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**REPORT OF AN OECD WORKSHOP ON PERFLUOROCARBOXYLIC ACIDS (PFCAs) AND  
PRECURSORS**

Stockholm, Sweden, 20 - 22 November 2006

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**No. 23**

**Report of an OECD Workshop on  
Perfluorocarboxylic Acids (PFCAs) and Precursors**

**Stockholm, Sweden, 20 – 22 November 2006**

**IOMC**

**INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS**

**A cooperative agreement among UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD**

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## FOREWORD

The 39<sup>th</sup> Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology (15-17 February 2006) welcomed the offer by Sweden to host a workshop on “PFOA and Related Substances” and noted that a workshop back-to-back to the November 2006 Joint Meeting would be opportune. A Steering Group for organising this workshop was established with Australia, Canada, Germany, Italy, Japan, Sweden, Switzerland, the US, the EC, BIAC, DuPont, 3M, Environmental NGO and the Secretariat. The OECD Workshop on Perfluorocarboxylic acids (PFCAs) and Precursors was held on 20-22 November 2006 in Stockholm, Sweden.

This document provides a report of the workshop. It was compiled by the OECD Secretariat in close collaboration with Sweden and the Steering Group, on the basis of the material provided to and in the workshop.

This document is published on the responsibility of the Joint Meeting of the Chemicals Committee and Working Party on Chemicals, Pesticides and Biotechnology.

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## EXECUTIVE SUMMARY

### Objectives of the Workshop

The objectives of the workshop were to:

- Exchange information on on-going activities in OECD member countries regarding research, environmental monitoring, risk assessment and risk reduction related to PFCAs and precursors;
- Identify gaps in knowledge and assessment needs for both long and short-chain PFCAs and precursors;
- Discuss which circumstances contribute to our concerns and how they could be mitigated; and
- Develop recommendations for future activities. However, risk management recommendations were outside the scope of the workshop.

### Context of the Workshop

The widespread occurrence of certain perfluorinated compounds in the environment, in certain animal species, as well as in humans, has attracted great attention. Perfluorinated compounds are known to be persistent. Some of these compounds are bioaccumulating, in particular those with long carbon chains, and some have been reported to cause toxic effects in laboratory animals.

Perfluorooctane sulfonate (PFOS) was the first among the perfluorinated compounds to be found in significant levels in various environmental media. The major US producer of precursors to PFOS ceased the manufacture of these compounds a number of years ago. PFOS has been regulated within the US, is reviewed for risk reduction measures within the EU and is under discussion as a candidate substance for the Stockholm Convention, and for the Convention on Long-range Transboundary Air Pollution (LRTAP) Protocol on Persistent Organic Pollutants (POPs Protocol). PFOS belongs to the PFAS-group of chemicals.

Another group of perfluorinated substances, perfluorocarboxylic acids (PFCAs), has recently been reported to increase over time in the environment, in particular in the Arctic. The occurrence of these substances in animal species and in man has been reported in many countries.

PFCAs in the environment come from different sources. Examples of point sources are production plants, e.g. production of fluorotelomers, fluoropolymers, or APFO. Another source of the wide occurrence of PFCAs in the environment has been reported to be releases of PFCA-precursors, such as fluorotelomer alcohols, from products. PFCA-precursors are present in the products either as residuals or can possibly be formed through degradation of fluorotelomer-based substances. Another source that has been identified is release of PFCAs from the manufacture of fluoropolymers, such as polytetrafluoroethylene (PTFE).

In Canada, the Ministers for Health and Environment have imposed a temporary prohibition of four fluorotelomer-based polymers. Environment Canada and Health Canada have recently proposed an action plan for assessment and management of PFCAs and precursors.

In the United States, the Environmental Protection Agency (EPA) has launched a global stewardship programme inviting companies to reduce facility emissions and product content levels of perfluorooctanoic acid (PFOA), PFOA-precursors and higher homologue chemicals. All eight companies that were contacted have committed to participate in this programme. EPA has also entered into Enforceable Consent Agreements and Memoranda of Understanding with industry to generate certain data, including studies on incineration of fluoropolymers and fluorotelomer-based polymers, and environmental sampling and monitoring in the vicinity of fluoropolymer manufacturing facilities. PFOS, PFOA, and related chemicals have been included in the US national human biomonitoring programme. PFOA belongs to the PFCA group of chemicals

In the EU, PFOA is currently prioritised for hazard classification concerning health and environmental effects. Several research programmes regarding sources, exposure and effects of these substances are ongoing in Canada, USA and in other countries. In EU a research programme (PERFORCE) is aiming at the European exposure assessment based on field data and modelling.

### **Workshop Agenda and Participation**

The focus of the workshop was on perfluorocarboxylic acids (PFCAs) and their precursors. Session 1 consisted of 7 *scientific and technical reviews* provided by leading scholars, NGOs and governmental experts in this area, and focusing on the production and use of PFCs, their environmental monitoring, environmental long-range transport and fate, their health and environmental implications and societal value.

Session 2 reviewed the *ongoing risk mitigation activities* in the OECD, EU, the US, Canada and Japan.

Session 3 consisted of *breakout group discussions* and Session 4 on the *outcomes of breakout group discussions*, concentrating on the assessment and research needs, risk reduction approaches and the use, trends and alternative chemistries for PFCs. The discussions were held in four parallel breakout groups, on the basis of a separate set of questions for each group.

Session 5 focused on the conclusions and recommendations of the workshop.

In total 55 experts attended this Workshop, representing 11 OECD countries, European Commission, academia, industry and environmental NGOs.

### **Recommendations**

The workshop identified recommendations to OECD, Member Governments, Academia and Industry. It was recognised, however, that the identified information needs should not be misinterpreted as preventing conclusions in a regulatory context concerning risk assessment or management decision-making.

#### ***Recommendations to the OECD***

- Start an activity aiming at examination of international harmonisation of methods regarding bioaccumulation (possibly including biomagnification) determination of certain perfluorinated substances;

- The OECD and BIAC need to define a cooperative process of how to collect more reliable data on the OECD survey; there is a need to find a way to improve the collection of information from companies. Correlation between the use and production volumes of PFCs is important to be able to identify and prioritise chemicals from a potential exposure perspective; and
- An Information Sharing or Clearing House repository under the auspices of the OECD should include scientific information reported from Member countries and Industry.

#### ***Recommendations to the OECD to work with Governments and Industry***

- Encourage member countries to launch outreach efforts to promote risk reduction programmes (in particular the present US/Canada Stewardship Programmes) and play a coordinating role in collating information on available programmes;
- Encourage BRIC-countries and other non-OECD countries to be involved in programmes similar to the US Stewardship Programme aimed at reducing exposure levels. Governments and Industry should report to the OECD ongoing scientific risk assessments and risk reduction programmes in place that are aimed at reducing potential exposures;
- Encourage Industry to share information on technologies effective in reducing environmental releases;
- Advise Governments to encourage companies to provide information on the chemical content of articles in the form of labelling or web-based product content disclosures; and
- Advise Governments to encourage Industry to apply the basic principles of Green Chemistry to new product development.

#### ***Recommendations to Industry***

- Information on the composition of commercial substances which are potential sources of PFCAs and their precursors should be made available. Similarly, to assess end use articles' contribution to the emission of PFCAs and their precursors, information should be made available including identity of the substances applied to the articles and the level of residual PFCA precursors present;
- Report to the OECD ongoing scientific risk assessments and risk reduction programmes in place; and
- Consider adding toxicity data into a global portal e.g. an existing database such as US EPA AQUIRE (or the new OECD Global Portal).

#### ***Recommendations to Industry, Governments and Academia on Assessment and Research Needs***

The workshop identified several data gaps and research needs in areas such as monitoring, emissions, exposure, environmental fate and transport as well as potential effects on human health and the environment. Governments, Industry and Academia should take note of the recommendations and initiate activities aimed at closing the most important data gaps. Below is a summary of the recommendations:

- Further studies, such as biomonitoring studies and multi-media studies, are needed to clarify direct and indirect sources of PFCAs and to inform on human end environmental exposure assessment
- Toxicity studies are needed especially on PFCAs with chain lengths other than C4 and C8, and on precursors to PFCAs;
- Further studies are needed regarding toxicokinetics, growth, development, hepatic effects tumorigenicity and other endpoints (e.g. circulating sex hormones); and
- Further studies are needed to address bioaccumulation and biomagnification potential in wildlife other than fish.

**GLOSSARY OF ACRONYMS**

PFCA	Perfluorocarboxylic acids, PFOA is one example
PFHxA	Perfluorohexanoic acid
PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnA	Perfluoroundecanoic acid
PFDoA	Perfluorododecanoic acid
PFTTrA	Perfluorotridecanoic acid
PFTA	Perfluorotetradecanoic acid
PFPeA	Perfluoropentadecanoic acid
PFAS	Perfluoroalkyl sulfonates, one example is PFOS
PFOS	Perfluorooctane sulfonate
PFBS	Perfluorobutane sulfonate
PFOS-related substances	All substances that can break down to PFOS
PFOA-related substances	All substances that can break down to PFOA
FTCA	Fluorotelomer carboxylic acid
FTOH	Fluorotelomer alcohol, component in commercial products that can break down to PFCAs
PTFE	Polytetrafluoroethylene
ETFE	Ethylenetetrafluoroethylene
PVDF	Polyvinylidene fluoride
ECF	Electrochemical fluorination

## WORKSHOP REPORT

### 1. Objectives of the Workshop

The objectives of the workshop were to:

1. Exchange information on on-going activities in OECD member countries regarding research, environmental monitoring, risk assessment and risk reduction related to PFCAs and precursors;
2. Identify gaps in knowledge and assessment needs for both long and short-chain PFCAs and precursors;
3. Discuss which circumstances contribute to our concerns and how they could be mitigated; and
4. Develop recommendations for future activities. However, risk management recommendations are outside the scope of the workshop.

### 2. Context of the Workshop

#### 2.1 Background

Perfluorinated substances have been produced and used since the 1950s for their unique properties, e.g. resistance to high temperatures and water, stain and oil and grease repellence. They are sometimes spoken of as 'new' environmental pollutants. The reason for this is probably that it has only been possible to analyse perfluorinated substances in the environment and in humans since the late 1990s. Before that, analytical methods were not sufficiently refined.

Perfluorooctane sulfonate (PFOS) and PFOS-related substances have received a lot of attention since the year 2000 when the major global manufacturer, 3M, decided to cease the production of these substances. The production and use of PFOS-related substances have decreased substantially since that time. The risks of PFOS have been assessed in several different jurisdictions, and by some of them PFOS have been found to be persistent, bioaccumulative and toxic (PBT). Risk reduction measures exist or are being developed in several countries, in the EU and globally. Several producers are supplying other perfluorinated substances as substitutes, mainly fluorinated telomers, which have the same attractive technical properties. Although some of these replacement substances have shorter chain lengths, and are expected to have a more favourable hazard profile, some of them could potentially have adverse effects on health and the environment.

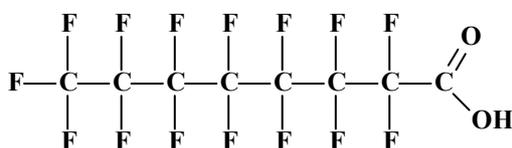
Perfluorocarboxylic acids (PFCAs) and fluorotelomer-based substances have been used for various purposes for several decades, and with the move toward ceasing PFOS production,

## 2.2 Perfluorinated Substances

Substances within the group of perfluorinated substances are characterised by containing a fully fluorinated carbon chain; all hydrogens in that part of the chain are exchanged for fluorine atoms.<sup>1</sup> The bond between carbon and fluorine is a very strong chemical bond, making perfluorinated substances persistent. Examples of perfluorinated substances are perfluoroalkyl sulfonates (e.g. PFOS) and perfluorocarboxylic acids (e.g. PFOA).

PFAS is a generic term used to describe any fully fluorinated carbon chain length sulfonate, and includes higher and lower homologues as well as PFOS. PFAS-related substances may be simple salts or polymers that contain the PFAS as only a portion of the entire polymer.

Perfluorocarboxylic acids (PFCAs) are fully fluorinated carboxylic acids, perfluorooctanoic acid (PFOA) (see Fig. 1) having attracted the most attention due to its structural similarity with PFOS. Other PFCAs include perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), and so on, which are named according to the length of the carbon chain.

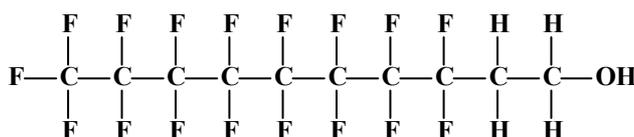


**Figure 1. Perfluorooctanoic acid, PFOA**

PFCAs, themselves rarely used in products, have been used commercially since the 1950s as fluoropolymerization aids (FPAs) to make fluoropolymers. Commercially, however, there are commonly used substances known as fluorotelomers, e.g. substances derived from fluorotelomer alcohols (FTOHs), or other fluorotelomer-based substances, some of which can degrade to PFCAs. Fluorotelomers are a subgroup of perfluorinated substances that are produced by a process called telomerisation, and can occur in a range of fluorocarbon chain lengths.

Fluorotelomer alcohols are not fully fluorinated since they have a 2C hydrocarbon chain linked to the perfluorinated carbon chain (e.g. 8:2 FTOH depicted in Figure 2). Fluorotelomer epoxides, olefins or alcohols are often used as building blocks in the production of fluorotelomer-based substances. Fluorinated chains are thus built into the substances, giving them oil, grease, water and stain repellent properties. Some fluorotelomer-based substances can be further exploited as monomers to generate polymeric fluorotelomer substances with the same characteristic properties.

<sup>1</sup> Kissa, E. (2001), *Fluorinated Surfactants and Repellents*, Second edition, Marcel Dekker Inc., New York.



**Figure 2. 8:2 Fluorotelomer alcohol-building block for fluorotelomer-based polymeric product**

The OECD has compiled a preliminary list of approximately 850 known perfluorinated substances to facilitate future data collection on their production and use, including chemicals that can potentially break down to PFCAs.<sup>2</sup>

Fluoropolymers such as polytetrafluoroethylene (PTFE) are considered stable and thus not a PFCA precursor. Certain PFCAs are however used as processing aids in the production of fluoropolymers and very low concentrations of PFCAs may be present in the finished products, but PFCA is not incorporated into the polymer structure.

### 2.2.1 Production

There are two major production methods for the production of perfluorinated substances: electrochemical fluorination (ECF) and telomerisation.<sup>3</sup> A difference between the two process methods is that the ECF process gives both linear and branched substances, and telomerisation only leads to linear substances. The perfluorinated substances formed in these processes can then be further processed to different derivatives and polymers.<sup>4</sup>

The largest producers of fluorotelomers are DuPont, Daikin, Clariant and Asahi Glass. During 2004 an estimated 72 000 tonnes of product were sold, containing 11 250 - 13 500 tonnes of active fluorotelomer ingredients.<sup>5</sup> Another source estimates that the production of fluorotelomer alcohols is 12 000 tonnes per year.<sup>6</sup> Additional sources indicate that the production and use of fluorotelomer alcohols are more in the order of 6000 tonnes per year<sup>7</sup>

There were four producers of APFO (the ammonium salt of PFOA) in 2005: Miteni, DuPont, Daikin and a Chinese producer. The yearly production of APFO during 1995-2002 has been estimated to be 200-300 tonnes.<sup>8</sup>

<sup>2</sup> Preliminary Lists of PFOS, PFAS, PFOA and related compounds and Chemicals that may degrade to PFCA, ENV/JM/MONO(2006)15 (<http://www.oecd.org/env/riskmanagement>).

<sup>3</sup> Prevedouros K., I. T. Cousins, R. C. Buck and S. H. Korzeniowski (2006), Sources, fate and transport of perfluorocarboxylates, *Environ. Sci. Technol.*, 40:32-43.

<sup>4</sup> Kissa, E. (2001), *Fluorinated Surfactants and Repellents*, second edition., Marcel Dekker Inc., New York.

<sup>5</sup> NERA Economic Consulting (2006), *Societal benefits assessment for fluoropolymers and fluorotelomers*, Prepared for DuPont fluoroproducts and DuPont Chemical Solutions Enterprise.

<sup>6</sup> Dupont Global PFOA Strategy Update: Presentation to USEPA-OPPT, January, 31, 2005, *US Public Docket AR226-1914*, US Environmental Protection Agency.

