major alternative product used is a telomersulphonate where 6 of the total of 8 carbon atoms are perfluorinated (generally referred to as a 6:2 fluorotelomer sulphontate) and therefore residual levels of PFOA will already be taken into account with the US EPA PFOA Stewardship data as already mentioned earlier.

However, the current basic fluorotelomer surfactants used in concentrations up to 0.5% in AFFF do contain traces of PFOA. It should be emphasized that the traces of PFOA in these PFOS-alternatives are much lower than the 200-1600 ppm of PFOA that might be present in PFOS-based AFFF. Current fluorotelomer based AFFF suppliers are in a continuous effort towards lowering the PFOA quantities below 1 mg/kg in the fluorotelomers that are present at maximum levels of 0.5% in AFFF. In other words, even if PFOA is present in concentrations <100 mg/kg fluorotelomer (used as an alternative to PFOS and related substances), the maximum concentration of PFOA due to trace levels in the PFOS-alternative fluorotelomer used in the final AFFF product will be <1 mg/kg and minimal risks are to be expected especially compared to the previously mentioned levels of 200-1600 mg PFOA/kg PFOS-based AFFF.

Currently non-fluorinated (organohalogen free) AFFF are on the market meeting the toughest amongst the fire fighting standards.

Conclusions

Alternatives for the direct uses of PFOA and for the other indirect sources of PFOA

Data on PFBS (perfluorbutanesulfonate) and PFHxA (perfluorohexanoic acid) have shown different pharmacokinetics (shorter half-life) and lower toxicity than PFOA (Workshop Safer Alternatives, 2009). However, because of the very different chemistries of various perfluorinated chemicals it is not possible to group them and impossible to properly compare the alternatives with PFOA for many years to come.

During the UNEP SAICM Workshop for Safer Alternatives, held in February 2009 in Geneva, Switzerland (UNEP, Geneva, 2009) four companies presented their alternatives to both PFOS (without possible indirect sources of PFOA) and the direct use of PFOA, including their health and environmental profiles, and when these alternatives will be ready for the market. Table 20 gives an overview of their alternatives and phase out date. As the alternatives will all be ready for market before 2015 the alternatives are available before that date and will be technical and economical feasible.

Table 20 Overview alternatives for both PFOS (without a possible indirect source of PFOA) and directly used PFOA as presented during the UNEP SAICM Workshop for Safer Alternatives

Company	PFOS-alternatives	Ready for market	PFOA-alternatives in fluoropolymer manufacturing	Ready for market
Company 4	Electrochemical fluorination (EFC) – PFBS “C4” $\text{H}(\text{CH}_2)_n\text{SH}$ aliphatic mercaptan $\downarrow \text{HF, e}^-$ $\text{F}(\text{CF}_2)_n\text{SO}_2\text{F} \longrightarrow \text{F}(\text{CF}_2)_n\text{SO}_3\text{X}$ Sulfonyl fluoride \downarrow $\text{F}(\text{CF}_2)_n\text{SO}_2\text{N(R)CH}_2\text{CH}_2\text{OH}$ Perfluoroalkyl sulfonamido ethanol PFDS $n = 10$ PFOS $n = 8$ PFH ₂ S $n = 6$ PFBS $n = 4$		Yes	2008
Company 2	C6-based fluorotelomer $\text{CF}_2=\text{CF}_2$ (TFE) \downarrow $\text{F}(\text{CF}_2)_6\text{I}$ Perfluoroalkyl iodide \downarrow $\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{I}$ Fluorotelomer iodide \downarrow $\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OH}$ Fluorotelomer Alcohol	2008	Yes	2015 or earlier if possible
Company 5	C6-based fluorotelomer	2006	Yes	2009
Company 6	C6-based telomer $\text{CF}_2=\text{CF}_2$ (TFE) \downarrow $\text{F}(\text{CF}_2)_6\text{I}$ Perfluoroalkyl iodide \downarrow $\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{I}$ Fluorotelomer iodide \downarrow $\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OH}$ Fluorotelomer Alcohol	2012	Yes	2012 (all product lines)

Information on alternatives to PFOA from the public domain shows already great improvements in the full environment, health and safety profile regarding their intrinsic properties when compared to PFOA and related substance. There seems to be a sharply decreased, if any, hazards for humans, workers and environment. However, most alternatives will be persistent although most of them show a lower persistency compared to PFOA. Therefore comparable abatement techniques used to reduce the emissions of PFOA will have to be applied for the alternatives. Further most applications are polymerised and releases for the consumer products will be limited.

There are some concerns regarding PFOA as contamination present in short-chain fluorotelomers. The US EPA evaluation of alternatives includes “contaminated significantly with longer chain-lengths perfluorinated substances of concern”. The polymerisation reaction to short-chain telomers is strictly regulated and further purified by a distillation procedure. The contamination level of PFOA may be <1% in the formulation that

will be used in the range of 100 mg/kg consumer products that as a consequence may contain sub-ppm amounts (below current detection levels) of PFOA.

Also, there may be some concerns regarding the formation of PFOA formed from perfluorinated compounds with shorter carbon chains, e.g. C6, C4 and C2. However, there is no information from the peer reviewed scientific literature indicating that such reactions are possible under environmental conditions. The conditions necessary to produce perfluorinated compounds (high temperature and high pressure) will not be met under the average environmental conditions.

It should be emphasized that the current minimum standards that are currently set by the US EPA and that these minimum standards are or will be applied in Europe and on a global scale by the participating companies in the US EPA PFOA Stewardship Program. This will most probably imply that PFOA and related substances will not be manufactured nor used (except for certain critical uses in photographic and/or semiconductor industry) any longer as from 2015.