<sup>7</sup> Personal communication, DuPont, 2006

<sup>8</sup> Prevedouros, K., I. T. Cousins, R. C. Buck and S. H. Korzeniowski (2006), Sources, fate and transport of perfluorocarboxylates, *Environ. Sci. Technol.*, 40:32-43.

### 2.2.2 Use

Perfluorinated substances are used in many types of products where their capacity to form smooth water, oil, grease, and stain repellent surfaces is desirable.

Fluorotelomers are used in products as surfactants or surface treatment chemicals. They are either used as major active ingredients in a formulation (e.g. in fire fighting foams) or as a very minor component in more complex formulations (e.g. in impregnating products).

Examples of fluorotelomer uses are:<sup>9</sup>

- As wetting agents, anti-foaming agents and impregnating agents for **textiles**; according to DuPont, textile applications are the largest use of fluorotelomers<sup>10</sup>; examples of end products are sportswear, workwear, carpets and soft furnishings;
- As a grease resistant barrier in e.g. **paper** wrapping for oily or greasy food;
- In **fire fighting foams**; fluorotelomer surfactants with six perfluorinated carbons are commonly used; and
- As a levelling agent or surfactant in coatings, polishes, waxes, window cleaners and other **cleaning products**, for consumer or industrial use.

PFOS and PFOS derivatives were used in many of these same applications prior to the recent phase-out of most PFOS-based products.

The main use of PFOA is as a processing aid in the production of fluoropolymers, e.g. polytetrafluoroethylene (PTFE). Another PFCA, perfluorononanoic acid (PFNA), is used in a similar way, mainly in the production of polyvinylidene fluoride (PVDF).<sup>11</sup> Fluoropolymers are typically used in non-stick cookware, electronics, textiles, wire and cables coating, semiconductors, etc.

### 2.3 Existing Alternative Substances

Fluorotelomer alcohols and other precursors of fluorotelomer substances, which can degrade to PFCAs, have been produced since the 1970s, and were simultaneously on the market with PFOS. Notably, with the phase-out of PFOS, the primary manufacturer (3M) chose to substitute PFOS with either short chain perfluoroalkyl sulfonates, e.g. perfluorobutane sulfonate (PFBS), or fluorotelomers.

Several companies are now developing products with shorter carbon chain lengths. PFBS has been produced commercially by 3M since 2003 and seems to have lower potential for bioaccumulation than longer chain perfluorinated substances, but is very persistent in the environment.

Fluorine free alternatives (chemicals and techniques) are available and in use for certain applications, e.g. for some textile and paper applications in Sweden. However, perfluorinated substances have unique properties and in many cases, companies have found it difficult to develop alternatives that are

<sup>9</sup> Perfluorinated substances –The use in Sweden, KemI report 2006 (forthcoming).

<sup>10</sup> Personal communication, DuPont, 2006.

<sup>11</sup>Prevedouros, K., I. T. Cousins, R. C. Buck and S. H. Korzeniowski (2006), Sources, fate and transport of perfluorocarboxylates, *Environ. Sci. Technol.*, 40:32-43.

as functional and efficient.<sup>12</sup> Some of the possible alternatives may also cause adverse effects and need further investigation. Examples of such alternatives are found among siloxanes and nanomaterials.

## 2.4 Hazard Assessment

More can be learned about the hazardous properties of many PFCAs, such as how they are dispersed in the environment and how we are exposed to them. It can be said with certainty that this is a group of extremely persistent substances. Some demonstrate bioaccumulative or bioaccumulation-like properties and there are indications that concentrations of PFCAs in certain Arctic animals are increasing.

### 2.4.1 Chemical properties

Perfluorinated substances are very stable due to the very strong chemical bond between carbon and fluorine. This bond is not broken by acids or bases and it resists oxidation and reduction, even at high temperatures.<sup>13</sup> It is also resistant to photolysis.<sup>14</sup>

The solubility of neutral perfluorinated substances (e.g. perfluorooctane, fluorotelomer alcohol) is low in both water and organic solvents (e.g. octanol). In contrast, anionic perfluorinated substances (e.g. PFCAs, perfluoroalkyl sulfonates) contain both hydrophobic and a hydrophilic end, and can be very water soluble. In all cases the perfluoroalkyl chain is of such low surface energy it preferentially seeks interfaces e.g. between water and organic solvents or between a fluid and a solid surface. As a result of this the partitioning between octanol and water,  $K_{ow}$ , is less useful and difficult to determine for this group of substances.<sup>15</sup>

### 2.4.2 Persistence

Fluorotelomer alcohols and other PFCA precursors may be degraded in the environment to PFCAs which are extremely persistent. Available data indicate there are no known degradation mechanisms for PFCAs under environmentally relevant conditions.

### 2.4.3 Bioaccumulation

Increasing the carbon chain length of PFCAs tends to increase their bioaccumulation in fish and clearance time in certain mammals. Based on bioconcentration factors and biomonitoring studies, some of the longer carbon chain PFCAs (>8C) are considered bioaccumulative. Monitoring data show the widespread presence of low levels of PFCAs in wildlife, and based on archived tissue samples, increasing concentrations in certain species over time. There are field studies providing evidence of biomagnification, meaning higher concentrations are found in organisms at higher levels of the food chain.

While laboratory based studies indicate PFOA (C8) does not bioaccumulate in fish, data suggests a potential for PFOA (C8) to biomagnify in certain marine food chains or biota.<sup>16,17</sup> PFOA has been

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<sup>12</sup> Perfluorinated substances –The use in Sweden, KemI report 2006 (forthcoming).

<sup>13</sup> Kissa, E. (2001), *Fluorinated Surfactants and Repellents*, Second edition., Marcel Dekker, Inc., New York.

<sup>14</sup> von Stedingk, H. and Å. Bergman (2004), En miljökemisk översikt av polyfluorerade kemikalier (PFCs). Institutionen för miljökemi, Stockholms Universitet, Stockholm.

<sup>15</sup> Kissa, E. (2001), *Fluorinated Surfactants and Repellents*, Second edition, Marcel Dekker, Inc., New York.

<sup>16</sup> Houde, M., J. Martin, R. J. Letcher, K. R. Solomon and D. C. G. Muir (2006), Biological Monitoring of Polyfluoroalkyl Substances: A Review, *Environ.Sci. Technol.*, 40:3463-3473.

detected in higher trophic level biota such as polar bears. Furthermore, it is noted that higher homologues are also detected in arctic animals and their contamination levels are significantly higher than that of PFOA.<sup>18</sup>

Due to the water, oil and grease repellent properties of PFCAs, they are not primarily accumulated in fat tissue like many other bioaccumulating substances. PFCAs preferentially bind to proteins and accumulate primarily in the liver and in the blood. The potential for bioaccumulation also differs significantly between animal species. The half-life of PFOA in human serum is 3.8 years, whereas the half-life in rats varies between 3 hours and 9 days depending on the individual and sex. Traditional testing methods for bioaccumulation may therefore give insufficient information, and may not account for observed levels in organisms at higher levels of food chains.

#### 2.4.4 Toxicity

The US EPA<sup>19</sup> is carrying out an extensive human health hazard assessment of PFOA and is also conducting research on other PFCAs. An evaluation (SIDS, Screening Information Data Set) of PFOA is also being carried out under the auspices of the OECD's High Volume Chemical Programme (although PFOA is not classified as a high production volume, HPV, chemical).

The EU Technical Committee on Classification and Labelling of Dangerous Substances has agreed that PFOA should be classified as follows (Summary Record of the Technical Committee Meeting of 3rd October 2006): Carc. Cat. 3; R40, Repr. Cat 2; R61, NC Repr. Cat. 3; R62, T; R48/23, Xn; R20/22, Xn; R48/22, Xi; R36.

For mammalian species, PFOA and its salts have been found to cause cancer in rats and adverse effects on the immune system in mice. In addition, PFOA and its salts can display reproductive or developmental toxicity in rodents at moderate levels of exposure, and moderate to high systemic toxicity in rodents and monkeys following long-term exposure by the oral route. The Science Advisory Board PFOA Review Panel of the US EPA has recommended that PFOA be classified as 'likely to be carcinogenic' to humans and that cancer risk assessment be performed.

Except for PFOA, there is very little information on the health and environmental effects of PFCAs. Despite the absence of robust toxicity data for longer chain PFCAs (C9 and greater) these substances could be reasonably expected to be of greater concern than PFOA as a result of their known slower clearance rates and higher bioaccumulation potential. It is suggested that longer chain PFCAs exhibit properties of persistent organic pollutants (POPs) as they are persistent, bioaccumulative, widespread through Arctic biota and based on data for PFOA, associated with adverse effects in laboratory animals.<sup>20</sup>

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<sup>17</sup> Tomy, G. T., W. Budakowski, T. Halldorson, P. A. Helm, G. A. Stern, K. Friesen, K. Pepper, S. A. Tittlemier and A. T. Fisk (2004), Fluorinated Organic Compounds in an Eastern Arctic Marine Food Web, *Environ. Sci. Technol.*, 38:6475-6481.

<sup>18</sup> Martin, J.W., M. M. Smithwick, B. M. Braune, P. F. Hoekstra, D. C. G. Muir and S. A. Mabury (2004), "Identification of long-chain perfluorinated acids in biota from the Canadian arctic, *Environ. Sci. Technol.* 38:373-380.

<sup>19</sup> US EPA, PFOA Homepage: <http://www.epa.gov/opptintr/pfoa/index.htm>.

<sup>20</sup> Action plan on perfluorocarboxylic acids and precursors, Environment Canada and Health Canada, <http://www.ec.gc.ca/nopp/DOCS/consult/PFCA/EN/actionPlan.cfm>

## 2.5 Sources, transport and exposure

### 2.5.1 Sources

PFCAs in the environment come from different sources. Examples of point sources are production plants, e.g. from the production of fluorotelomers, fluoropolymers, or APFO.

The use of fluorotelomer-based substances in different products is a diffuse source of PFCAs. Studies have shown that fluorotelomer alcohols can break down to PFCAs via atmospheric degradation as well as biological degradation. Studies from wastewater treatment plants with active sludge also show that final effluent concentrations of PFCAs are sometimes higher than the incoming concentrations.<sup>21</sup> The high occurrence of linear isomers of PFCAs in blood, as compared to branched isomers, also indicates that substances produced by telomerisation are an important source.<sup>22</sup>

PFCA precursors can be released from fluorotelomer-based substances in two ways:

- Through their release, because they are present as “residual” unreacted building blocks of fluorotelomer-based substances; and
- Through their release upon degradation of fluorotelomer-based substances; there are uncertainties regarding mechanisms and rates of degradation; consequently, the relative contribution of this source to environmental levels of PFCAs is uncertain.

Because the commercial fluorotelomer-based substances contain a range of fluorinated carbon chain lengths, the resulting PFCAs also contain a range of carbon chain lengths.

Studies of indoor air have shown the presence of PFCA precursors associated with dust particles, which suggests sources such as treated carpets or textiles. Analyses of textiles have shown that fluorotelomer alcohols, and also small amounts of PFCA and perfluoroalkyl sulfonate (PFAS) compounds, can be released from clothing and other textiles. The textile samples contained up to 10.7 mg/m<sup>2</sup> of FTOH.<sup>23, 24</sup>

In a set of survey-type experiments, PFCA precursors have also been reported at levels up to 3.8% in a study of several industrial and consumer products containing fluorotelomer-based substances, including certain surfactants, carpet protector products and windshield wiper fluid.<sup>25</sup>

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<sup>21</sup> Sinclair, E. and K. Kannan (2006), Mass Loading and Fate of Perfluoroalkyl Surfactants in Wastewater Treatment Plants, *Environ. Sci. Technol.*, 40:1408-1414.

<sup>22</sup> De Silva, A. O. and S. A. Mabury (2006), Isomer Distribution of Perfluorocarboxylates in Human Blood: Potential Correlation to Source, *Environ. Sci. Technol.*, 40:2904-2909.

<sup>23</sup> Statens Forensningstillsyn, Kartlegging av perfluoralkylstoffer i utvalgte tekstiler, Oslo, 2006. (English summary).

<sup>24</sup> Fluorerade miljögifter i allväderskläder, Svenska Naturskyddsföreningen, Rapport 2006. (English summary).

<sup>25</sup> Dinglasan-Panlilio, M. J. A. and S. A. Mabury (2006), Significant residual fluorinated alcohols present in various fluorinated materials, *Environ. Sci. Technol.*, 40:1447 -1453.

### 2.5.2 *Transport*

Several sources, such as discharges of industrial and municipal wastewater, fire-fighting operations at military bases and airports, and landfill leachate may all be responsible for the elevated exposure to perfluorinated substances in urban areas.

However, perfluorinated substances are also detected in remote regions such as the Arctic and the mid-Pacific, far from known sources. Evidence indicates certain PFCA precursors, e.g. fluorotelomer alcohols, are volatile and subject to long-range transport via the atmosphere<sup>26</sup>, and that this may be a possible explanation for the increasing concentrations in the Arctic.<sup>27</sup> PFCAs themselves may also be subject to long-range transport via oceanic currents.<sup>28</sup>

### 2.5.3 *Exposure*

PFCAs are found in a variety of environmental media such as indoor air, dust, food and drinking water that may contribute to human exposure.

Fish have been found to be a source of exposure in humans.<sup>29</sup> Overall, the patterns of exposure to perfluorinated substances are different between humans and animals, indicating that fish and mammals may not be the major source of exposure in humans. Personal care and cleaning products, in addition to indoor dust, may constitute additional exposure routes. A potential source of exposure to PFOA is migration from food-packaging, e.g. microwave popcorn bags, through metabolism of fluorotelomer-based precursors.<sup>30</sup> Studies of PFOA release from non-stick cookware did not show detectable amounts of PFOA.<sup>31</sup>

### 2.5.4 *Monitoring*

There are studies indicating that PFOA is present in human blood with a rather even global distribution, while other perfluorinated substances show higher concentrations in the vicinity of industrialised areas<sup>32</sup>.

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<sup>26</sup> Ellis, D. A., J. Martin, A. O. De Silva, M. D. Hurley, S. A. Mabury, M. P. Sulbaek Andersen and T. J. Wallington (2004), Degradation of fluorotelomer alcohols: a likely atmospheric source of PFCA, *Environ. Sci. Technol.*, 38:3316-3321.

<sup>27</sup> Renner, R (2006), 3-D modelling substantiates perfluorinated theory, *Environ. Sci. Technol.*, 40: 632- 633.

<sup>28</sup> Prevedouros K., I. T. Cousins, R. C. Buck and S. H. Korzeniowski (2006), Sources, fate and transport of perfluorocarboxylates, *Environ. Sci. Technol.*, 40:32-43.

<sup>29</sup> Falandysz, J., S. Taniyasu, A. Gulkowska, N. Yamashita and U. Schulte-Oehlmann (2006), Is fish a major source of fluorinated surfactants and repellents in humans living on the Baltic coast?, *Environ. Sci. Technol.*, 40:748-751.

<sup>30</sup> Begley, T. H., P. Honigfort, M. L. Twaroski, R. Neches and R. A. Walker (2005), Perfluorochemicals: potential sources of and migration from food packaging, *Food. Addit. Contam.*, 22:1023-1031.

<sup>31</sup> Powley, C. R., M. J. Michalczyk, M. A. Kaiser and L. W. Buxton (2005), Determination of PFOA extractable from the surface of commercial cookware under simulated cooking conditions by LC/MS/MS, *Analyst*, 130:1299-1302.

<sup>32</sup> Houde, M, J. W. Martin, R. J. Letcher, K. R. Solomon and D. C. G. Muir (2006), Biological Monitoring of Polyfluoroalkyl Substances: A Review, *Environ. Sci. Technol.*, 40:3463-3473.

Other monitoring data show widespread low concentrations of PFCAs (C8 to C15) throughout Arctic biota. Increased concentrations were measured in wildlife feeding at higher trophic levels (e.g. polar bears, seals), suggesting biomagnification. There is evidence that for C9 and C10 PFCAs, the concentrations found in polar bear liver have been doubling every 5 to 8 years, indicating increasing PFCA levels in the environment.<sup>33</sup>

## **2.6 Risk characterisation**

It is clear that PFCAs are a group of very persistent substances and that some PFCAs are bioaccumulative and toxic. There are indications of increasing concentrations in mammals in the Arctic. There is thus reason for concern that serious long-term problems may arise from these long-lived substances, already wide-spread in the environment, and with known hazardous properties, as demonstrated in laboratory animals. The increasing concentrations may rise even further if the use of PFCAs and PFCA precursors increase further.

Additional research will improve our understanding of their hazardous properties, environmental transport and exposure to humans as well as exposure to wildlife and organisms in the environment.

## **3. Setting the Scene – Presentation Summaries**

### **3.1 OECD 2006 Survey on Production and Use of Perfluorinated Compounds (PFCs)**

*Dr. Sneha Satya, NICNAS, Australia: OECD 2006 Survey on Production and Use of PFOS, PFAS, PFOA, PFCA, their Related Substances and Products/Mixtures Containing these Substances*

In 2006, the OECD surveyed the manufacture, importation and use of perfluorinated compounds and mixtures containing these substances in member and non-member countries [See ENV/JM/MONO(2006)36]. The 2006 OECD survey was a follow up of the 2004 survey. The perfluorinated chemicals covered the perfluoroalkyl sulfonate (PFAS) compounds including perfluorooctane sulfonate (PFOS) and perfluorocarboxylic acid (PFCA) compounds including perfluorooctanoic acid (PFOA). Data were collected on production, import and use of the above substances for the year 2005 (or 2004 if 2005 data did not exist). Seventeen OECD countries, 6 non-OECD countries and 2 companies responded to the survey. In addition, the European Chemicals Bureau (ECB) forwarded information on these chemicals from the IUCLID database. Most countries provided information on volumes manufactured and/or imported as ranges due to confidentiality of business information or regulatory restrictions. Australia prepared a report based on the responses to the survey for the 40<sup>th</sup> OECD Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology in November 2006.

The responses to the survey did not provide a comprehensive picture of the manufacture, importation or use of perfluorinated chemicals, however, it gives a general trend of the global use of these chemicals. There is a decrease in the numbers and quantities of PFOS and PFOA-related substances manufactured and used globally. Most countries that responded to the survey indicated that PFBS-based substances (C4) were the main PFAS compounds used and that these are replacing PFOS/PFOA related substances. The production volume of PFBS based compounds has increased markedly since the 2004 survey.

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<sup>33</sup> Action plan on perfluorocarboxylic acids and precursors, Environment Canada and Health Canada, <http://www.ec.gc.ca/nopp/DOCS/consult/PFCA/EN/actionPlan.cfm>

Only one PFCA-related substance was reported in the 2006 survey. However, the quantities and numbers of PFCA precursors were much greater than those reported in the other chemical groups surveyed. Greater focus will be on chemicals in this group specifically relating to the degradation mechanisms, toxicity, definition of PFCA precursors and the subclasses of precursors.

The quality of responses to the 2006 survey, particularly regarding chemical names and CAS numbers, has improved as compared to the 2004 survey. This improvement may be due to the publication of the OECD "Preliminary Lists of PFOS, PFAS, PFOA and Related Compounds and Chemicals that may degrade to PFCA" [ENV/JM/MONO(2006)15].

### 3.2 *Environmental Monitoring, including Biomonitoring*

*Ass. Prof. Pim de Voogt, IBED, University of Amsterdam: Results of the Perforce Project*

The PERFORCE project started in July 2004 and covered a period of two years. Its principal aim was to make an exposure assessment of perfluorinated organic compounds (PFCs) in the European environment. Several tools were considered necessary to fulfil the task indicated above. These included the development of chemical analytical and bioanalytical tools for identification and quantification of the compounds, the validation of these methods, and the collection of relevant physicochemical compound property data that would serve to understand their fate and to model and explain their behaviour in environmental compartments. The tools were then used in a Europe-wide monitoring campaign that included sampling of surface waters, air, sediments, biota, and wastewater treatment plants. The campaign was aimed at identifying possible sources of PFCs, and establishing spatial and temporal trends in Europe.

The physicochemical data collected in this work confirm that atmospheric transport may be important for certain PFCs, notably the fluorotelomer alcohols. In addition they showed that the two major representatives of the PFCs, vis. PFOA and PFOS, do not accumulate in sediments, and that sorption to sediment does not strongly affect water-mediated transport of these PFCs. Sediment is probably not a major sink for PFOS, PFOA and shorter chain homologues. Sorption does increase with carbon chain length, however, and thus becomes more important in the environmental fate of longer chain PFAS.

The results of the sampling campaigns show that PFCs are ubiquitously present in the European environment. Sewage treatment plants probably serve as sources of PFAS both for the aquatic ecosystems (through effluent discharges) and the terrestrial environment (through application of sewage sludge in agriculture). Spatial differences were observed particularly in biota. PFOS and PFOSA concentrations were higher in North Sea cod liver than in cod liver from the Kattegat and the Baltic. In marine mammals, concentrations of PFOS are higher in species feeding close to the shore or in estuaries than in off shore feeders. A relationship appears to exist between concentrations of PFOS and trophic levels in marine mammals. In these mammals perfluorinated carboxylic acids are relatively low in all species and tissues analysed. PFOS, PFDA and PFUnA bioaccumulate in a simple estuarine food chain, while PFOA accumulates significantly less.

*Dr. Urs Berger, ITM, Stockholm University: Results from Water and Air Samples*

Within the PERFORCE project, PFCAs were analysed in the major European rivers. Rivers are expected to be the predominant pathway for PFCAs to the marine environment. PFOA was the dominating carboxylate with concentrations up to 23 ng/l, followed by PFHxA (typically up to 18 ng/l, with a maximum value in the Thames of 32 ng/l). PFHpA, PFNA, PFDcA and PFUnA were additionally detected in many river water samples. The annual European riverine fluxes of PFHxA, PFHpA, PFOA and PFNA were estimated to be in the order of 10, 2, 20 and 0.5 tonnes. The Danube and Rhine watersheds are

particularly important source regions, whereby the Elbe and Po also make a significant contribution for PFHxA and PFHpA/PFOA, respectively.

In European air, fluorotelomer alcohols (FTOHs) were the prevailing fluorinated compounds. FTOHs are possible precursor compounds for PFCAs. Due to their high volatility, they may undergo long-range atmospheric transport, and contribute to the load of long-chain PFCAs detected in remote regions like the Arctic. 6:2 FTOH and 8:2 FTOH were the dominating FTOHs found in the gas phase, with typical concentrations of 50-150 pg/m<sup>3</sup>. Alkylated perfluorooctane sulfonamides and sulfonamido ethanols were also present in the gas phase. Even these can be degraded to form PFCAs. PFOA was often the predominant PFCA found in the particulate phase. In the vicinity of industrial plants producing fluorinated compounds, particle associated PFOA was even the dominant fluorinated compound in air samples. In indoor air, FTOH concentrations were typically a factor 100 higher than in outdoor air, suggesting that the main source for FTOHs to the environment is evaporation from products and goods used in offices and homes.

### 3.3 *Environmental Long Range Transport*

*Prof. Scott Mabury, University of Toronto: Environmental Chemistry, Transport and Fate of Fluorinated Alcohols ~ the Indirect Route to Global Contamination*

The coating of carpets, fabrics and paper products with fluorinated polymers and surfactants imparts the water, stain, and oil repellency so highly desired for a variety of consumer products. Of significant scientific and regulatory interest is whether the world-wide occurrence of the highly persistent and bioaccumulative perfluorinated acids, such as PFOS<sup>34</sup> and PFOA, is connected to the use of these popular materials. PFOA and related long-chain perfluorinated alkylcarboxylates (PFCAs)<sup>35</sup> are of current interest to Environment Canada, US EPA, and other regulators. A working theory was constructed around the potential role of fluoroalcohols, the functioning component of the surface active materials, to serve as travel agents and precursors for the dissemination of these chemicals to the global environment.<sup>36</sup> Additional measurements and studies now provide substantial support for the 'precursor alcohol atmospheric reaction and transport' or PAART theory, though further work remains to fully clarify the relevant sources and reactions to ultimately solve the problem of environmental contamination of these persistent chemicals. Contamination of humans appears more complicated and is currently less clear.

Initial lab studies quickly indicated the chemical personality of the most prevalent poly-fluorinated chemicals, the fluorotelomer alcohols (FTOHs; typically linear perfluorinated chains) and fluorinated sulfamidoethanols (electrochemical production of significant branched chain isomers), was characterized by relatively high volatility. Though substantial differences exist in the published literature,<sup>37,38,39</sup> the published and available data suggest the air:particle-partitioning of these chemicals in

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<sup>34</sup> Giesy J. P., Kannan K. (2001), *Environ. Sci. Technol.*, 35:1339-1342.

<sup>35</sup> Martin, J. W., M. M. Smithwick, B. Braune, P. F. Hoekstra, D. C. G. Muir, S. A. Mabury. 2004. *Environ. Sci. Technol.*, 38:373-380.

<sup>36</sup> Ellis, D. A., J. W. Martin, A. O. DeSilva, S. A. Mabury, M. D. Hurley, M. P. Sulbaek Andersen, T. J. Wallington (2004), *Environ. Sci. Technol.*, 38: 3316-3321.

<sup>37</sup> Stock, N., D. A. Ellis, L. Deleebeek, D. C. G. Muir and S. A. Mabury (2004), *Environ. Sci. Technol.*, 38:693-1699.

<sup>38</sup> Lei, Y. D., F. Wania, D. Mathers and S. A. Mabury (2004), *J. Chem. Eng. Data.*, 49:1013-1022.

<sup>39</sup> Kaiser, M. A., D. A. Cobranchi, C.-P. Chai Kao, J. Krusic, A. A. Marchione and R. C. Buck (2004), *J. Chem. Eng. Data.*

the atmosphere is primarily or exclusively (6:2 and 8:2 FTOHs) in the gas phase.<sup>40,41,42</sup> This suggested the FTOHs would readily partition to air if allowed to escape from the consumer materials containing the fluorinated polymers and surfactants; residuals have been shown to be significant (few % by weight) in multiple industrial and consumer products and are suggested to be a significant source of fugitive emissions.<sup>43</sup> An air sampling campaign across North America (including the Arctic) indicated the fluorinated alcohols were ubiquitous<sup>40,41,42</sup> with slightly higher values in urban areas and those known to be significant for carpet production.

Extensive smog chamber studies, which mimicked the atmosphere, determined the atmospheric lifetime and helped elucidate the mechanisms through which the fluorinated alcohols (FTOHs and fluorinated sulfamidoethanols) could be converted to the perfluorinated acids (PFCAs and PFOS). Lifetimes are relatively long for the FTOHs (~20 days) and relatively shorter for the fluorinated sulfamidoethanols (~2 to 4 days) though the des-ethanol intermediates are quite long-lived (~50 days); ultimately atmospheric persistence is sufficient to explain transport to remote regions.<sup>44,45,46</sup> Hydroxyl driven transformation of FTOHs is reasonably well developed. More work is required to evaluate the importance of aldehyde photolysis and the role of any hydrates formed, though the potential exists for both pathways to lead to even higher PFCA production<sup>47</sup> which we recently showed for the hydrates themselves. A three-dimensional modeling study, based on published smog chamber studies and known atmospheric pathways, concluded that FTOHs could be a significant source of PFCAs to remote regions.<sup>48</sup> More recently, the fluorinated sulfamidoethanols were shown to yield both PFOS and PFCAs via OH-derived reactions under smog chamber conditions,<sup>49,50</sup> this discovery provides a mechanism for the electrochemical (isomer laden) PFOA observed in Polar Bears.<sup>51</sup>

Multiple lines of evidence support the PAART theory and will be highlighted in the talk. They include the detection of PFCAs and FTCAs in rainwater<sup>52</sup> and the preliminary determination that the PFOA in rain was primarily from a linear (telomerization) source though ~20% of the PFOA did appear to

<sup>40</sup> Martin, J. W., D. C. G. Muir, W.C. Kwan, C. A. Moody, K. R. Solomon and S. A. Mabury (2002), *Anal. Chem.*, 74:584-590.

<sup>41</sup> Stock, N., F. K. Lau, D. A. Ellis, J. W. Martin, D. C. G. Muir and S. A. Mabury (2004), *Environ. Sci. Technol.*, 38:991-996.

<sup>42</sup> Stock, N., D. C. G. Muir and S. A. Mabury (2006), to be submitted to *Environ. Sci. Technol.*

<sup>43</sup> Dinglasan, M. J. A. and S. A. Mabury (2006), *Environ. Sci. Technol.*, 40:447-1453.

<sup>44</sup> Ellis, D. A., J. W. Martin, S. A. Mabury, M. D. Hurley, M. P. Sulbaek Andersen and T. J. Wallington (2003), *Environ. Sci. Technol.*, 37:3816-3820.

<sup>45</sup> Ellis, D. A., J. W. Martin, A. O. DeSilva, S. A. Mabury, M. D. Hurley, M. P. Sulbaek Andersen, T. J. Wallington (2004), *Environ. Sci. Technol.*, 38: 3316-3321.

<sup>46</sup> Hurley, M. D., M. P. Sulbaek Andersen, T. J. Wallington, D. A. Ellis, J. W. Martin, S. A. Mabury (2004), *J. Phys. Chem. A*, 108:1973-1979.

<sup>47</sup> Sulbaek-Andersen, M. P., A. Toft, O. J. Nielsen, M. D. Hurley, T. J. Wallington, H. Chishima, K. Tonkorua, S. A. Mabury, J. W. Martin and D. A. Ellis (2006), *J. Phys. Chem. A*, in press.

<sup>48</sup> Wallington, T. J., M. D. Hurley, J. Xia, D. J. Wuebbles, S. Sillman, A. Ito, J. E. Penner, D. A. Ellis, S. A. Mabury, O. J. Nielsen and M. P. Sulbaek Andersen (2006), *Environ. Sci. Technol.*, 40:924-930.

<sup>49</sup> Martin, J. W., S. A. Mabury and P. J. O'Brien (2005), *Chemico-Biological Inter.*, 155:165-180.

<sup>50</sup> D'eon, J., M. Hurley, T. J. Wallington and S. A. Mabury (2006), *Environ. Sci. Technol.*, 40:1862-1868.

<sup>51</sup> DeSilva, A. O. and S. A. Mabury (2004), *Environ. Sci. Technol.*, 38:6538-6545.

<sup>52</sup> Scott, B. F., C. Spencer, S. A. Mabury and D.C. G. Muir (2006), submitted to *Environ. Sci. Technol.*

be electrochemical; this is broadly consistent with the reactivity and atmospheric concentrations of the FTOHs and fluorinated sulfamidoethanols. Atmospherically derived flux of PFCAs and PFOS to remote regions was confirmed through measurement of these chemicals in ice cores on Devon ice cap and in analysing multiple isolated inland lake water and sediments; PFCAs concentrations were within a factor of 10 for PFOA, PFNA, PFDA, and PFUnA which is suggestive of an atmospheric source via FTOH degradation. Flux measurements in ice on Devon (~0.3 tonnes/year for PFOA) closely mirrored the model values (~0.4 tonnes/year) provided by Wallington and colleagues. Long-range transport and conversion of the FTOHs to PFCAs is supported by our discovery that Polar Bears and Ringed Seals in the Arctic are highly contaminated with the PFCA levels doubling every 6 to 13 years since the early 1990s. Interestingly, PFOS also increased until around 2001 after which it has declined significantly, presumably due to the production cessation of PFOS and PFOS-related substances by the manufacturer; this reduction has now been confirmed in two locations (Resolute and Arviat) over two successive years.<sup>53</sup> Further detection work indicated the congener and isomer fingerprint of the PFCAs in Polar Bears suggested that FTOHs were the likely source.<sup>51</sup> Overall the experiments and data available provide persuasive support for the PAART theory, thus an indirect source of these pollutants; much of this evidence does not support a significant source of transport of PFCAs/PFOS to the Arctic via an oceanic route. The PAART theory suggests that controlling the inadvertent release of FTOHs from consumer materials could serve to significantly reduce the continued contamination of the Arctic.