Further, after 2018 REACH will serve as a control mechanism for these accomplishments because from that point in time any PFOA imported as from 1 tonne per annum needs to be registered. Sufficient enforcement capacity needs to be in place to ensure that PFOA will not be put on the EU market via imports as from 2018.

Additionally, the OECD is expected to take over the US EPA PFOA Stewardship campaign. Currently the OECD is considering how best to develop, facilitate and promote national and international product stewardship programmes and regulatory approaches for perfluorinated chemicals based on their existing work programmes and in association with other participating organizations of the IOMC.

9. DEROGATIONS FOR CERTAIN CRITICAL USES WITHOUT ALTERNATIVES (TASK 4)

Direct uses – Fluoropolymer manufacturing

Leading fluoropolymer manufacturers in the EU are committed toward the US EPA PFOA Stewardship Programme and work toward elimination of PFOA from emissions and products by 2015. As mentioned in the previous chapter these companies have already been notifying alternatives for evaluation toward the US EPA. These companies will most probably achieve to bring viable drop-in alternatives for the use of PFOA and related substances as a surfactant to market before 2015.

Direct Uses – Semiconductor industry (based on information received from EECA-ESIA European Semiconductor Industry Association)

Semiconductor industry uses PFOA related substances as a constituent material of a process chemical formulation in very specialized sensitive technical manufacturing application steps, such as in the photolithographic applications.

Photolithography is the critical process in defining the level of sophistication and performance of semiconductor devices. PFOA where it is used is stringently managed in the photolithography process. There is no release to the work place due to the use of closed systems processes. Solvent waste is collected at the factories and sent for incineration. Further exhaust systems with abatement equipment (scrubber) are used. There is very minimal release to the environment in wastewater. Based on an industry figure of usage per annum of <50kg, overall emissions through wastewater based on expert engineer knowledge of the process technology and waste stream would give rise to an estimated 4kg per annum. This is a conservative estimation – a worst case scenario.

The semiconductor industry and its supply chain are aware of the concerns regarding these chemicals, and efforts are underway to reduce, and where technically feasible, eliminate the current uses of the relatively minor nature of such uses.

Non-critical applications (i.e. where non-PFOA based alternatives exist, or may become available) include:

- the uses as a surfactant. Like PFOS, PFOA may be used as a wetting agent to enhance adhesion properties in various chemistries across different industry sectors. The trend in the semiconductor industry is to phase out PFOA for non critical uses as happened with the phase out on non critical uses of PFOS over the past decade. It is important to consider that the semiconductor industry has taken proactive steps to move away from PFOS usage where possible in the non critical applications in the past decade. This does not refer to the necessary continued use which the semiconductor industry exemptions/derogation of PFOS for critical photolithography uses in photoresist and antireflective coatings (these are in derogation to EC Marketing and use directive (2006/122/EC) and also exempted in the recent Stockholm Convention POP amendment).
- Uses outside of semiconductor production chemicals. There may be trace amounts of PFOA in materials such as glues, foils, tapes, where PFOA could be a very minor below ppm constituent.

Direct Uses – Photographic and imaging industry (based on information received from the EPIA, the European Photo and Imaging Association)

Since 2000 the photographic industry is conducting research, development and testing on possible alternatives. If available PFOA/APFO based products are replaced by alternatives. These alternatives are mostly fluorotelomers and other per- or polyfluorinated substances.

However, there are some remaining critical uses for which there are no suitable alternatives available yet. Research, development and testing for alternatives is still ongoing for these remaining critical uses. If restrictions are to be recommended for PFOA and related substances, photographic industry needs comparable derogations as are now in place for PFOS and related substances for certain critical uses as well because for these critical uses no alternatives exist at this point in time. Additionally, photographic industry will continue to ensure that exposure of man and the environment to PFOA and related substances will be limited to the remaining critical applications which are likely to reduce further as the trend to digital imaging continues.

The average use per company decreased from 1000kg PFOA/APFO and related substances per year per company to < 500kg per year per company between 2004 and 2008.

Other possible direct uses

No other possible critical uses of PFOA are identified by the study team. It is confirmed by the company 10 that PFOA is not contained in any of their products in the electroplating processes. Also various manufactures of hydraulic fluids confirmed that PFOA is not used in hydraulic fluids. Therefore no derogations for PFOA will be required for these applications.

Indirect sources

Fluorotelomer and fluoropolymer products

With regard to alternatives developed within the US EPA PFOA Stewardship Program, US EPA has received mainly shorter chain-length fluorotelomeric substances (Workshop Safer Alternatives, 2009). In consistency with the US EPA PFOA Stewardship Program, it is required that alternatives do not contain significant levels longer chain-length perfluorinated substances of concern as unintended by-products. The fluoropolymers made within the companies committed toward the US EPA PFOA Stewardship Program will in 2015 manufacture fluoropolymers without PFOA as polymerisation aid. Therefore the residual levels of PFOA will be taken into account with the US EPA PFOA Stewardship.

If fluorotelomers and fluoropolymer products are imported from outside the EU these products may still contain PFOA as unintended by-product. Additional activities should be undertaken for global PFOA elimination.

10. CONCLUSIONS AND RECOMMENDATIONS (TASK 5)

During the kick-off meeting the following tasks have been identified:

- Task 1: Market analysis
- Task 2: General assessment and analysis
- Task 3: Evaluation of the risk profiles for PFOA and APFO
- Task 4: Identification & definition specific uses without alternatives
- Task 5: Recommendations on specific uses without substitutes

Based on work of the team, working in close co-operation with the DG Enterprise Project Manager, we have come to following conclusions:

PFOA and related substances are probably the best studied chemicals. Even at this point in time, on average, a new peer reviewed scientific study is published every working day. Although already a lot is known on PFOA there seems to be only limited scientific consensus.

Task 1: Market analysis

The market volume of PFOA and related substances has a decreasing trend from 2002 onwards in the EU-27 Member States. For the period 2004-2008 the average market volume is estimated at maximal 100 tonnes per annum, direct and indirect sources included. The trend of the use of PFOA and related compounds is further decreasing and the market volume outlook for 2010 will most probably be less than 50 tonnes per annum, direct and indirect sources included.

Uncertainties of the Market Analysis

The largest uncertainty in the market analysis lies in the levels of PFOA as an unintended by-product in imported fluorotelomer based products used in consumer products and in the residual levels of PFOA in imported consumer articles. For EU Member States currently a legal framework is lacking to further investigate these levels of PFOA in consumer articles.

Further it should be noted that the information presented in this report is based on the questionnaires received from the industrial stakeholders and that due to the commercially sensitive (CBI) nature of this information only a range or rounded figure could be presented in this report.

Task 2: General assessment and analysis

Using a strict interpretation of the results of the PFOA risk assessment in this report leads to the conclusion that there seems to be no risk for human health in the EU-27 Member States. However, due to uncertainties with regard to carcinogenic and developmental effects firm conclusions on health risks are not possible. Furthermore, PFOA and APFO at the present level of understanding do not meet the criteria as given in Annex XIII of the REACH regulation EC/1907/2006 for PBT or vPvB substances.

Regarding the risk for the environment, it can be concluded that there seems to be no risk for the aquatic, terrestrial and atmospheric compartment. No risk could be identified for the microbial activity in sewage treatment systems.

However, these outcomes may be challenged due to various uncertainties which can be summarised as follows.

Uncertainties in the human health risk assessment

First of all there is evidence that PFOA shows developmental toxicity in experimental animals. From general human health studies there is a suggestion of a negative association between estimates of maternal exposure to PFOA and fetal growth or fertility in humans. However, a number of concerns have been raised about these data including the possibility that they may not be the result of a true causal relationship.

Challenges remain in interpreting human biomonitoring study results (Emmett et al 2006a,b; Calafat et al. 2007a,b). A more biologically complete kinetic model will support risk assessment and interpretation of human biomonitoring results.

From epidemiological occupational exposure and general human health studies there is only an association between PFOA and prostate cancer, the evidence is not conclusive. Some increases in prostate cancer have been seen, but the cause is not certain.

From Canadian sources a final report on the possible carcinogenic properties is expected by the end of 2009. Furthermore, other epidemiological results from the US C8 research project are expected to be published by the end of 2009 as well.

From the above information it seems to be clear that PFOA and related compounds will most probably be classified as a Category 2 Reprotoxicant. This classification of PFOA as Reprotoxicant 2 is also foreseen in the Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009). The classification of PFOA and its salts as Reprotoxicity Category 2 was agreed in the former TC C&L group in exECB 2006 after the closure of the 31ATP to Directive 67/548/EEC, and was therefore not included in the 1ATP to the CLP Regulation 1272/2008/EC. The Norwegian rapporteur will update their Annex XV C&L dossier on PFOA and send it to ECHA in December 2009. This updated dossier might serve as a basis for possible restrictions for the direct and/or indirect use of PFOA.

Uncertainties regarding the PBT-criteria

Although in the strict sense PFOA is not bioaccumulative according to the REACH Annex XIII criteria, another bioaccumulation mechanism seems to take place due to the fact that PFOA is found in the blood of the general public with a half-life of approximately 4 years. This effect might be judged as of equivalent concern although blood levels of PFOA seem to be decreasing. The decrease might be a result of the decreasing trend in the direct use of PFOA from 2002 onwards.

Uncertainties regarding the environmental risk assessment

From the information in the Risk assessment of perfluorooctanic Acid (PFOA) as part of a strategic partnership between German authorities and industry (2009) there seems to be no risk for the environment. No new data were found which could be used for the revision of risk assessment for the environment.

Task 3: Alternatives evaluation

Alternatives for the direct uses of PFOA in fluoropolymer production

It is clear that given the commitment of industry to the US EPA PFOA Stewardship Programme it is important that alternatives must perform technically and meet HSE conditions as a first priority and that the cost of the alternative although important is a secondary issue. It should be recognised that there are

different processes and different process conditions which are needed to be met. It is highly unlikely that there will be only one single alternative of PFOA that can be applied for all the different processes and different process conditions in which PFOA is presently being used. Only experience gained on the longer term will allow to determine the optimum replacements.

At this moment accurate information on the economic feasibility of alternatives could not be given as most alternatives are still under development for the different processes and different process conditions. One alternative is already being produced. However, the pricing information of this alternative could not be provided as the manufacturer does not sell it on the open market and considers this information as confidential business information (CBI). This manufacturer pointed out that the use of the alternative is not a major cost/pricing component in the fluoropolymer production.

The fluoropolymer production is the major direct user of PFOA as processing aid. In this production sector alternatives of PFOA are being developed. Other direct uses include that in the semiconductor industry and in the photographic industry. In these industries no suitable alternative for PFOA for some critical applications are available yet. See task 4.

Alternatives of other indirect sources of PFOA

The direct uses of PFOA in the fluoropolymer production, the semiconductor industry and the photographic industry are considered as direct sources of PFOA in the environment.

Indirect sources of PFOA in the environment are related to fluorotelomer production as unintended by-product, use of resins and dispersions contaminated with PFOA and the use of alternatives to PFOS which may contain trace levels of PFOA in fluoropolymer industry. The development of short-chain fluorotelomer products without PFOA as unintended by-product and the development of alternatives to PFOS without trace levels of PFOA are already available or will become available before 2015.

Task 4: Identification & definition of specific uses without alternatives

In photographic industry as well as semiconductor industry certain critical uses of PFOA are identified.