The presence of PFOA in human blood at relatively high concentrations is not yet fully explained. The chemical fingerprint is consistent with the FTOHs as a source but is also suggestive of modest exposure to PFOA itself.<sup>54</sup> Direct exposure to FTOHs has been shown to produce a suite of intermediates and fluorinated telomer acids, and minor quantities of PFOA<sup>55,56</sup>; the bulk of FTOHs are likely excreted via secondary metabolism (e.g. glucuronide and sulfate). We also showed that both the acrylic aldehyde and telomer acids were reactive towards glutathione indicating a putative mechanism for potential toxicity.<sup>49</sup> It has been shown that at least one reactive intermediate, the saturated FTCA, is significantly more toxic than the corresponding PFCA to aquatic invertebrates, presumably via production of HF.<sup>57</sup>

Exposure could arise out of out-gassing of the FTOHs from carpets or fabrics or ingestion of fluorinated surfactants used widely in the food packaging industry. Current experiments are focused on addressing these questions. Our initial efforts in this area are focused on telomer based phosphate surfactants. Both the mono- and di-8:2 FTOH alkylphosphate have been synthesized and purified to remove any residual alcohol. Rat dosing studies, oral gavage, are now complete and indicate both the mono and di-phosphates are bioavailable and are ultimately metabolised to the full suite of fluorinated intermediates and acids previously identified from the 8:2 FTOH itself. These results suggest that food packaging coated with fluorinated materials could be a significant source of both PFCAs and their reactive precursors.<sup>58</sup>

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<sup>53</sup> Butt, C. M., D. C. G. Muir, I. Stirling, M. Kwan and S. A. Mabury (2006), *Environ. Sci. Technol.*, in press.

<sup>54</sup> DeSilva, A. O. and S. A. Mabury (2006), *Environ. Sci. Technol.*, 40:2903-2909.

<sup>55</sup> Dinglasan, M. J., Ye, Y., Edwards, E. and S. A. Mabury (2004), *Environ. Sci. Technol.*, 38:2857-2864.

<sup>56</sup> Wang, N., B. Szostek, P. W. Folsom, L. M. Sulecki, V. Capka, R. C. Buck, W. R. Berti, J. T. Gannon (2005), *Environ. Sci. Technol.*, 39:531-538.

<sup>57</sup> MacDonald, M. M., M. J. A. Dinglasan-Panlilio, S. A. Mabury, K. R. Solomon and P. K. Sibley (2006), submitted to *Environ. Sci. Technol.*

<sup>58</sup> Deon, J. and S. A. Mabury (2006), in preparation for *Environ. Sci. Technol.*

### 3.4 *Health Implications*

*Dr. Jennifer Seed, US EPA: Overview of the Toxicology of PFOA:*

The potential effects of perfluorocarboxylic acids on human health is an area of active research. To date, most of the work has focused on perfluorooctanoic acid (PFOA). Several occupational studies have been conducted, and no clear association between PFOA exposure and health outcomes has been found. However, these studies are limited in that the animal toxicology studies indicate that the developing organism is a target, and most of the workers followed in the occupational studies are adult men.

In animal studies, PFOA has been shown to be well absorbed orally. It is not metabolised, and distributes mainly to the serum and liver. It is bound to proteins such as albumin. There are species differences, and in some cases gender differences, in the excretion of PFOA. Rats show a profound difference in that the half-life of PFOA in females is hours, while the half-life in males is 4-5 days. Furthermore, the ontogeny of this pattern of excretion is developmentally regulated. The half-life is several weeks in mice, while it is close to one month in non-human primates. In contrast, humans have a very long half-life – estimates are around 3.8 years.

Repeat dose studies in rats have shown that the liver is a primary target. Two-year bioassays in rats have shown an increase in liver, Leydig cell, and pancreatic acinar cell tumors. The liver tumors seem to be due to a PPAR $\alpha$ -agonist mode of action. However, liver enlargement may also be associated with a PPAR $\alpha$ -independent mode of action. A two generation reproductive toxicity study in rats has shown post-weaning mortality, reduced growth, and delayed sexual maturation. Follow-up developmental toxicity studies in mice have shown a pattern of neonatal mortality similar to that observed in mice; this consists of a dose-related increase in mortality during the first several days after birth. Cross-fostering studies have shown that the critical period of exposure is during the prenatal period. Further studies have shown delayed development of the mammary glands in both the dams and female offspring. Preliminary unpublished studies also indicate that prenatal exposure in mice leads to obesity later in life.

### 3.5 *Environmental Implications*

*Ass. Prof. Jonathan Martin, University of Alberta: Environmental Implications of PFCAs*

PFCAs are a persistent and widespread class of environmental contaminants that are detectable in the ambient environment at trace concentrations. These chemicals, and their precursors (PFCA-precursors), are not expected to have any effects on the abiotic environment based on their negligible stratospheric ozone depletion potential and expectedly low global warming potential. More relevant concerns for PFCAs are their environmental behaviour (persistence, long-range transport, and bioaccumulation potential) and potential to cause toxic effects in exposed organisms.

The persistence and long-range transport potential of PFCAs and/or PFCA-precursors (in soil, water, and air) are substantial and exceed most national or international regulatory criteria irrespective of chain-length. PFCA bioaccumulation potential depends on chain-length and also on the organisms under examination. Laboratory bioconcentration factor (BCF) studies with small fish indicate that BCFs are negligible for PFCAs shorter than C8, while C11 and larger PFCAs have BCFs that meet or exceed the common '5000 criteria' for regulation. Laboratory biomagnification factor (BMF) studies with small fish indicate negligible (<1) BMFs for all PFCAs, however, trophic magnification factors in the Lake Ontario indicate significant trophic magnification for C10 and C11, and bioaccumulation factors (BAFs) in Great Lakes lake trout also exceed the common 5000 criteria for C8, C9, and C10. Some of the ambiguity related to PFCA accumulation in aquatic food webs may be related to fish size and PFCA-precursors.

Biomagnification of PFCAs in terrestrial (or marine mammals) food webs is likely much higher than in fish, but limited data is available for quantification of these feeding relationships to date.

Compared to humans, the PFCA profiles in wildlife are dramatically different, and concentrations can be orders of magnitude higher in terrestrial, fresh-water aquatic and marine organisms living far from emission sources. Despite these facts, relatively little has been published on the toxicological effects that PFCAs may have on ecosystems or on the most highly exposed organisms. Existing data regarding the (eco-)toxicological effects of C8 were reviewed and compared to environmental exposures in a simple hazard assessment. Negligible hazard was evident for aquatic organisms except for those close to spill sites or PFCA manufacturing. For the most highly exposed marine mammals (based on liver concentrations), the hazards are highly uncertain due to a lack of relevant toxicological data, and extrapolation from rodent studies is difficult since liver concentrations are rarely reported at the toxicological threshold. An eco-epidemiology approach has demonstrated a relationship between sea-otter liver C8 concentrations and their risk of dying from infectious disease, thus more subtle effects should be examined in toxicological studies. Furthermore, the carcinogenic risk for wildlife remains as uncertain as it currently is for humans. The hazard posed by all longer PFCAs cannot currently be assessed due to minimal exposure and effect data, and there is evidence that chain-length affects many endpoints, including tumorigenicity, thus it is not possible to extrapolate from data on C8.

### 3.6 *Uses, Sources and Societal Value of Perfluorinated Chemistry*

*Dr. Robert C. Buck, DuPont: Uses, Sources and Societal Value of Perfluorinated Chemistry*

The family of fluorinated chemicals is broad and diverse, including substances very different in properties like the family of hydrocarbons (e.g. octane, sodium lauryl sulfate, benzene, polyethylene). The general term “fluorochemical” is often used to describe this family. Within the family are substances that are extremely different in their properties, uses and benefits. Fluoropolymers and fluorotelomer-based products are truly unique in their physical and chemical properties largely based upon the thermal and chemical stability of carbon-fluorine bonds. They are generally used in applications where their functionality and societal benefits are unique and cannot be achieved with alternative technologies. They protect people and property and substantially increase the useful lifetime of consumer goods.

Fluoropolymers (e.g. polytetrafluoroethylene, PTFE) are high molecular weight polymers with the inherent properties of chemical resistance and thermal stability which cannot be achieved with any other known substances.<sup>59,60</sup> They have high thermal stability, are non-flammable and are resistant to chemical attack in addition to having low friction (e.g. slippery) and excellent electrical insulation properties. Fluoropolymers are manufactured using PFCAs as a polymerization aid (surfactant). PFCAs are neither reacted with nor incorporated into the fluoropolymer. PTFE does not degrade to form PFCAs. High heat treatment during fluoropolymer processing thermally destroys traces of PFCAs. Polymer fume fever arises from small particles created as a result of thermal degradation of PTFE and is not related to or caused by PFCAs.

Ammonium- perfluorooctanoate (APFO) and -perfluorononanoate (APFN) are the major PFCAs manufactured globally. Their primary use is in the manufacture of fluoropolymers and they have been widely used as surfactants in both industrial and consumer applications.<sup>61</sup> They are manufactured by a

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<sup>59</sup> Hougham, G., P. E. Cassidy, K. Johns, and T. Davidson (eds.) (1999), *Fluoropolymers 2: Properties*, 408 p.

<sup>60</sup> Hougham, G., P. E. Cassidy, K. Johns, and T. Davidson (eds.) (1999), *Fluoropolymers 1: Synthesis*, 329 p.

<sup>61</sup> Prevedouros, K., I. T. Cousins, R. C. Buck and S. H. Korzeniowski (2006), Sources, Fate and Transport of Perfluorocarboxylates, *Environ. Sci. Technol.*, 40: 32-44.

number of processes and are mixtures of carbon chain length homologues. The electrochemical fluorination (ECF) process has been the most widely used to manufacture APFO and results in both a homologue mixture of PFCAs and up to 30% branched PFCAs isomers.<sup>62</sup>

The family of “fluorinated organics” is comprised of substances principally built upon hydrocarbons to which a “short” fluorocarbon chain (e.g.  $F(CF_2)_n-$  where  $n \geq 4$ ) has been chemically attached, most often a hydrocarbon polymeric backbone such as a polyacrylate.<sup>62,63</sup> These substances are designed to provide unique surface modification properties associated with the unique low surface energy of the fluorocarbon chain. When applied to a substrate such as a textile fabric, these products provide stain and soil protection as well as oil and water repellency. The two manufacturing processes most widely used to make the fluorinated functionality in these products are electrochemical fluorination (ECF) and telomerization. In addition to the polymeric products, fluorinated surfactants are also made using these technologies.<sup>64,65</sup>

Recently, studies have been conducted to assess the safety of consumer products that may contain trace levels of perfluorooctanoate (PFO).<sup>66</sup> The work included an extensive assessment of a large number of consumer articles which contain fluoropolymers and fluorotelomer-based products to quantify potential exposure.<sup>67,68,69</sup> These data were combined with recent PFO hazard assessment data.<sup>70,71</sup> Using a margin of safety approach, the study concluded that consumer exposure to PFO from use of the articles evaluated in the study is not expected to cause health effects

Concerns regarding the persistence of PFCAs in the environment have spurred industry to take voluntary action. The major electrochemical fluorination manufacturer announced the phase out of

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<sup>62</sup> Kissa, E. (2001), *Fluorinated Surfactants and Repellents*, Second edition, Marcel Dekker Inc., New York.

<sup>63</sup> Rao, N. S., B. E. Baker, (1994), *Textile Finishes & Fluorosurfactants* in B. E. Smart and J. C. Tatlow (eds.), *Organofluorine Chemistry: Principles and Commercial Applications*, Plenum Press, New York, pp. 321-336.

<sup>64</sup> Taylor, C. K. (1999), Fluorinated surfactants in practice, *Annual Surfactants Review 2*: 271-316.

<sup>65</sup> 3M Company (1995), 3M Fluorad Surfactants: Product Bulletin, St. Paul, MN.

<sup>66</sup> Washburn, S. T., T.S. Bingman, S. K. Braithwaite, R. C. Buck, L. W. Buxton, H. J. Clewell, L.A. Haroun, J. E. Kester, R. W. Rickard and A. M. Shipp (2005), Exposure Assessment and Risk Characterization for Perfluorooctanoate in Selected Consumer Articles, *Environ. Sci. Technol.* 39:3904-3910.

<sup>67</sup> Mawn, M. P., R. G. McKay, T. W. Ryan, B. Szostek, C. R. Powley and R. C. Buck (2005), Determination of extractable perfluorooctanoic acid (PFOA) in water, sweat simulant, saliva simulant, and methanol from textile and carpet samples by LC/MS/MS. *Analyst (Cambridge, United Kingdom)*, 130:670-678.

<sup>68</sup> Powley, C. R., M. J. Michalczyk, M. A. Kaiser and L.W. Buxton (2005), Determination of perfluorooctanoic acid (PFOA) extractable from the surface of commercial cookware under simulated cooking conditions by LC/MS/MS, *Analyst (Cambridge, United Kingdom)*, 130:1299-1302.

<sup>69</sup> Larsen, B. S., M. A. Kaiser, M. A. Botelho, S. F. Bachmura and L. W. Buxton (2006), Efficient ("total") extraction of perfluorooctanoate from polytetrafluoroethylene fluoropolymer, *Analyst (Cambridge, United Kingdom)*, 131:1105-1108.

<sup>70</sup> Butenhoff, J. L., D. W. Gaylor, J. A. Moore, G. W. Olsen, J. Rodricks, J. H. Mandel and L. R. Zobel (2004), Characterization of risk for general population exposure to perfluorooctanoate, *Regulatory Toxicology and Pharmacology*, 39:363-380.

<sup>71</sup> Kennedy, G. L., Jr., J. L. Butenhoff, G. W. Olsen, J. C. O'Connor, A. M. Seacat, R. G. Perkins, L. B. Biegel, S. R. Murphy and D. G. Farrar (2004), The Toxicology of Perfluorooctanoate, *Critical Reviews in Toxicology* 34:351-384.

perfluorooctanyl chemistry.<sup>72</sup> Manufacturers have made substantial voluntary emissions reductions.<sup>73,74,75</sup> Extensive scientific studies have been conducted and sponsored by industry and there has been global sharing of technologies to reduce PFCA emissions. In January 2006, many of the global PFCA, fluoropolymer, ECF and fluorotelomer producers made a voluntary commitment to reduce PFCA emissions and product content and to work toward the elimination of PFCAs and potential precursors with eight carbons or higher.<sup>76</sup>

The fate and transport of PFCAs is an active area of ongoing scientific research. The physical-chemical properties of PFCAs and their potential precursors are not well understood and have proven difficult to determine in some cases. PFCAs themselves can exist in both anionic, acid and salt forms, each with distinct properties.<sup>76,77</sup> Fluorotelomer alcohols and olefins have also been investigated.<sup>78,79</sup> A comprehensive review of PFCA sources, fate and transport has recently been published.<sup>61</sup> A complete assessment of both PFCAs and precursors which degrade and contribute to PFCAs in the environment was made. The largest global historical emissions of PFCAs are from direct manufacture of PFCAs and their use in fluoropolymer manufacture. Indirect PFCA sources, including degradation of perfluoroalkyl sulfonyl and fluorotelomer raw materials and products, were estimated to be small but remain an area of active ongoing research. Water is the principal environmental “reservoir” for PFCAs in the environment. Global transport of PFCAs and precursors occurs in coupled processes involving both water and air. Recent studies have explored the direct transport of PFCAs in water<sup>80</sup> and fluorotelomer alcohols in air.<sup>81</sup> Clearly, much more work is needed to better characterize emissions and assess all of the identified sources in order to elucidate their relative contribution, pathways for environmental transport and ultimate fate of PFCAs and their potential precursors. Systematic, multi-media spatial and temporal studies are needed in order to accomplish this objective.

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<sup>72</sup> 3M Company (2000), Phase-Out Plan for POSF-Based Products, *US EPA Administrative Record AR226-0600*, <http://www.regulations.gov>.

<sup>73</sup> Fluoropolymer Manufacturing Group (2002), Fluoropolymer Manufacturers Group Presentation, *U.S. EPA Administrative Record AR226-1094*, <http://www.regulations.gov>.

<sup>74</sup> Fluoropolymer Manufacturing Group (2005), “Dispersion Processors Mass Balance Report”, *U.S. EPA E-Docket OPPT2003-0012-0900, -0901, -0902, -0903, -0904*, <http://www.regulations.gov>.

<sup>75</sup> DuPont Company (2005), DuPont Global PFOA Strategy, *U.S. EPA Administrative Record AR226-1914*, <http://www.regulations.gov>.

<sup>76</sup> Kaiser, M. A., B. S. Larsen, C.-P. Kao and R. C. Buck (2005), Vapor Pressures of Perfluorooctanoic, -nonanoic, -decanoic, -undecanoic, and -dodecanoic Acids, *Journal of Chemical and Engineering Data*, 50:1841-1843.