In the semiconductor industry non-PFOA based alternatives appear to be available for some non-critical applications like the uses as a surfactant. However, there still remain critical uses in the semiconductor industry. These mainly concern uses of PFOA related substances as a constituent material in process chemical formulations for very specialized application steps, such as for the photolithographic applications.

In the photographic industry PFOS and PFOA have comparable critical photographic applications but can not be substitutes by each other. Some individual companies use PFOS for their critical photographic application while others use PFOA for comparable photographic applications. For those companies which use PFOA within their critical photographic applications the same derogations based on the same argumentation as for PFOS will be necessary to continue their production.

In both other derogated uses of PFOS that is in the hydraulic fluids and in the electroplating process, no PFOA is presently being used and therefore no derogations for PFOA will be required for these specific applications.

Task 5: Conclusions and Task 5: Recommendations on specific uses without alternatives

For critical uses without current alternatives in photographic and semiconductor industry, the study team proposes derogations if PFOA is used under strictly controlled conditions as set out in Art 18(4) of REACH and referred to in Annex XI section 3.

In general, authorisation of PFOA will not be a sensitive instrument to control PFOA in consumer products as residues of PFOA in finished products, which are typically between 0.1 and 1% of the total content of fluorinated substances.

Recommendations for restrictions, including derogations for uses without suitable alternatives (TASK 5) Based on the new data used for the hazard and environmental risk assessment of PFOA/APFO during this study there seems to be no foundation to impose further restrictions on the use of PFOA/APFO. However, due to the uncertainty in PFOA levels in imported consumer articles it is recommended that detailed research is done on the levels of PFOA in consumer articles, especially those consumer articles that are not produced in the EU-27. From discussions with competent authorities in the various EU Member States it has become clear that a legal framework is lacking to further investigate these levels of PFOA in consumer articles. In case a legal framework is to be developed for this purpose the nomenclature for perfluorinated compounds need to be made more uniform. Industry and its associations are currently working on this aspect. Furthermore, a normalised analytical standard needs to be developed to enable comparison of the results from the various EU Member States.

Further, uncertainty appears to be unclarity as to whether and to which extent PFOA may be formed from precursor substances, and which are the most relevant precursor substances. It is recommended that more research will have to be done on the precursors of PFOA and more efforts have to be made to gather information on international level using the available information of the various international bodies to come to a internationally/globally recognised list of precursor substances. The OECD could be the platform best used for bringing together all this international information. However, the OECD has already put up a list of possible precursor substances that is used by international bodies as well as industry.

When new information on the risks for human health and environment will become available and when based on that information further restrictions on the use of PFOA will be imposed, a number of derogations might be considered. These derogations are to be time-limited based on the expectations that the PFOA Stewardship Programme when executed by the OECD will have a more global coverage. Time limited derogations might include a number of critical uses:

- The direct uses of APFO and APFN in the fluoropolymer industry as a direct source in the environment;
- The proces applications as indirect sources of PFOA in fluorotelomer production as unintended by-product, use of resins and dispersions contaminated with PFOA and the use of alternatives to PFOS which may contain trace levels of PFOA in fluoropolymer industry.
- Certain critical **uses** of PFOA and related substances in photographic and semiconductor industry.

It is required that these industries further define these critical uses and that PFOA and related substances are only used under strictly controlled conditions.

Given the goal of the PFOA Stewardship Programme the ultimate phase-out deadline for the direct use of PFOA and related compounds of 2015 might be considered as a starting point.

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APPENDIX 1

List of potential PFOA precursors

FINAL REPORT

LIST OF POTENTIAL PFOA PRECURSORS

Fluoropolymers such as polytetrafluoroethylene (PTFE) are considered stable and thus not a PFOA precursor. PFOA and related substances are used as surfactants in the production of fluoropolymers and very low concentrations of PFOA and related substances may be present in the finished products, but PFOA and related substances are not incorporated into the polymer structure.

In this project we used the following list of possible PFOA precursors and higher homologue chemicals that may degrade to PFOA. The study team did not receive any information, although it was asked in our questionnaire, that other PFOA precursors and/or higher homologue structures that may degrade to PFOA were used in the EU-27 member states.

<i>PFOA precursors</i>		
Methyl perfluorooctanoate	376-27-2	206-808-1
1,1,1,2,2,3,3,4,4,5,5,6,6,7,7, 8,8-Heptadecafluoro-8-iodo-octane	507-63-1	208-079-5
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl acrylate	27905-45-9	248-722-7
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl methacrylate	1996-88-9	217-877-2
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-decanol	678-39-7	211-648-0
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-decene	21652-58-4	244-503-5
<i>Higher homologues that may degrade to PFOA</i>		
1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-Pentacosafuoro-12-iodo-dodecane	307-60-8	206-205-3
1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Henicosafuoro-10-iodo-decane	423-62-1	207-030-5
Heptadecafluoro-nonanoic acid	375-95-1	206-801-3
Nonadecafluoro-decanoic acid	335-76-2	206-400-3
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-decanol	678-39-7	211-648-0
1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-10-iodo-decane	2043-53-0	218-053-5
1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Henicosafuoro-12-iodo-dodecane	2043-54-1	218-054-0
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Nonacosafuorohexadecyl methacrylate	4980-53-4	225-627-9
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Henicosafuorododecyl acrylate	17741-60-5	241-732-2
Carboxylic acids, C7-13, perfluoro, ammonium salts	72968-38-8	277-138-5

Further, there is consensus in industry that the Lists of PFOS, PFAS, PFOA, PFCA, Related compounds and Chemicals that may degrade to PFCA (OECD, 2007) provides, at this current point in time the best overview of the substances that are recognised as PFOA and its related substances and the substances that may possibly degrade to PFOA.