<sup>77</sup> Goss, K.-U. and G. Bronner (2006), What Is So Special about the Sorption Behavior of Highly Fluorinated Compounds?, *Journal of Physical Chemistry A*, 110:9518-9522.

<sup>78</sup> Goss, K.-U., G. Bronner, T. Harner, M. Hertel and T. C. Schmidt (2006), The Partition Behavior of Fluorotelomer Alcohols and Olefins, *Environ. Sci. Technol.* 40:3572-3577.

<sup>79</sup> Arp, H. P. H., C. Niederer and K.-U. Goss (2006), Predicting the Partitioning Behavior of Various Highly Fluorinated Compounds, *Environ. Sci. Technol.*, 40:7298-7304.

<sup>80</sup> Armitage, J., I. T. Cousins, R. C. Buck, K. Prevedouros, M. H. Russell, M. MacLeod and S. H. Korzeniowski (2006), Modeling Global-Scale Fate and Transport of Perfluorooctanoate Emitted from Direct Sources, *Environ. Sci. Technol.*, 40:6969-6975.

<sup>81</sup> Wallington, T. J., M. D. Hurley, J. Xia, D. J. Wuebbles, S. Sillman, A. Ito, J. E. Penner, D. A. Ellis, J. Martin, S. A. Mabury, O. J. Nielsen and M. P. S. Andersen (2006), Formation of C7F15COOH (PFOA) and Other Perfluorocarboxylic Acids during the Atmospheric Oxidation of 8:2 Fluorotelomer Alcohol, *Environ. Sci. Technol.*, 40:924-930.

Studies to determine PFCA trends in the environment are limited. Human blood studies suggest a high statistical correlation between PFOA and perfluorooctane sulfonate (PFOS) concentration.<sup>82</sup> Longitudinal results do not correlate with fluoropolymer or fluorotelomer historic production and are inconsistent with degradation of fluorotelomer products. No statistical correlation has been reported between PFCAs and any fluorotelomer-based substance. Limited wildlife monitoring data suggests decreasing concentrations of PFCAs and PFOS in arctic biota.<sup>83,84</sup> Water is an important exposure medium. In wildlife, some strong statistical correlations between PFCAs and PFOS have been observed. Generally, PFOA and PFCAs with eight or less carbons are either not observed or observed in low quantities suggesting they have negligible bioaccumulation and biomagnification potential largely due to their very high water solubility. These monitoring interpretations are based on a limited number of studies. Additional longitudinal human studies and spatially and temporally integrated biota monitoring which includes exposure media is needed to more fully understand PFCA levels and trends.

### 3.7 *Environmental NGO Viewpoint*

*Dr. Mariann Lloyd-Smith, National Toxics Network inc.: PFCAs and Precursors - Why international action is needed*

At the International Conference on Chemical Management in Dubai 2006, the international community endorsed the Strategic Approach to International Chemical Management. Building on this, the International POPs Elimination Network released its declaration for a Toxic Free Future. We committed “to work for and achieve by the year 2020, a Toxics-Free Future, in which all chemicals are produced and used in ways that eliminate significant adverse effects on human health and the environment,” and most importantly, “where persistent organic pollutants (POPs) and chemicals of equivalent concern no longer pollute our local and global environments, and no longer contaminate our communities, our food, our bodies, or the bodies of our children and future generations.”

It is against these commitments we evaluate the assessment, use, management and final destruction of the perfluorocarboxylic acids (PFCAs) and their precursors. PFCAs’ persistency and long-range transport via precursors has meant they are now widespread throughout the environment and in wildlife, far from sources of production. PFCAs are found in human blood demonstrating their potential for bioaccumulation and the increasing concentrations of long chain PFCAs, particularly in wildlife high on the foodchain strongly suggest biomagnification. The evidence that the levels of some PFCAs have been doubling every 5 to 8 years in the highly vulnerable polar bear population is of major concern.

While for some PFCAs, there are known adverse health impacts, for example, perfluorooctanoate (PFOA) has shown to be tumourigenic and immunotoxic in laboratory animals, however for others, there is no toxicological or ecotox data available.

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<sup>82</sup> Olsen, G. W., H.-Y. Huang, K. J. Helzlsouer, K. J. Hansen, J. L. Butenhoff and J. H. Mandel (2005), Historical comparison of perfluorooctanesulfonate, perfluorooctanoate, and other fluorochemicals in human blood, *Environ. Health Persp.*, 113:539-545.

<sup>83</sup> Butt, C. M., D. C. G. Muir, I. Stirling, M. Kwan and S. A. Mabury (2007), Rapid Response of Arctic Ringed Seals to Changes in Perfluoroalkyl Production, *Environ. Sci. Technol.* 41: 42-49.

<sup>84</sup> Kannan, K., S. H. Yun and T. J. Evans (2005), Chlorinated, Brominated, and Perfluorinated Contaminants in Livers of Polar Bears from Alaska, *Environ. Sci. Technol.* 39: 9057-9063.

This lack of information highlights the four critical components of ‘world’s best practice’ chemical regulatory policy: *Precautionary Principle*, *No data - No market*, *Right to Know* and the *Substitution Principle*. This paper will review the PFCAs against these criteria.

As some of the PFCAs have already been found to exhibit the properties of persistent organic pollutants (POPs), the need for precaution and prevention is paramount, as is civil society’s right to know. We consider that activities to identify substitutes for essential uses should be a requirement of their use and proactively supported.

PFCAs via their precursors are “*Poisons without Passports*” with no respect for territorial borders. Countries or even regions alone cannot respond effectively. PFCAs and their precursors, like their sister chemical perfluorooctanesulfonate (PFOS), need priority global action under the Stockholm Convention on Persistent Organic Pollutants 2001.

#### **4. Ongoing Risk Reduction Activities**

##### **4.1 *The United States***

In January 2006, the US Environmental Protection Agency (EPA) invited producers of fluorotelomers and fluoropolymers to participate in a PFOA Stewardship Programme. The participating companies committed to achieve, no later than 2010, 95% reductions of both facility emissions and product content of PFOA, precursors that can break down to PFOA and related higher homologue chemicals in their US and world-wide operations. They also agreed to work toward the elimination of the same substances from emissions and products no later than 2015.

All the companies that were approached, and which make up the main part of the world market, have agreed to participate. The companies are E.I. DuPont de Nemours and Company, 3M/Dyneon, Arkema Inc., AGC Chemicals/Asahi Glass, Ciba Speciality Chemicals, Clariant Corporation, Daikin and Solvay Solexis. The “PFOA Stewardship Programme” is a voluntary agreement. Several of the companies have reported that they are already close to fulfilling the goal for 2010 since they have recently developed new techniques to reduce fluorotelomer residuals in their products. They have also indicated their willingness to share these techniques with other manufacturers. More detailed information is provided in Annex 1.

##### **4.2 *Canada***

In 2004, Environment Canada prohibited the import and production of four new fluorotelomer-based substances. The temporary prohibitions were based on evaluations made within the Canadian notification system for new substances. These restrictions remain in force and Environment Canada has now published a proposal for permanent prohibitions for the four substances. The proposed regulations will prohibit the manufacture, use, sale, offer for sale and importation of the four fluorotelomer-based substances.

Environment Canada and Health Canada have developed an action plan to address the assessment and management of PFCAs and their precursors. The action plan includes maintaining the current approach of prohibiting the introduction into Canada of new sources of long-chain PFCAs ( $\geq C9$ ) and addressing confirmed sources of certain PFCAs associated with substances already in Canadian commerce. More detailed information is provided in Annex 2.

### **4.3 European Union**

To date, PFCAs have not received as much attention in the EU as in North America.

EU regulation No 648/2004 on detergents, which entered into force in 2005, led to certain restrictions in the use of perfluorinated substances in detergents. According to the regulation, surfactants in detergents must be readily biodegradable or primarily degradable. Fluorosurfactants cannot comply with these criteria and may not be used in detergents. However, the criteria are only applicable to products with a cleaning effect. They do not apply to polishes that only condition a surface without cleaning it, but they do apply to detergents acting as combined cleaning and conditioning agents.

In 2004, there were a large number of products containing fluorosurfactants registered as cleaning agents in the Swedish products register.

The European Food Safety Administration (EFSA) is currently evaluating PFOS and PFOA. The EU also has a research programme for perfluorinated substances, PERFORCE, with researchers from the Netherlands, Sweden, Norway, Belgium and DuPont.

In the proposed European Parliament and Council directive on PFOS within the framework of directive 76/769/EEC, it is included that the Commission shall keep under review the ongoing risk assessments of PFOA and propose appropriate risk managing measures where justified.

EU Technical Committee on Classification and Labelling of Dangerous Substances has agreed that PFOA should be classified as follows (Summary Record of the Technical Committee Meeting of 3rd October 2006): Carc. Cat. 3; R40, Repr. Cat 2; R61, NC Repr. Cat. 3; R62, T; R48/23, Xn; R20/22, Xn; R48/22, Xi; R36. More detailed information is provided in Annex 3.

### **4.4 Japan**

In 2002, Japan designated PFOA and some of these salts as class 2 monitoring substances under the Chemical Substance Control Law which are judged as not biodegradable, not highly bio-accumulative, and has the potential to be hazardous to human health if taken in continuously. PFOA ammonium salt was also designated as a class 2 monitoring substance in 2006.

In 2005, responding to the US EPA stewardship programme, METI requested those PFOA suppliers that participate in the US programme, to inform the Japanese public of their actions. Joint announcements by these suppliers were published on the Japanese Fluoropolymers Industry Association's website.

METI has conducted a series of BCF tests of PFCA and its higher homologues, and the result revealed that BCF values of PFCA (C=12 and C=14) are higher than 10 000 while the BCF values of PFOA and PFCA (C=18) are below 100 and that of PFCA (C=16) is some 5 000 (Annex 4).

### **4.5 OECD**

In 2004, the OECD carried out a survey on the production and use of PFOS, PFAS, PFOA, PFCA and related substances in its member states. The survey is currently being repeated, with PFCA-precursors included in the 2006 version.

The OECD Joint Meeting agreed in November 2004 to prepare a hazard assessment of PFOA as a joint project between the US EPA and German UBA. The first draft SIAR (Initial Assessment Report) was submitted in January 2006 for discussion at SIAM 22. According to the comments received, the documents needed to be revised including more recent findings and other additional information available in the member countries.

The revised SIAP (Initial Assessment Profile) and SIAR (human health part), and also a proposal for amending the environmental part to include the recent findings, were sent to Germany for finalisation in mid-September 2006. The draft is nearly completed, but still needs to be approved by both Sponsor countries.

At SIAM 23, Korea, October 17-20, 2006, Germany confirmed that the revised documents will be submitted to the SIAM CDG as soon as the draft is approved by the Sponsor countries. The revised documents (SIAR, SIAP, SIDS) will then be finalised in 2007 via the written procedure on the SIAM CDG. More detailed information is provided in Annex 5.

## **5. Breakout Group Discussions**

### ***5.1 Assessment and Research Needs: Monitoring, Emissions, Environmental Fate and Transport (Group 1)***

The aim of the discussion was to identify needs for monitoring and research that would reduce uncertainties and support further assessment.

#### *5.1.1 Questions for the break-out group*

1. What does available empirical monitoring data tell us about:
2. Humans
3. Wildlife
4. Environmental media (non-biotic), indoor air and dust, water, sediment etc.
5. Production, use and waste phases
6. What understanding do we have on different sources and what additional information would help to advance our understanding?
7. Currently studied sources
8. Articles?
9. Other chemistries?
10. What biodegradation studies, fate studies and models would assist to describe fate and transport of PFCAs.
11. What spatial and temporal monitoring studies do best answer questions about sources, fate and transport and effectiveness of mitigation measures?

### 5.1.2 *Conclusions of Discussion*

Humans and wildlife are exposed to PFCAs. There are differences in exposure patterns, as indicated by the prevalence of PFOA in human monitoring and longer chain PFCAs in wildlife.

Work toward certified standard reference materials for PFCA analysis through the continuation of round robin laboratory activities. This is needed to facilitate comparisons of monitoring data generated in different laboratories although intra-laboratory data, subject appropriate quality assurance steps, continues to be useful in trend analysis.

For monitoring activities in general, analytes should be considered which broadly cover the suite of PFCAs, known and potential precursors, and analytes which will help inform sources. An example of the latter would be the analysis of branched and linear fluorocarbon chains (an indicator of production method), and intermediates of precursor conversion to PFCAs (e.g. presence of FTCA's suggesting PFCA formation from fluorotelomer sources).

Human exposure to PFCAs and their precursors will be informed by multi-media assessment which considers exposure via food, drinking water, household dust, indoor air as well as exposure to consumer articles.

Further analysis, including measurements in oceans and soils will help elucidate the reservoirs of PFCAs. It will also help describe the environmental fate of PFOA, which appears to mainly reside in water (on a mass basis) and PFCAs of different chain lengths where less data is available to fully understand their environmental fate and distribution.

Differences in physical chemical behaviour of PFCAs of different chain lengths can affect behaviour in the environment. Additional characterization of these properties will inform our understanding of fate and transport.

Studying commercial substances will help determine their significance as potential sources of PFCAs. To facilitate the prioritisation and design of these studies, information on the composition including residual PFCA precursors, stability, commercial applications and production volume of these substances will contribute to experimental design and data interpretation. Similarly, in assessing end use articles' contribution to the emission of PFCAs and their precursors, information including identity of the substances applied to the articles and the level of residual PFCA precursors present will be of assistance. Although not discussed in much detail, the potential for contributions to environmental emissions at the end of the life cycle of a product, e.g. during its waste stage, should also be considered.

Public availability of such information, recognising the boundaries set by Intellectual Property Rights, would be consistent with the SAICM overarching policy strategy, paragraph 15 (b).

Concentrations in environmental media and the total mass those concentrations represent will inform exposure analysis.

Recognising steps are being undertaken to reduce point source emissions and certain volatile precursors, continuation of monitoring of precipitation and air may offer an early measure of effectiveness. Monitoring of humans and wildlife will inform about the ultimate effectiveness of measures taken, and it was recognised this may take a longer time.

## 5.2 *Assessment and Research Needs: Effects (Group 2)*

The aim of the discussion was to identify needs for monitoring and research that would reduce uncertainties and support further assessment.

### 5.2.1 *Questions for the Break-out Group*

1. Are the toxicity and pharmacokinetics studies available sufficient to conclude for human health risk assessments for all PFCAs? What are the key data gaps?
2. Are the available ecotoxicity, bioaccumulation and biomagnification studies sufficient to conclude for environmental risk assessments for all PFCAs? What are the key data gaps?
3. How can we use read-across data (surrogates)?
4. What additional studies might be helpful for PFCAs of different chain lengths or intermediates?
5. How can we address potential cumulative effects with respect to human health and wildlife exposure?

### 5.2.2 *Conclusions of Discussion*

The break out group has identified conclusions for assessment and research needs concerning effects on human health and the environment. It is recognised, however, that the identified information needs should not be misinterpreted as preventing conclusions in a regulatory context concerning risk assessment or management decision-making. The discussion was driven by questions 1-4.

**Conclusions of discussion on question 1:** To assess PFCAs different from PFOA, the focus should be on specific chain lengths of known environmental or commercial relevance, e.g. C4-C14<sup>85</sup> PFCAs.

Available data indicate different effects for different chain lengths (e.g. data for C4 and C10 demonstrate this) which may depend in part on physico-chemical properties and pharmacokinetics (PK). At least for C4, C6, and C8, PK information is available. Although there may be common modes of action (e.g. peroxisome proliferation for C4, C6, C8, C9, C11) there may also be differences for different PFCAs (e.g. body fat differences with different compounds and life stages).

In the absence of any other information, data on C8 on mammalian toxicity could be used as a worst case scenario surrogate data for lower homologues e.g. C6, depending on the purposes. It was stated by some participants that a weight-of-evidence approach should be taken. C4 and C6 data will be available shortly (as reported by 3M<sup>86</sup>).

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<sup>85</sup> For PFCAs, the number of carbons found in the chain length is designated by the number following C, e.g. the abbreviation C8 indicates a PFCA with an 8 carbon chain length (of which 7 carbons would be fully fluorinated).

<sup>86</sup> 3M is aware of data on C6 toxicity and pharmacokinetics that have been developed by another company, but the only reports available to 3M on C6 are the "sanitized" reports available through the "Freedom of Information Act" process from EPA. 3M has developed pharmacokinetic data on C4 and C6 as well as toxicology data on C4, all of which will be made public. The C4 and C6 pharmacokinetic data was presented at European SETAC in 2006.

In general, pharmacokinetics (PK), growth and development, hepatic effects would be of interest for other PFCAs, based on data we have seen for PFOA. When conducting animal PK studies, these should include faecal and urine analyses to attempt to achieve mass-balance; radiolabelled PK studies would be helpful.

One of the most important concerns for PFOA is the long elimination half-life from human blood. Some participants stated this indicates persistence and potential bioaccumulation in humans (PFOA appears to remain in the human body for a long time, with examples of reported half-lives of 3.8 years (Olsen *et al.* 2005) and 4.37 years (Kudo and Kawashima, 2003)). Some participants stated that based on recent field data (Emmett *et al.*, 2006.) PFOA cannot be considered to meet the traditional profile of a highly bioaccumulative agent in humans.

In the absence of human elimination half-life data on other chain lengths, there is a need to develop a means of extrapolating from animal pharmacokinetic (PK) data to humans.

There are substantive tumour data in rats for PFOA, however, there remains a range of uncertainty regarding the mode(s) of action.

As there are limited tumour data on substances other than PFOA (C8) and we cannot assume other chains are similar to C8, further tumorigenicity data are needed for other PFCA chain lengths.

There are only immunotoxicity data for PFOA, but the significance of this finding is not clear at this stage.

Although most studies indicate PFOA is not genotoxic it is unknown whether this is true for other PFCAs.

Studies regarding structure activity for different chain lengths for a variety of endpoints would be helpful.

More global human biomonitoring studies are needed for PFCAs. Norwegian blood samples from pregnant women indicate C9 levels similar to PFOA and PFOS. It can't be assumed data from one country (e.g. US) are reflective of other countries.

**Conclusions of discussion on question 2/ecotoxicity:** The ecotoxicological data available for PFOA appear sufficient to perform an appropriate assessment concerning the risks for pelagic aquatic ecosystems.

PFOA toxicity data indicate low toxicity for pelagic aquatic species. The risk to other organisms is uncertain. For example, other organisms (e.g. soil nematodes) may be more sensitive than standard study species. It is noted for nematodes that C9 is more toxic than C8.

Avian toxicity is a data gap and should be considered further, given that some avian species are known to be contaminated with perfluorinated substances. Reproductive endpoints are needed, considering the available data from other vertebrates.

While there are data for PFOA, there are limited data on other chain lengths. There is a need for additional toxicity data (e.g. phytotoxicity data on algae) beyond PFOA, particularly as lower chains may be used as replacements commercially. Other endpoints may be helpful in addition to standard endpoints e.g. circulating sex hormones (effects in fish noted).

There is a need to assess body burdens; studies on PFOA and other PFCAs need to report liver and blood concentrations e.g. at the end of studies.

**Conclusions of discussion on question 2/bioaccumulation:** Existing data do not appear sufficient to address bioaccumulation potential in wildlife other than fish. Fish data generally do not indicate high bioaccumulation potential for PFOA, however, this may not be adequate to address what occurs in other organisms (e.g. air breathing organisms at the top of food chains and contaminated with perfluorinated substances).

For longer chain PFCAs, there are indications for bioaccumulative properties (e.g. some C9-C14 PFCAs show high bioaccumulation potential in aquatic organisms). In studies in fish, chain-length dependent bioconcentration of PFCAs was observed – increasing from C8 up to C14, then decreasing. Chain lengths  $\leq$  C8 do not appear to bioconcentrate based on available data from laboratory studies on fish. However, as noted above, fish data (e.g. a laboratory-derived bioconcentration factor (BCF)) may not adequately address potential bioaccumulation in other organisms. A fish laboratory-derived BCF may be considered by some participants as an insufficient criterion on which to base a bioaccumulation determination for certain perfluorinated acids (including C8), given their unusual partitioning behaviour and reported biomagnification in the environment.

For some perfluorinated substances, there may be data to indicate bioaccumulative properties even if strict regulatory criteria are not met.

With regard to bioaccumulation, there is a need for more emphasis on monitoring/accumulation data for different trophic levels. When doing so, a focus should also be biomagnification in organisms at the top of food chains (e.g. certain terrestrial or marine mammals; fish-eating avian species). Air-breathing organisms need to be considered.

In addition, a need for international harmonisation regarding bioaccumulation determination in general and especially for perfluorinated substances is recognised.

**Conclusions of discussion on question 3:** Using surrogate toxicity data may be more complicated for perfluorinated substances. In some cases for toxicity data, e.g. liver-peroxisome proliferation data, you may be able to make inferences for other chain lengths. In some cases, chain lengths may be more toxic than PFOA, e.g. it is noted that for nematodes, C9 is more toxic than C8.

As concluded under ecotoxicity, further tumourogenicity data is needed for other PFCA chain lengths beyond PFOA as it cannot be assumed other chains behave similar to C8.

There is a need for open information sharing and improved access to toxicity data across jurisdictions. Some stakeholders are aware of additional toxicity data (e.g. on C4, C6, C9 and C10) but the data is not easily accessible to all.

Data on different PFCA salts (with same chain length) are more likely to be accepted as surrogate data.

C8 (mammalian toxicity) could be used as a worst case scenario surrogate data for lower homologues e.g. C6, but depends on your purposes.

*In vitro* data is needed for longer chain PFCAs. Some participants stated this could include mode of action data.

If the structure activity for certain chain lengths is known, it may be possible to interpolate.

**Conclusions of discussion on question 4:** As noted in the discussion, toxicity data for substances other than C4 and C8 are needed (limited C6, C9 and C10 data exist).

Priority endpoints would be: pharmacokinetics (PK), growth and development, and hepatic effects. PK studies on other PFCAs are needed (there is only limited PK data; studies for C4 acid underway; C4 and C6 sulfonates data exist; C6 acid data also exist in public docket); fluorotelomer alcohol (FTOH) metabolism studies exist for the 8:2 FTOH<sup>87</sup>.

In addition to standard endpoints, other endpoints to consider include circulating sex hormones (effects noted in fish). Avian reproductive effects are needed. Studies regarding structure activity for different chain lengths for a variety of endpoints would be helpful.

If exposure scenarios exist for intermediates (e.g. aldehydes) then it would be useful to have corresponding toxicity data for such substances.

The environmental fate of unsaturated acids has not been studied; depending on persistence, this may be of interest from effects perspective.

### 5.3 *Risk reduction approaches (Group 3)*

The aim was to discuss ways to mitigate our concerns. The group's task was to identify risk reduction measures or approaches that could be considered and list their advantages and disadvantages. However, the workshop was not tasked with producing risk reduction recommendations.

#### 5.3.1 *Questions for the break-out group*

1. What are the advantages and disadvantages of the risk reduction approaches such as voluntary, regulatory, economic incentive driven, etc.
2. What is expected from different risk reduction measures on PFCAs undertaken in specific member countries (e.g. the US, Canada).
3. What factors should be considered in assessing applicability in other countries on a multi-national or global basis?
4. What alternative or complementary risk reduction measures or approaches could be considered? (Brainstorm possible alternatives.)

#### 5.3.2 *Conclusions of Discussion*

The goal of this breakout group discussion was to identify risk reduction measures and list their advantages and disadvantages. While risk assessment efforts are in process, prudent actions can be taken to reduce the environmental footprint of PFCAs and various approaches can be considered to attain that reduction. It is important to point out that risk reduction approaches or strategies were to be identified and evaluated, but the group was not charged with making specific risk reduction recommendations, i.e. which option or options should be selected.

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<sup>87</sup> Fluorotelomer alcohols are polyfluorinated compounds that have the generic formula  $F(CF_2)_nCH_2CH_2OH$ , where  $n$  is an even number, and are named according to the relative number of fluorinated to hydrogenated carbons: e.g.,  $F(CF_2)_8CH_2CH_2OH$  is 8:2 FTOH. Their name is derived from the telomerization process from which they are produced.

The risk reduction approaches that were identified include voluntary efforts, regulatory action, and market driven or economic incentives. In the case of voluntary programmes, the USEPA Stewardship programme was highlighted as a model approach to obtain significant commitments from industry, make progress in an accelerated time frame and allow flexibility in achieving the results. However, this approach may result in an uneven playing field if not all companies in all parts of the international community participate. Regulatory actions generally do assure a level playing field in countries where enacted, and can target a broader range of companies in the supply chain. They can also include strong enforcement measures. They can create similar uneven playing fields however, if not generally adopted in most countries. Additionally, regulatory actions require an extended time frame compared to voluntary measures to establish justification, can target a broader range of companies in the supply chain, and can include strong enforcement measures. These regulatory actions require an extended time frame to establish justification, develop and promulgate regulations, and provide time for compliance. This approach tends to discourage private-public partnerships.

Other approaches in the area of market driven incentives and economic instruments were addressed. These included: taxation on emissions or hazardous chemicals, incentives to encourage “Green Chemistry” by streamlining regulatory notification of alternative chemistries, cap and trade approaches, and voluntary product content disclosures on websites and on product labels so that consumers can access product information more easily. In addition, alternative or complimentary risk reduction approaches were discussed and included, using a mix of the various tools, setting industry standards, and certification requirements to accompany consignments. These approaches are generally more indirect compared to the structured voluntary or regulatory approaches described above, and therefore less able to attain uniform progress internationally. However, they are more flexible and can yield cost effective solutions.

Regardless of the approach, the expectations around risk reduction efforts were agreed: reduce exposure and the environmental footprint quickly, make scientifically based reduction decisions, stimulate new technology development, and share the information on the technologies effective in reducing environmental releases.

The group also addressed the factors that should be considered in assessing applicability on a global basis. These included harmonised technology-based standards for residuals in manufactured articles and harmonised pollution prevention principles in developed and developing countries, standardised data criteria and hazard assessment and the need for transparency, verification and enforcement. Obstacles included incomplete data on manufacturers and emission levels, and lack of interest in some countries to adopt these measures. Outreach to the international community was endorsed as a key factor in addressing the global constraints and uncertainties.

#### **5.4 *Uses, trends and alternative chemistries (Group 4)***

This group was to discuss the larger group of perfluorinated substances (including PFAS), their current uses, trends in use, the suitability of short-chain perfluorinated compounds and possible non-fluorinated alternatives. The aim was to identify difficulties, possibilities and opportunities for substitution of (long chain) perfluorinated compounds for specific uses.

##### **5.4.1 *Questions for the break-out Group***

1. What is the full range of current uses for different perfluorinated compounds? What are the use trends of perfluorinated compounds in different products?
2. How can we identify some of the lesser-known uses?

3. What short-chained PFCs or non-fluorinated alternatives are available from a functional, economic, human health and environmental perspective? (Are there specific uses where alternatives are particularly difficult to identify?)
4. What guidance would be needed on designing alternatives to different perfluorinated compounds? What criteria would be needed to make decisions on these alternatives?
5. What incentives could support the development of alternatives to different poly- or perfluorinated compounds?

#### 5.4.2 *Conclusions of Discussion*

The global trend shows that PFC and fluoropolymer use is increasing. These individual chemistries have very specific applications and uses that are tied to their performance. Due to the societal pressure on persistent and/or potentially bioaccumulative substances such as these fluorinated products, pro-active companies are driven into researching and developing alternatives to these applications. The difficulties discussing alternatives are due, in large degree, to competing needs of transparency and protecting confidential business information. In addition, the OECD survey discussion indicated that more specific information on the chemistries and uses are needed to prioritise the key chemistries from an exposure perspective.

**Conclusions of discussion on question 1:** These individual chemistries have very specific applications and uses that are tied to their performance.

Industry has grouped polyfluorinated substances into three main categories. Understanding the differences in chemistry, uses, and potential environmental and toxicity concerns are important to discussing the search for alternatives:

- **Fluoropolymers** – PTFE and ETFE polymers, for example, have very long chains and are either per- or poly-fluorinated with a molecular weight typically ranging from  $10^5$  -  $10^7$ . Uses include: wire and cable, semi-conductor, coatings (Non-stick pans, mechanical parts), personal care use, membranes/films, additives (e.g. paint), industrial applications (e.g. liners pumps, pipes and valves);
- **Polyfluorinated chemicals, including surfactants** – These can have, for example, sulfonate, phosphate functional groups. Some other examples are: PFOS, PFOA, PFNA, etc. Note: some ethers fall into group. Small polyfluorinated organics, but not HFCs. Uses include manufacturing aids, firefighting foams, surfactants in paints, inks, cleaning products, and personal care products, paper coatings, and metal treatment.
- **Polyfluorinated polymers**– Includes polymers with C2 – C14 side-chains (with some larger ones) on a polymer (non-fluorinated) backbone (Ethers, esters, urethanes, acrylics, etc.). Uses include coatings for textiles, paper, carpets, and leather.

The global trend shows that PFC and fluoropolymer use is increasing. Registrations of new PFCs are also increasing, however, volume data on these new substances is currently lacking.

In order to better address the first question, the OECD survey needs to provide information on the chemistries and uses (specifically enough to be useful to regulators and other key stakeholders). The use and production volume correlation of PFCs is important to be able to identify and prioritise the key chemistries from an exposure perspective. OECD does not have the mandate or means to go directly to

companies, but response from companies and countries is crucial. There are major difficulties in identifying key players.

**Conclusions of discussion on question 2:** The number of chemicals registrations as alternatives to potentially problematic PFCAs and precursors is increasing, but no volume data is available currently.

Due to the societal pressure on persistent and/or potentially bioaccumulative substances such as these fluorinated products, pro-active companies are driven into researching and developing alternatives to these applications. Certain new chemistries are appearing or have appeared on the market to replace existing applications. Paper coatings now have alternative fluorinated and non-fluorinated solutions already on the market.

A number of technologies are known to reduce the residual concentrations of PFCAs as unintended by-products.

It remains an open question whether polyfluorinated polymers and polyfluorinated chemicals as defined above break down into PFCAs and/or precursors under expected conditions during or after product lifetimes.

The difficulties discussing alternatives are due, in large degree, to the competing needs of transparency and protecting confidential business information.

Another challenge to alternatives is the need for both regulatory approval of chemistries (registration and permitting) and qualification of products for highly specialised applications.

**Conclusions of discussion on question 3:** In looking for alternatives, the original and/or degradation products must demonstrate decreased:

- Persistence;
- Bioaccumulation - (human and environmental);
- Toxicity/Hazard (human and environmental);
- Exposure (human and environmental) through use and end-of-life; and
- Exposure (human and environmental) during production.

For an alternative to be effective there must be an overall improvement of safety (hazards and risk information mentioned above) and, if possible, seek a reduction of uncertainty versus present chemicals. Of course, alternatives need to meet the functionality and performance requirements of an application. There are limiting factors in finding alternatives such as costs and application range (see conclusions under question 2).

**Conclusions of discussion on question 4:** In order to promote development of alternative processes and products, there are several incentives, both implicit and explicit, that can be encouraged:

- Direct financial incentives to alternatives;
- Increased environmental and bio-monitoring and research into the effects of PFCAs and precursors;

- Increased general knowledge to promote environmental responsible action;
- Regulatory incentives;
- Training incentives for green chemistry education;
- Transparency to consumers regarding product information;
- Accelerated product-approval process; and
- Multi-party stakeholder processes such as the US Design for the Environment.

The aims of the present Stewardship Programmes (US/Canada) need to be implemented globally to maintain the momentum of the emission reductions and in the development of alternative chemistries. It is especially important to engage BRIC (Brazil, Russia, India, and China), and other potential PFC producing countries in order not to undermine efforts in major chemical manufacturing states, since PFCs are a global issue.