This document can be found using the following link:

[http://www.ois.oecd.org/ois/2006doc.nsf/LinkTo/NT00000F9A/\\$FILE/JT03231059.PDF](http://www.ois.oecd.org/ois/2006doc.nsf/LinkTo/NT00000F9A/$FILE/JT03231059.PDF)

APPENDIX 2

List of consumer products that may contain a source of PFOA

FINAL REPORT

LIST OF CONSUMER PRODUCTS THAT MAY CONTAIN A SOURCE OF PFOA

(Sources: Kemi, 2006; SFT, 2007, Washburn et al, 2005, Begley et al 2005, Danish EPA, 2008, Guo et al, 2009)

Direct use of APFO in (imported) consumer products:

- non-stick (PTFE-coated) cookware
- flexible (PTFE) inlays for frying pans
- non-stick (PTFE-coated) kitchen utensils
- tread sealant (PTFE) and tape
- apparel membranes
- dental floss and tape
- fluoro-ethylene propylene copolymer (FEP) tubing

Indirect PFOA (trace) levels possible:

- Various household cleaning products with water, oil, grease & dirt resistance/protection and/or anti-static properties:
 - o Floor polish and wax products
 - o Floor sealant products
 - o Wood sealant products
 - o Stone (tile, marble, granite) sealer/protection products (sprays, polish)
 - o Carpet protector products (concentrate, spray, shampoo)
 - o Carpet spot & stain remover products
 - o Polish for plastics
 - o Glass & hotplate cleaning products
 - o Leather protection products
 - o Upholstery cleaning/protection products
- Stain repellent home textile & upholstery
 - o microfiber fabric
 - o carpet
 - o mat
 - o slip cover
 - o mattress pad
 - o table cloth
 - o ironing board cover
 - o cotton throw
 - o impregnation products for carpets & mats
 - o impregnation products for furniture (textile and leather)
- Stain & water repellent (all weather) clothing (textile and leather)
 - o Pants (insulated, regular)
 - o Shorts
 - o Skirts
 - o Dresses
 - o Shirts (including polo shirts, T-shirts, blouses)
 - o Coats, jackets, parka's
 - o Hats & caps
 - o Umbrellas
 - o Gloves
 - o Shoes & boots
 - o Impregnating products for (breathable) textile
 - o Impregnating products for leather
 - o Impregnating products for footwear

- Bags and suitcases (leather & textile)
- Tents
- Sails
- Sunshades
- Shower curtains
- Fat resistant food contact materials
 - o wrapper paper
 - o paper bags
 - o cartons
 - o popcorn bags (microwave)
 - o baking paper
 - o Disposable paper tablecloths
 - o Disposable paper plates
- Animal food paper packaging
- Wallpaper
- Hand held foam fire extinguishers
- Latex paint
- Printing inks
- Tire shine
- Car spray wax
- Car wheel cleaner
- Deck cleaner
- Boat polish
- Ski wax
- Photographic film additives

APPENDIX 3

EPA's summary of 2009 Company Progress Report

EPA's Summary Tables for 2009 Company Progress Reports

Table 1. Reported Emissions and Product Content of PFOA, Precursors, and Higher Homologues from U.S. Operations

Company	Second Year Reductions	Chemical Category	Emissions		Product Content		
			Releases to all media from FP and Telomer Manufacturing (kg)	kg of release / kg of product produced	Dispersions (ppm wet-weight basis)	Other Fluoropolymers (ppm dry-weight basis)	Telomers (ppm dry-weight basis, unless stated otherwise)
Arkema	2008	PFOA and Higher Homologues	>1,000 – 10,000	>0.001 – 0.01	>100 - 300	>50 - 100	Not Applicable
		Precursors	Not Applicable				
Asahi	2008	PFOA, PFOA salts and Higher Homologues	0	Not Applicable	0	0	Not Applicable
		Precursors	Not Applicable				
Ciba	2008	PFOA	0 kg (total for emissions and product content)				
		Higher Homologues	0 kg (total for emissions and product content)				
		Precursors	0 kg (total for emissions and product content)				
Clariant	2008	PFOA and PFOA salts	Not Applicable				
		Direct Precursors					
Daikin	2008	PFOA	<100	None reported	<10	<15	<5 kg
		Precursor and Higher Homologues	<50	None reported	Not Applicable	Not Applicable	CBI
DuPont	2008	PFOA and PFOA Salts	686	None reported	9	13	16 kg ^a
		Higher Homologues	None Reported	None reported			None reported
		Precursors	CBI	None reported	None reported	None reported	<3 kg ^b
Dyneon/3M	2008	PFOA, PFOA salts and Higher Homologues	0	0	0	0	No Telomer Production
		Precursors	0				
Solvay Solexis, Inc	2008	PFOA, PFOA salts	Not Applicable	Not Applicable	<25ppm	170-200	Not Applicable
		Higher Homologues	>1,000- 10,000	0.01 -0.001			
		Precursors	Not Applicable				

Table 2. Reported Emissions and Product Content of PFOA, Precursors, and Higher Homologues from Non-U.S. Operations