## 6. Recommendations

The Workshop identified recommendations to the OECD, Member Governments, Academia and Industry (as indicated in parenthesis below). *It is recognised, however, that the identified information should not be misinterpreted as preventing conclusions in a regulatory context concerning risk assessment or management decision-making.*

Assessment and research needs: monitoring, emissions, exposure, environmental fate and transport:

- Information on the composition of commercial substances which are potential sources of PFCAs and their precursors should be made available, thereby contributing to experimental design and data interpretation. Similarly, to assess end use articles' contribution to the emission of PFCAs and their precursors, information should be made available including identity of the substances applied to the articles and the level of residual PFCA precursors present. This recommendation is consistent with the SAICM overarching policy strategy, paragraph 15 (b), and recognises the boundaries set by Intellectual Property Rights (**Industry, OECD**).
- Encourage studies to clarify direct and indirect sources of PFCAs (**Industry, Academia**).
- Global human biomonitoring studies are needed for PFCAs. Apart from studies on blood samples from adults, breast milk, umbilical cord blood and meconium are of particular interest (**Industry, Member Governments, Academia**).
- Multi-media studies are needed (e.g. food, drinking water, indoor air and dust, and consumer articles) to inform human exposure assessment (**Industry, Member Governments, Academia**).
- Temporal analysis should be performed as a means to estimate the effectiveness of measures now being implemented to reduce emissions and product content of PFCA (**Industry, Member Governments, Academia**).
- In monitoring activities, consider analytes which broadly cover the suite of PFCAs, known and potential precursors, and those which will help inform sources/uses (for example branched vs.

linear fluorocarbon chains and intermediates of precursor conversion to PFCAs e.g. presence of FTCAs during PFCA formation from telomer sources). Include exposure originating from articles (**Industry, Member Governments, Academia**).

- Work toward certified standard reference materials for PFCA analysis through the continuation of round robin (inter-laboratory comparison) laboratory activities (**Industry, Member Governments, Academia**).
- There is recognition of the differences in the physical/chemical properties of PFCAs of different chain length, and physical/chemical properties of known and potential precursors. Encourage further studies in order to develop understanding of how these differences impact environmental distribution and presence in humans and wildlife (**Industry, Member Governments, Academia**).

## **6.1 Assessment and Research needs: Effects**

### *6.1.1 Chemicals of Interest*

The chain lengths of known environmental or commercial relevance are C4-C14 PFCAs. Data for substances other than C4 and C8 are needed. Though not discussed at the Workshop due to time constraints, it was recognised there is a general lack of knowledge on precursors (**Industry, Member Governments, Academia**).

### *6.1.2 Toxicological and Toxicokinetic Studies*

- Further research should be focused on toxicokinetics, growth, development, hepatic effects, tumorigenicity, as well as other endpoints (e.g. circulating sex hormones). Considering the known effects on other vertebrates, reproductive endpoints should be included. Toxicity studies for substances other than C4 and C8 are needed (**Industry, Member Governments, Academia**).
- Since the long elimination half-life from human blood is an important concern for PFOA, this needs to be clarified for other PFCAs with high priority. In the absence of human elimination half-life data on other chain lengths, there is a need to develop a means of extrapolation of animal toxicokinetic (pharmacokinetic) data to humans. When conducting animal toxicokinetic (pharmacokinetic) studies, these should include faecal and urine analyses to attempt to achieve mass-balance; toxicokinetic (pharmacokinetic) studies using radiolabelled substances would be helpful. Future toxicity studies on PFCAs and precursors thus need to consider body burden; there is a need to report liver and blood concentrations e.g. at the end of the study (**Industry, Member Governments, Academia**).
- Species different from pelagic aquatic species need to be considered when performing additional studies on ecotoxic effects for PFCAs different from PFOA; non-standard study species may be more sensitive (e.g. soil nematodes). Avian toxicity tests need to be considered, given that some avian species are contaminated (**Industry, Member Governments, Academia**).
- Environmental fate of unsaturated acids, depending on persistence, may be of interest (**Industry, Member Governments, Academia**).
- More data on different trophic levels in terrestrial organisms, marine mammals and fish-eating avian species, i.e. air-breathing organisms, particularly at top of food chains, would be of interest

to address bioaccumulation and biomagnification potential in wildlife other than fish (**Industry, Member Governments, Academia**).

- OECD should start an activity aiming at examination of international harmonisation of methods regarding bioaccumulation (possibly including biomagnification) determination of certain perfluorinated substances (OECD).
- Industry should be encouraged to make studies more readily available. OECD countries should collate scientific information available in member countries; an Information Sharing or Clearing House repository under the auspices of the OECD, would make user friendly information available to member countries. Industry could consider adding toxicity data into a global portal e.g. an existing database such as Aquire (**Industry, OECD**).

## 6.2 *Risk Reduction Approaches*

- OECD should encourage member countries to launch outreach efforts to promote risk reduction programmes and play a coordinating role in collating information on available programmes (OECD).
- Though companies currently involved in the US Stewardship Programme were to achieve the goals on a global basis it is important for the OECD and Industry to encourage BRIICS-countries and other relevant non-member countries to be involved in similar programmes to reduce exposure levels. Governments and Industry should report to the OECD ongoing scientific risk assessments and risk reduction programmes in place that are aimed at reducing potential exposures (**Industry, OECD**).
- The OECD should encourage Industry to share the information on technologies effective in reducing environmental releases (OECD).
- The OECD should advise Governments to encourage companies to provide information on the chemical content of articles in the form of labelling or web-based product content disclosures (OECD).

## 6.3 *Uses, trends and alternative chemistries*

- The OECD and UN organisations should advise Governments to implement the present Stewardships Programmes (US/Canada) globally to maintain the momentum of development of alternative chemistries and emission reductions (OECD, UN).
- The OECD should advise Governments to encourage Industry to apply the basic principles of Green Chemistry to new product development. In particular, in looking for alternatives, the original and/or degradation products should demonstrate decreased:
  - Persistence;
  - Bioaccumulation – (human and environmental);
  - Toxicity/Hazard (human and environmental);
  - Exposure (human and environmental) through use and end of life; and

- Exposure (human and environmental) during production (**OECD**).
- For an alternative to be effective there should be an overall improvement of safety (hazards and risk information mentioned above) and, if possible, seek a reduction of uncertainty versus present chemicals. Alternatives need to meet the functionality and performance of an application. There are limiting factors in finding alternatives such as costs and application range (**Industry**).
- The OECD survey needs to provide information on the chemistries and uses, specifically enough to be useful to regulators. The use and volume correlation of PFCs is important to be able to identify and prioritise the chemistries from a potential exposure perspective (**OECD**).
- The OECD and BIAC need to define a cooperative process of how to collect more reliable data on the OECD survey; there is a need to find a way to improve the collection of information from companies (**Industry, OECD**).

**ANNEX 1:  
PFOA AND RELATED COMPOUNDS IN THE UNITED STATES OF AMERICA**

**Background Document for the OECD Workshop on PFCAs and Precursors, 20-22 November 2006**

The U.S. Environmental Protection Agency (USEPA) began its investigation of perfluorinated compounds in 1999, following the receipt of information submitted by the 3M Company (3M) under section 8(e) of the Toxic Substances Control Act (TSCA). TSCA section 8(e) requires companies to submit to USEPA any information which reasonably supports the conclusion that a substance presents a substantial risk of injury to human health or the environment.<sup>88</sup> The new 3M data indicated that exposure to perfluorooctane sulfonate (PFOS) caused reproductive and developmental toxicity in rats.<sup>89</sup> Additional information from 3M indicated that PFOS was extremely persistent in the environment, was being found at low parts per billion (ppb) levels in the environment worldwide and in the blood of the general U.S. population, and demonstrated a half-life in humans measured in years.<sup>90</sup>

Several of the monitoring reports from 3M on the presence of PFOS in human blood serum and in the environment also included data on perfluorooctanoic acid (PFOA). USEPA expanded its investigation to include PFOA, other related perfluorinated sulfonic and carboxylic acids, and their precursor chemicals early in 2000, to determine whether these chemicals might present a profile similar to PFOS and give rise to similar concerns for persistence, toxicity, and potential bioaccumulation.<sup>91</sup>

The U.S. investigation is still ongoing, but the USEPA has also taken both voluntary and regulatory chemical management activities intended to reduce releases of and exposures to these chemicals while the assessment process is underway. This background paper provides information on the U.S. investigation and on the specific actions that are being taken, and is intended to supplement the basic background paper on perfluorinated carboxylic acids (PFCAs) prepared for this Workshop by Sweden.

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<sup>88</sup> 14 USC 2607(e).

<sup>89</sup> Christian, M.S., Hoberman, A.M., and York, R.G. 1999b. Argus Research Laboratories, Inc. Protocol Number: 418-008, Sponsor Study Number: 6295.9, June 10, 1999. "Combined Oral (Gavage) Fertility, Developmental and Perinatal/Postnatal Reproduction Toxicity Study of PFOS in Rats." (TSCA Section 8(e) submission 8EHQ-0200-00374).

<sup>90</sup> (AR226-0548) Perfluorooctane Sulfonate: Current Summary of Human Sera, Health and Toxicology Data. 3M. St. Paul, MN. January 21, 1999. (Document Number EPA-HQ-OPPT-2002-0043-0007). Please note that any reference including an EPA docket number can be accessed at the U.S. Federal Docket website, <http://www.regulations.gov>, by using the "Advanced Search" feature to search for the complete document number.

<sup>91</sup> (AR226-0639) PFOS Presentation to CMA. Auer, Charles M., USEPA. Washington, DC. June 19, 2000. (Document number EPA-HQ-OPPT-2003-0012-0004).

## U.S. Actions Concerning PFOS

### *Voluntary Action and Regulatory Response*

3M, the principal global producer of PFOS and the only producer of PFOS and PFOS-related compounds in the U.S., decided voluntarily in 2000 to cease global production of both PFOS and PFOA by the end of 2002.<sup>92</sup> USEPA followed up this voluntary phaseout of PFOS with significant new use rules (SNURs) under TSCA section 5 in 2000 and 2002.<sup>93</sup> TSCA section 5 gives USEPA authority to review and regulate the manufacture, importation, and processing of new chemicals, and to regulate significant new uses of existing chemicals that may change or increase the exposure of humans and the environment to the chemicals.

These rules restrict the reintroduction into the U.S. market of 88 perfluoroalkyl sulfonate (PFAS) PFOS-related compounds that were specifically identified in the 3M phaseout for all but four specifically defined continuing uses.<sup>94</sup> The manufacture or importation of these chemicals for any other use would require prior review by the USEPA. The four uses excluded from this regulation, and thus allowed to continue in the U.S. without prior review, are:

- Use as an anti-erosion additive in fire-resistant phosphate ester aviation hydraulic fluids.
- Use as a component of a photoresist substance, including a photo acid generator or surfactant, or as a component of an anti-reflective coating, used in a photomicrolithography process to produce semiconductors or similar components of electronic or other miniaturised devices.
- Use in coatings for surface tension, static discharge, and adhesion control for analog and digital imaging films, papers, and printing plates, or as a surfactant in mixtures used to process imaging films.
- Use as an intermediate only to produce other chemical substances to be used solely for these specific uses.

All of these still-ongoing uses were characterized by low volume, low exposure potential, and low releases, and the affected industries, in their comments on the regulation, pledged continuing reductions in the volume and release of these chemicals as potential alternatives could be developed and qualified.<sup>95</sup>

### *Additional Regulatory Action*

USEPA proposed a follow-up SNUR on 183 additional PFOS-related chemicals appearing on the TSCA Inventory in March 2006, to subject those chemicals to the same restrictions as contained in the

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<sup>92</sup> 3M Phasing Out Some of its Specialty Materials. 3M News. 3M. St. Paul, MN. May 16, 2000.

<sup>93</sup> 65 FR 62319 (October 18, 2000); 67 FR 11008 (March 11, 2002); 67 FR 11014 (March 11, 2002); and 67 FR 72854 (December 9, 2002). These publications are also available on the Federal Docket website, <http://www.regulations.gov>, as document numbers EPA-HQ-OPPT-2002-0043-0001, EPA-HQ-OPPT-2002-0043-0003 and EPA-HQ-OPPT-2002-0043-0004.

<sup>94</sup> 40 CFR 721.9582.

<sup>95</sup> Illustrative comments appear on the Federal Docket website as document numbers EPA-HQ-OPPT-2002-0043-0011 through -0017.

2002 regulation.<sup>96</sup> The chemicals listed in the 2006 SNUR include PFAS chemicals comprising a range of carbon chain lengths. Comments on that proposed rule are currently under review.

The SNUR regulations do not affect the continued use of existing stocks of the listed chemicals that had been manufactured or imported into the U.S. prior to the effective date of the SNURs. Existing products and formulations already in the U.S. containing these chemicals – for example, PFOS-based fire fighting foams produced before the rules took effect in 2002 – can still be used.

## **U.S. Actions Concerning PFOA**

### ***Background***

At the time of the original PFOS phaseout by 3M in 2000, the data set for PFOA was less complete than for PFOS. Further, although 3M phased out their manufacture of PFOA, PFOA continued to be produced in the U.S. by E.I. DuPont de Nemours and Company (DuPont), and to be imported and used by other companies. EPA began efforts in June 2000 to assess PFOA to determine whether it might present the same undesirable environmental profile as PFOS, and to identify the sources of PFOA in the environment and the pathways leading to human and environmental exposures. Substantial data have been developed and risk assessments prepared which support that PFOA is of concern, although uncertainties remain.

In the United States, according to documents submitted by industry, PFOA – usually in the form of its ammonium salt, ammonium perfluorooctanoate (APFO) – is used intentionally only in the production of fluoropolymers, such as polytetrafluoroethylene (PTFE). APFO, when released to the environment, rapidly dissociates into the acid, PFOA. Examples of fluoropolymer products include non-stick coatings on cookware; the membranes that make waterproof, breathable clothing; fire-resistant casings for plenum cable; fire and chemical-resistant tubing; and plumbing thread sealant tape. At the present time, viable alternatives to PFOA for this fluoropolymer manufacturing use have not been identified.

As noted in the background paper produced for this Workshop by Sweden, PFOA can also be produced by the breakdown of some fluorinated telomers. These telomers are fluorinated polymers produced through a specific process called telomerization, in which a chain-ending chemical is introduced to stop the reaction at a specified carbon chain length. Most telomers are relatively small polymers, and are used in surface treatment products to impart soil, stain, grease, and water resistance to carpets, textiles, paper, stone, and leather. Some are used as high performance surfactants in products that must flow evenly, such as paints, coatings, and cleaning products, fire-fighting foams for use on liquid fuel fires, or the engineering coatings used in semiconductor manufacture.

The 8-2 telomer alcohol, which is often used in the telomerization process, is volatile and readily breaks down to PFOA. Residual alcohols, iodides, and related monomers remaining as impurities in final telomer products can also break down to PFOA and related perfluorinated carboxylic acids. It is not yet known whether the telomer polymer backbone itself can break to release PFOA and related acids.

These fluorinated compounds possess unique functionality and are extremely valuable for myriad uses. Their unusual physical and chemical properties also make them extremely challenging and expensive to study.

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<sup>96</sup> 71 FR 12311 (March 10, 2006). (EPA-HQ-OPPT-2005-0015-0001)

### ***The PFOA Enforceable Consent Agreement (ECA) Process***

Studies on PFOA and the 8-2 telomer alcohol were undertaken voluntarily by the industry in response to the issues raised by USEPA in 2000. Additional data provided by these studies, particularly including a two-generation reproductive study of PFOA in rats indicating developmental toxicity, prompted USEPA to designate PFOA for a priority review beginning in September 2002.<sup>97</sup>

In March 2003, individual companies and industry groups submitted Letters of Intent (LOI) to USEPA outlining their voluntary commitments to emission reductions and to additional research on PFOA and telomers.<sup>98</sup> With uncertainties and data gaps remaining in the PFOA assessment, particularly with regard to source and pathway information, USEPA initiated a public process in April 2003 to pursue the negotiation of enforceable consent agreements (ECAs) to generate missing data.<sup>99</sup> The public ECA process, which involves USEPA, other Federal and State agencies, industry, and environmental and public interest groups in the development of study protocols for legally enforceable testing programmes, is an alternative to obtaining testing via notice and comment rulemaking under section 4 of TSCA.

Early meetings in the PFOA ECA process identified specific data gaps concerning both fluoropolymers and fluorinated telomers.<sup>100</sup> Industry voluntarily provided information to fill certain of these gaps, including chemical identification and physical/chemical properties information, production volume data, and product stewardship information. Two ECAs for laboratory-scale incineration testing on fluoropolymers and on fluorotelomer-based polymers were signed and published in July 2005, to determine whether the incineration of these substances, particularly in municipal waste incinerators, could be a source of PFOA and contribute to PFOA exposures.<sup>101</sup> That testing is currently underway, and the data produced will be submitted to the public docket. A third ECA to determine whether fluoropolymers could generate PFOA as they age is still under negotiation.