Company	Second Year Reductions	Chemical Category	Emissions		Product Content		
			Releases to all media from FP and Telomer Manufacturing (kg)	kg of release / kg of product produced	Dispersions (ppm wet-weight basis)	Other Fluoropolymers (ppm dry-weight basis)	Telomers (ppm dry-weight basis, unless stated otherwise)
Arkema	2008	PFOA and Higher Homologues	>1,000 – 10,000	For FP Production: (>0.1-1) kg/100kg	Not Applicable	>50 – 100	Not Applicable
		Precursors	Not Applicable				
Asahi	2008	PFOA, PFOA salts and Higher Homologues	3,885	For FP Production: <1%	5-2,900	18	Negligible as compared to precursors
		Precursors	1,921	For Telomer Production: <1%	Not Applicable	Not Applicable	Average 50% (range: 0-100%)
Ciba	2008	PFOA	13.5 kg (total for emissions and product content)				
		Higher Homologues	11.2 lbs (total for emissions and product content)				
		Precursors	1172.3 kg (total for emissions and product content)				
Clariant	2008	PFOA and PFOA salts	0.5	For Telomer Production: 0.00000015	None Reported	None Reported	>2
		Direct Precursors	<2	For Telomer Production: 0.0000005	None Reported	None Reported	39
Daikin	2008	PFOA	<1,900	None reported	<100	<70	<5 kg
		Precursor and Higher Homologues	<700	None reported	Not Applicable	Not Applicable	CBI
DuPont	2008	PFOA and PFOA salts	779	None reported	58	0	16 kg ^c
		Higher homologues	None reported	None reported			None reported
		Precursors	None reported	None reported	None reported	None reported	<3 kg ^d
Dyneon/3M	2008	PFOA, PFOA salts and Higher Homologues	1,020	For FP Production: <1kg/100kg	4	3	No Telomer Production
		Precursors	0				
Solvay Solexis, Inc	2008	PFOA, PFOA salts and Higher Homologues	Not Applicable				
		Precursors	Not Applicable				

Reported Percent Reductions in Emissions and Product Content

Table 3. Reported Percent Reductions in Emissions and Product Content of PFOA, Precursors, and Higher Homologues from U.S. Operations (cumulative percent reductions from baseline year through end of 2008)

Company	Second Year Reductions	Chemical Category	% Reduction in Emissions	% Reduction in Product Content		
			% Reductions in total quantity of chemical(s) released from baseline year	Fluoropolymer Dispersions	Other Fluoropolymers	Telomer based products
Arkema	2008	PFOA and Higher Homologues	30%	66%	44%	Not Applicable
		Precursors	Not Applicable			
Asahi	2008	PFOA, PFOA salts and Higher Homologues	100%	100%	100%	Not Applicable
		Precursors	Not Applicable			
Ciba	2008	PFOA	100% (total for emissions and product content)			
		Higher Homologues	100% (total for emissions and product content)			
		Precursors	100% (total for emissions and product content)			
Clariant	2008	PFOA and PFOA Salts	Not Applicable			
		Direct Precursors				
Daikin	2008	PFOA	99%	99%	>25%	>80%
		Precursor and Higher Homologues	>95%	Not Applicable	Not Applicable	>90%
DuPont	2008	PFOA and PFOA Salts	99%	99%	96%	97%
		Higher Homologues	None reported			
		Precursors	CBI	None reported	None reported	97%
Dyneon/3M	2008	PFOA, PFOA salts and Higher Homologues	100%	100%	Not Applicable	No Telomer Production
		Precursors	No Precursor Production			
Solvay Solexis, Inc	2008	PFOA, PFOA salts Ad Higher Homologues	36%	98%	0%	Not Applicable
		Precursors	Not Applicable			

Table 4. Reported Percent Reductions in Emissions and Product Content of PFOA, Precursors, and Higher Homologues from Non-U.S. Operations (cumulative percent reductions from baseline year through end of 2008)

Non-U.S. Operations (Cumulative percent reductions from baseline year through end of 2008)						
Company	Second Year Reductions	Chemical Category	% Reduction in Emissions % Reductions in total quantity of chemical(s) released from baseline year	% Reduction in Product Content		
				Fluoropolymer Dispersions	Other Fluoropolymers	Telomer based products
Arkema	2008	PFOA and Higher Homologues	CBI	Not Applicable	CBI	Not Applicable
		Precursors	Not Applicable			
Asahi	2008	PFOA, PFOA salts and Higher Homologues	61%	54%	PFOA content in this product is negligible as compared to that in dispersions	Negligible as compared to precursors
		Precursors	51%	Not Applicable	Not Applicable	
Ciba	2008	PFOA	97.1% (total for emissions and product content)			
		Higher Homologues	97.5% (total for emissions and product content)			
		Precursors	Increase of 67.7 % (total for emissions and product content)			
Clariant	2008	PFOA and PFOA Salts	95%	None Reported	None Reported	60%
		Direct Precursors	>60%	None Reported	None Reported	61%
Daikin	2008	PFOA	>85%	>95%	>60%	>80%
		Precursor and Higher Homologues	>80%	Not Applicable	Not Applicable	>80%
DuPont	2008	PFOA and PFOA Salts	96%	95%	100%	97%
		Higher Homologues	None reported			
		Precursors	None reported	None reported	None reported	97%
Dyneon/3M	2008	PFOA, PFOA salts and Higher Homologues	93%	99%	0%	No Telomer Production
		Precursors	No Precursor Production			
Solvay Solexis, Inc	2008	PFOA, PFOA salts and Higher Homologues	Not Applicable			
		Precursors	Not Applicable			

^a Number represents global emissions of telomer manufacturing.

^b Number represents global emissions of telomer manufacturing.

^c Number represents global emissions of telomer manufacturing.

^d Number represents global emissions of telomer manufacturing.

APPENDIX 4

List of consulted stakeholders

FINAL REPORT

The following organisations and institutions were contacted in developing the market analysis and risk assessment of PFOA/APFO. An asterisk indicates organisations that have responded either by providing information or by completing questionnaire that was subsequently passed to us.

EU Member State Competent Authorities

Austria
Belgium*
Bulgaria
Cyprus*
Czech Republic*
Denmark*
Estonia*
Finland*
France*
Germany*
Greece
Hungary*
Ireland*
Italy*
Latvia*
Lithuania*
Luxembourg
Malta*
Netherlands*
Norway*
Poland
Portugal
Romania
Slovakia
Slovenia*
Spain
Sweden*
Switzerland
United Kingdom*

EU Trade Associations

Association Internationale de la Savonnerie de la Detergence et des Produits d'Entretien (AISE)
 European Chemical Industry Council (CEFIC)*
 European Council of Paint, Printing Ink & Artists' Colours Industry (CEPE)*
 Confederation of European Paper Industries (CEPI)*
 Commission on Engineering & Technical Systems (CETS)
 European Association for Textile Polyolefins (EATP)
 EDANA*
 European Electronic Component Manufacturers Associations (EECA)
 European Industrial Gases Association (EIGA)*
 European Photo and Imaging Associated Industry Association (EPIA)*
 Euratex
 Eurocord
 EUROFEU
 European Semiconductor Industry Association (ESIA)*
 Fédération Européenne des Aérosols (FEA)
 Association of European adhesives and sealants manufacturers (FEICA)
 European Association of Chemical Distributors (FECC)*
 Plastics Europe Fluoropolymers Committee*

EU NGOs & Trade Unions

European Consumers' Organisation (BEUC)
 ChemSec
 ChemTrust
 EU Environmental Bureau*
 EU Health & Environment Alliance
 EU Trade Unions
 Friends of the Earth Europe
 Greenpeace
 Women in Europe for a Common Future (WECF)*
 WWF

National Trade Associations

Chemicals & Chemical traders

AECQ (Spain)
 ASSIC (Italy)
 BKCH (België)*
 CBA (UK)
 Essencia/Fedichem (België)*
 IBEC (IE)
 Groquifar (Portugal)
 Mavesz (Hungary)
 Schod (CzRep)
 TKL (Finland)
 UFCC (France)
 VCH (Germany)
 VCI
 VNCI (Netherlands)*

Textile associations

Organisation	Country
IBEC	Ireland
GZS	Slovenia
Textiles	Poland
Modint	Netherlands
Fedustria*	Belgium
Textile*	Finland
c-i-t-a	Germany
Heimtex	Germany
Hup	Bosnia
Miroglio	Italy
	UK
PKS	Yugoslavia
Textile	France
Textile-mode	Germany
Skee	Greece
Axelero	Hungary
	Latvia
	Turkey
PiPex	UK
Swiss Textiles	Switzerland
Teko	Sweden
Aitpa	Spain
Atop	Slovak Rep
	Romania
ATP	Portugal
Nors Industri	Norway
Latia	Lithuania
Textiel	Netherlands
	France
Amith	Marocco
SGC	Egypt
INSTM	Italy
HGK	Bosnia
FEI	Egypt
	France
Ros Textile	Russia
TMG	Portugal
Wernertex*	Belgium

Fire Extinguishers**Organisation**

Bgfire (Bulgaria)
 FIA (UK)*
 Pelco (Finland)
 Ffmi (France)
 Zvei (Germany)
 Anie (Italy)
 Fme (Netherlands)*
 Tac (Norway)
 Tecnifuego Aespi (Spain)
 Swelarm (Sweden)

Detergents**Organisation**

FEMIN

Fachverband der Chemischen Industrie Österreichs (F.C.I.O.)
 Association Belgo-Luxembourgeoise des Producteurs et des Distributeurs de Savons, Cosmétiques, Détergents, Produits d'Entretien, d'Hygiène et de Toilette, Colles, Produits et Matériel Connexes ASBL (DETIC)
 Bulgarian Association of the Detergent Industry (BADI)
 Cyprus Aerosol, Detergents & Cosmetics Manufacturers Association
 Committee for Detergents with the Czech Association for Branded Products (CSZV)
 Brancheforening for Saebe, Parfume og Teknisk/kemiske Artikler (SPT)
 Federation of Estonian Chemical Industries (EKTL)
 Teknokemian Yhdistys ry
 Association Française des Industries de la Détergence, de l'Entretien et des Produits d'Hygiène Industrielle (AFISE)
 Chambre Syndicale Nationale de l'Eau de Javel et des Produits Connexes (C.S.N.E.J.)
 İndustrieverband Hygiene und Oberflächenschutz Für Industrielle und Institutionelle Anwendung e.V. (I.H.O.)*
 Industrieverband Körperpflege- und Waschmittel e.V. (IKW)*
 Association of the Greek Industry of Detergents and Soaps (SEVAS)*
 Hungarian Cosmetic and Home Care Association (KOZMOS)
 Irish Cosmetics & Detergents Association (I.C.D.A.)
 Assocasa - Associazione Nazionale Detergenti e Specialità per l'Industria e per la Casa
 The Association of Latvian Chemical and Pharmaceutical Industry
 Lithuanian Cosmetics and Household Chemicals Producers Association (LIKOCHEMA)
 Nederlandse Vereniging van Zeepfabrikanten (N.V.Z.)
 Vaskemiddelleverandørenes Forening (V.L.F.)
 Polish Associations of Cosmetics and Home Care Products Producers
 Associação dos Industriais de Sabões, Detergentes e Produtos de Conservação e Limpeza – (A.I.S.D.P.C.L.)
 Romanian Union of Cosmetics and Detergent Manufacturers (RUCODEM)
 Slovenské zdruzenie pre znackové výrobky (SZZV)
 Association of Cosmetics and Detergents Producers of Slovenia (KPC)
 Asociación de Empresas de Detergentes y de Productos de Limpieza, Mantenimiento y Afines (ADELMA)*
 Branschföreningen för Industriell och Institutionell Hygien (I.I.H.)
 UK Cleaning Products Industry Association (UKCPI)*

Country

Italy
 Austria

 Belgium
 Bulgaria
 Cyprus
 Czech Rep
 Denmark
 Estonia
 Finland

 France
 France

 Germany
 Germany
 Greece
 Hungary
 Ireland
 Italy
 Latvia
 Lithuania
 Netherlands
 Norway
 Poland

 Portugal
 Romania
 Slovak
 Republic
 Slovenia

 Spain
 Sweden
 UK

Paper**Organisation**

FFIF
 AUSTROPAPIER
 COBELPA
 ACP
 COPACEL
 VDP
 Federation of the Hungarian
 Printers and Paper Makers
 ASSOCARTA
 Royal VNP
 Norsk Industri
 SPP
 CELPA
 ROMPAP
 ZCPP SR
 ASPAPEL
 SFIF
 CPI

Surface treatment**Organisation**

Mirashowers*
 IVF*
 EFORIT
 VOM
 VOM
 AIAS
 ASFIMET
 ASSICC
 ASSO Galvanica
 DFO
 Grenzow
 Ivente
 FME
 nickel institute
 Buczko
 Sea
 Syf
 Ucif
 Uits
 VDMA
 ZVO

Country

UK*
 Sweden*
 Finland
 Netherland
 Belgie
 AIAS (spain)
 Italy
 Italy
 Italy
 Germany
 Denmark
 Norway
 Netherlands
 UK
 Poland
 UK
 Sweden
 Italy
 France
 Germany
 Germany

Manufacturers, Importers & Downstream Users**Company name**

3M*
Dyneon/3M*
DuPont*
Miteni*
Arkema*
Azoty Tarnow
AGC Chemicals Europe*
Solvay Corporate/ Solvay Solexis
Bayer*
Clariant*
Chemtura*
Wacker Chemie*
PPG
PolyComply Hoechst*
BASF*
Ashland/Hercules*
Total
Schmalfluss
Exxon Mobil*
Avery Dennison*
FujiFilm Manufacturing*
Kolb
Eastman
Nalco*
Mobacc
Smit & Zoon
Bondia Tricot
Shell Chemicals
Atotech*
Sara Lee*
Akzo Nobel
Ciba*
Grupo Forquisa
Dow Corning Europe
Polyfluor Plastics

Fire Extinguishers

Company name

Ansul/Tyco*

Ansul

Solberg*

Autronautica

Chubb UTC

Saval

Fomtec

Anaf

ADT/Tyco

Hydraulic Fluids Aviation

Company name

Boeing*

StorkFokker*

ExxonMobil*

Saab*

Solutia

Shell

BP/Castrol

Kendall/PhillipsConoco

EADS

Bombardier

APPENDIX 5

Analytical challenges for the detection of PFOA

Development of analytical methods for the detection of PFOA

The below information is based on the information received by Stefan Posner (Swerea, Sweden), prof. Pim de Voogt (University of Amsterdam, The Netherlands) and Dr. Stefan van Leeuwen (Vrije Universiteit, Amsterdam, The Netherlands)

For the development of an analytical method for the detection of PFOA in the various matrices it is, as a first challenge, important to have a clear definition for PFOA. This definition is also very important in if put in a legal framework where the limit value of detectable PFOA in various fluoropolymer and fluorotelomer based products may be determined by the levels of non-chemically bound PFOA in- or excluding possible PFOA-precursors and fluorotelomer based products that may contain chemically bound perfluorinated 8 (or more) carbon atom chains that may degrade to PFOA as an unintentional by-product.

The development of an analytical standard for PFOA is probably as complex as the development of this standard for PFOS analysis.

If a analytical standard would include non-chemically bound and chemically bound PFOA or PFOA-releasers (precursors, homologues, degradation products) this would imply an analytical method that can liberate PFOA from polymeric chemically bound PFOA and/or PFOA from its possible degradation products.

The largest challenge will be the percentage of indirect PFOA (from precursors and higher homologues) and direct PFOA that can be possibly detected with a standardized analytical method.

The next analytical challenge lies in the separate quantification of branched & linear isomers. These isomers may sort different toxicological effects. Branched internal standards are now coming available. This might be a larger problem/challenge for sulfonates because linear PFOA isomers are the most commonly found PFOA isomers found in the environment.

The main contamination problems are within the (PTFE) tubing of the analytical instrumentation but could also include all-weather clothing, fluoropolymers used in laboratory gloves or treated laboratory textiles.

Matrices	Validated analytical methods available?	Limit of quantification?
<i>Consumer products</i>	No, parallels with PFOS can be drawn. Special attention for laboratory contaminants (gloves, clothing, tubing in analytical instruments)	
<i>Food products</i>		
Plants & vegetables	Not yet, under development (under PERFOOD)	
Meat	Not yet, under development (under PERFOOD)	
Milk	Not yet, under development (under PERFOOD)	
Fish	yes	0,1-1,0 ng/g fish (parts per billion)
<i>Water</i>		
Surface water	yes	0,1-1,0 ng/L (parts per trillion)
Marine water	yes	0,1-1,0 ng/L (parts per trillion)
Groundwater	Not yet	
Drinking water	probably not yet validated, under development (under PERFOOD);	
Soil/Sediment	Not validated yet; interlab validation not yet performed	
Air	Validation in progress	
House Dust	Not validated yet; in progress by University of Antwerp	
Waste Water Treatment Sludge	Not validated yet; interlab study in progress	

Most PFOA publications are on toxicology and only a very limited amount does provide the details of the analytical methods used. Protocols need to be developed first before levels of PFOA (either as residual contaminant or as an unintended by-product) in consumer products, food and various environmental matrices levels can be determined with a high degree of certainty. As a next step protocols need to be tested in ring studies and validated.

Currently most consumer product testing protocols, if any, are not validated.

The Modified Powley method may be used for clean-up of samples, especially for samples with very low levels of quantification of PFO. However, this method does not include any information on sample extraction, pre-treatment or instrumental analysis. It might be useful for the detection of PFOA in environmental & food products, but the exact modified method used needs to be described in as much detail as possible.

Finally, all analytical methods need to be described in detail to verify quality. Scientific assessment of the analytical description remains necessary to judge the ultimate quality of study.