### ***Establishing Memoranda of Understanding***

Environmental sampling and monitoring to further understand the sources of PFOA and its fate and transport in the environment were identified as data needs during the PFOA ECA process. Securing ECAs for this activity proved infeasible, but USEPA negotiated Memoranda of Understanding (MOUs) with 3M in October 2004<sup>102</sup> and with DuPont in November 2005<sup>103</sup> for monitoring in the vicinity of fluoropolymer manufacturing facilities located in Decatur, Alabama and Parkersburg, West Virginia, respectively. These monitoring programmes address the presence of PFOA in ground water, surface water, soil, sediment, air, and biota, including plants and small mammals. All of the data generated by the MOUs are being submitted to public dockets. Under the terms of the MOU, each company will produce exposure assessments based on their data, and the assessment documents will be submitted together with the data to

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<sup>97</sup> Revision of PFOA Hazard Assessment and Next Steps. Auer, Charles M. USEPA. Washington, DC. September 27, 2002. (EPA-HQ-OPPT-2003-0012-0005).

<sup>98</sup> LOI Letters appear in the Federal Docket at document numbers EPA-HQ-OPPT-2003-0012-0007, EPA-HQ-OPPT-2003-0012-0012, EPA-HQ-OPPT-2003-0012-0013, and EPA-HQ-OPPT-2003-0012-0016.

<sup>99</sup> 68 FR 18626 (April 16, 2003). (EPA-HQ-OPPT-2003-0012-0001).

<sup>100</sup> Preliminary Framework for ECA Data Development. USEPA. May 21, 2003. (EPA-HQ-OPPT-2003-0012-0056, pages 4-13.)

<sup>101</sup> Fluoropolymers, 70 FR 39630 (July 8, 2005) (EPA-HQ-OPPT-2003-0071-0001); Fluorotelomers, 70 FR 39624 (July 8, 2005) (EPA-HQ-OPPT-2004-0001-0001).

<sup>102</sup> EPA-HQ-OPPT-2004-0112-0002 (October 25, 2004).

<sup>103</sup> EPA-HQ-OPPT-2004-0113-0002 (November 3, 2005).

an independent third party, which will conduct a peer consultation with public input to evaluate the data. The peer consultation panel will offer recommendations for any further monitoring, information gathering, or other research needed to illuminate the question of how PFOA is getting into humans and the environment. The peer consultation information will also be available in the public docket.

### ***Additional Issues in the PFOA ECA Process***

The PFOA ECA process identified additional questions concerning potential PFOA sources and exposures attributable to the use, aging, and end-of-life disposal of fluoropolymers and of telomer-treated products and articles. Although the incineration ECAs seek to address the potential contribution of incineration of these items to PFOA exposures, the use and aging elements have not yet been addressed. USEPA continues to pursue the negotiation of an ECA for testing to determine whether fluoropolymers could produce additional PFOA as they age, distinct from any residual PFOA remaining from the manufacturing process. USEPA also announced in June 2006 that the Agency itself would conduct aged article testing on both fluoropolymers and telomers. The design of those article aging studies is currently underway. Various industry commitments to conduct similar testing were contained in the LOI documents submitted in March 2003, but data have not yet been developed.

The PFOA ECA process also failed to produce agreement on a testing programme to determine whether the polymer backbone structure of fluorinated telomers could degrade to yield PFOA. Separate testing programmes are underway by USEPA and by industry to address this question.

### ***PFOA Risk Assessment***

In April 2003, USEPA released a very preliminary draft risk assessment on the developmental toxicity of PFOA in conjunction with the publication of the notice commencing the PFOA ECA process.<sup>104</sup> Work on developing the assessment continued in parallel with the Agency's other PFOA-related activities. In January 2005, the USEPA Office of Pollution Prevention and Toxics submitted a more comprehensive draft risk assessment of PFOA to the USEPA Science Advisory Board (SAB) for public peer review by a panel of experts.<sup>105</sup> This draft assessment was preliminary and did not provide conclusions regarding potential levels of concern.

The draft assessment highlighted the scientific approaches to be used in developing the overall PFOA risk assessment. To determine whether environmental exposure to PFOA might pose a risk to human health, EPA's draft assessment provided an evaluation of available information on health effects and human exposures to PFOA. Since there are substantial species differences in the elimination of PFOA from the body, different species could have vastly different blood levels resulting from the same exposure level. Thus, for PFOA it is necessary to use an actual measure of PFOA in the body (known as internal dose) when comparing humans and animal test species. In the draft risk assessment, the animal studies were evaluated to determine the "no effect level" in mg/kg-day. If a "no effect level" was not established in a study, then the lowest "effect level" was used. In some of the animal studies, serum PFOA concentrations had been measured. For studies where serum concentrations were not measured, pharmacokinetic modeling was used to estimate serum concentrations of PFOA at the "no effect level," or if necessary, at the lowest "effect level." These measured or estimated serum concentrations were then compared to blood

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<sup>104</sup> Preliminary Risk Assessment of the Developmental Toxicity Associated With Exposure to Perfluorooctanoic Acid and Its Salts (PFOA). USEPA. Washington, DC. April 10, 2003. (EPA-HQ-OPPT-2003-0012-0002)

<sup>105</sup> Draft Risk Assessment of the Potential Human Health Effects Associated With Exposure to Perfluorooctanoic Acid and Its Salts (PFOA). USEPA. Washington, DC. January 4, 2005. (EPA-HQ-OPPT-2003-0012-0840). This document can also be accessed on the EPA website at <http://www.epa.gov/opptintr/pfoa/pubs/pfoarisk.pdf>

levels that had been measured in several human biomonitoring studies. USEPA sought review and comment from the SAB to ensure that these approaches would be scientifically sound.

The SAB completed its review and issued its report on the draft risk assessment on May 30, 2006.<sup>106</sup> In general, the SAB Panel endorsed USEPA's risk assessment approach, particularly the inclusion of multiple non-cancer health endpoints for risk assessment, and the use of PFOA blood levels as a measure of estimated dose in place of the administered dose in toxicologic studies. The Panel recommended the inclusion of additional non-cancer health endpoints for risk assessment, and the use of the Benchmark Dose method to better estimate the lowest observed effect levels and no observed effect levels for risk assessment. They also recommended that a risk assessment be conducted for carcinogenic effects. The SAB urged USEPA to strengthen its risk assessment by considering verified and peer reviewed new information found to be relevant and critical to the assessment.

Taking the SAB Panel's input into account, USEPA is continuing to develop a full and comprehensive assessment of the risks associated with PFOA. In the year and a half between the submission of the draft assessment to the SAB Panel and the release of the SAB's report, a considerable amount of additional research was initiated, and some has been completed. Some of this new research may impact the Panel's assessment of PFOA. For this reason, USEPA considers that it is premature to draw any conclusions on the potential risks, including cancer, from PFOA until this new testing is complete and the data are integrated into the risk assessment.

The United States and Germany currently share the lead on the development of a hazard assessment of PFOA for the OECD.

#### **Additional U.S. Studies Underway**

In 2003, USEPA requested that the U.S. Center for Disease Control and Prevention (CDC) include PFOS, PFOA, and related perfluorinated acids in the National Health and Nutrition Examination Survey (NHANES), an ongoing programme of national biomonitoring within the United States. CDC refined the analytical techniques required for large scale sampling and monitoring for these chemicals in human blood serum, and incorporated these chemicals into its monitoring programme. The first nationwide data on the presence of PFOS, PFOA, and related chemicals in the U.S. population will be published in the 2007 *National Report on Human Exposure to Environmental Chemicals*, due to be released in Spring 2007.<sup>107</sup> The CDC has published some retrospective analyses of stored serum samples from earlier sampling years, but the 2007 report will constitute the first national baseline data for the presence of these chemicals in the U.S. population. The *National Report* is published every two years. USEPA anticipates that this ongoing data collection will provide a valuable tool for assessing whether the risk management efforts undertaken by the USEPA and by industry to reduce emissions of and resulting exposures to these chemicals are having the desired effect.

Also in 2003, USEPA requested that the National Toxicology Programme (NTP) undertake a class study on perfluorinated sulfonic and carboxylic acids, as well as telomer derivatives that could degrade to these acids, with carbon chain lengths ranging from four through twelve carbons.<sup>108</sup> The intent

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<sup>106</sup> SAB Review of EPA's Draft Risk Assessment of Potential Human Health Effects Associated with PFOA and Its Salts, EPA-SAB-06-006. Washington, DC. May 30, 2006. This document can be accessed on the USEPA SAB website at [http://www.epa.gov/sab/pdf/sab\\_06\\_006.pdf](http://www.epa.gov/sab/pdf/sab_06_006.pdf)

<sup>107</sup> The CDC *National Report* can be accessed on the CDC website at <http://www.cdc.gov/exposurereport/>.

<sup>108</sup> Letter from Auer, Charles M., USEPA. Washington, DC. August 7, 2003. The letter can be accessed on the NTP website at [http://ntp.niehs.nih.gov/ntp/htdocs/Chem\\_Background/ExSumpdf/PerfluorinatedCmpds.pdf](http://ntp.niehs.nih.gov/ntp/htdocs/Chem_Background/ExSumpdf/PerfluorinatedCmpds.pdf).

of the class study is to identify and fill data gaps on these chemicals, particularly with respect to mechanisms of toxicity, bioaccumulative potential, and pharmacokinetics. NTP accepted the USEPA request, and this study is in a design phase. Information on the study will appear on the NTP website.<sup>109</sup> The NTP is comprised of members from the National Institute of Environmental Health Sciences from the National Institutes of Health (NIEHS/NIH), the National Institute for Occupational Safety and Health of the CDC (NIOSH/CDC), and the National Center for Toxicological Research of the Food and Drug Administration (NCTR/FDA).

The USEPA Office of Research and Development (ORD) has developed research programmes to characterize the toxicity of various perfluoroalkyl acids, to explore their modes of action, to develop analytical methods for their detection in various media, and to investigate the fate and transport of these chemicals in the environment. Completed studies are submitted for publication in peer-reviewed journals.

Multiple non-government studies are also underway, including studies examining human health data on exposed populations to determine whether any correlations may exist between elevated levels of PFOA exposure and any human health effects.<sup>110</sup> These studies are expected to continue for several years.

### **2010/15 PFOA Stewardship Programme**

Although the risk assessment process on PFOA and related chemicals is still underway and definitive answers on risk have not yet been developed, USEPA took action in January 2006 to invite all of the major companies in this industry doing business in the United States to commit to a voluntary global stewardship programme.<sup>111</sup> This programme contemplates working toward eliminating emissions and product content of these chemicals. The rationale for this programme is the recognition that PFOA is persistent in the environment, that it has been detected in human blood, and that animal studies indicate effects of concern. Given that profile, minimising future environmental loadings of and potential exposures to these chemicals appears a prudent course. The programme addresses PFOA, precursor chemicals that can break down or dissociate to PFOA, and related higher homologue – longer carbon chain length – chemicals. The higher homologues were included in the programme based on limited information indicating that eight-carbon and longer chain length acids were associated generally with higher toxicity and longer retention times in the body than shorter chain length chemicals.

Participation in the stewardship programme requires voluntary corporate commitment to two goals:

1. To commit to achieve, no later than 2010, a 95 % reduction, measured from a year 2000 baseline, in *both*: facility emissions to all media of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals, *and* product content levels of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals; and
2. To commit to working 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.

<sup>109</sup> Search for “perfluorinated” on the NTP website, <http://ntp.niehs.nih.gov/>, under “Testing Status of Agents at NTP.”

<sup>110</sup> Information on two of these studies can be accessed on the individual study organization websites at <http://www.c8sciencepanel.org/> and <http://www.lhwc8study.org/>.

<sup>111</sup> Letter from Johnson, Stephen A, USEPA. Washington, DC. January 25, 2006. (EPA-HQ-OPPT-2006- 0621-0002). This letter can also be accessed on the EPA website at <http://www.epa.gov/oppt/pfoa/pubs/pfoastewardship.htm>.

All eight of the invited companies – AGC Chemicals/Asahi Glass; Arkema, Inc.; Ciba Specialty Chemicals; Clariant Corporation; Daikin; 3M/Dyneon; DuPont; and Solvay Solexis – submitted letters of commitment to the stewardship programme by March 1, 2006.<sup>112</sup>

Companies participating in this 2010/15 PFOA Stewardship Programme are to submit their year 2000 baseline numbers for emissions and product content to USEPA by October 31, 2006. If the companies have no data on these chemicals from the year 2000, they would use the closest year for which data are available, and adopt that year as their baseline. To ensure transparency, the programme specifies that companies will submit annual public reports on their progress toward the goals in October of each succeeding year, expressing their progress in terms of company-wide percentage achievements both for U.S. operations and for the company's global business. Companies are also to provide to USEPA detailed information on their progress in support of their public reports. The public reports will be available on the USEPA website, while the detailed reports will be contained in the docket for the programme. Detailed information may be claimed as confidential business information where appropriate, but the programme encourages companies to minimise confidentiality claims.

USEPA has developed suggested guidance for information submissions under the programme, based on the voluntary Use and Exposure Information Project (UEIP) reporting form developed by USEPA in cooperation with industry during the 1990's.

These chemicals present considerable scientific challenges in ensuring accurate and reproducible results in chemical analyses. To ensure that the results reported under the 2010/15 PFOA Stewardship Programme are both comparable and reliable, each participating company was asked to commit to work with EPA, other PFOA Stewardship Programme participants, and others in order to establish scientifically credible analytical standards and laboratory methods for measuring the chemicals in the programme by 2010, the first goal attainment year. Participants were also requested to make a general commitment to continue research to better understand the sources, pathways of exposure, and potential risks of these chemicals.

USEPA has encouraged the participating companies to capture in their reporting under the stewardship programme the full range of their activities to reduce emissions of and exposures to all of these related chemicals, including PFOS and higher homologue PFAS as well as PFOA and other higher homologue perfluorinated carboxylic acids (PFCAs). The programme does not prescribe how companies should achieve these goals, but instead encourages maximum flexibility to allow companies to devise business plans and pursue technology development consistent with their capabilities.

The programme requested companies to commit to the programme goals on the basis of their global operations as well as their U.S. activities because these chemicals have been found in remote locations indicating the potential for long-range transport of these chemicals. The United States encourages other countries to support the activities of these companies to respond to the programme, and to invite other companies to take similar action.

### **Other Interim Actions**

Certain individual States within the United States have taken action to set interim standards for PFOS and/or PFOA in specific local areas particularly affected by chemical releases. The State of Minnesota, for example, where 3M had production facilities, set interim health-based values in 2005

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<sup>112</sup> These letters appear in the Federal Docket website as document numbers EPA-HQ-OPPT-2006-0621- 0004 through -0011, and can also be accessed on the EPA website at <http://www.epa.gov/opptintr/pfoa/pubs/commitments.htm>.

requiring the provision of alternative water supplies or water treatment for persons whose drinking water source contains PFOS in excess of 1 ppb, or PFOA in excess of 7 ppb.<sup>113</sup>

USEPA has not set a national standard limiting the presence of either PFOS or PFOA in drinking water. Risk assessment activities that will eventually produce reference dose information for these chemicals is underway, but regulatory action would be premature at this stage of the assessment activity.

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<sup>113</sup> Information on the Minnesota activities can be accessed on the Minnesota Department of Health website at <http://www.health.state.mn.us/divs/eh/hazardous/sites/washington/3Mcottagegrove.html>.

**ANNEX 2:  
ONGOING ACTIVITIES IN CANADA ON THE ASSESSMENT AND MANAGEMENT OF  
PFCAs AND THEIR PRECURSORS**

**Background Document for the OECD Workshop on PFCAs and Precursors  
20-22 November 2006, Stockholm, Sweden**

Canada's Action Plan for the Assessment and Management of Perfluorinated Carboxylic Acids and their Precursors, was published in the Canada Gazette on June 17, 2006. It outlines a series of measures that will further protect the health of Canadians and the environment from exposure to these substances. New information may result in amendments to these measures.

The Action Plan addresses the concern that PFCA precursors can enter the environment through 2 routes:

- Through their release because they are present as "residual" unreacted building blocks of fluorotelomer-based substances; and
- Through their release upon degradation of fluorotelomer-based substances.

This Action Plan focuses on the long chain PFCAs, *i.e.* those with nine or more carbons. However, consideration will be given to the inclusion of other chain lengths if information that justifies it becomes available.

The *Canadian Environmental Protection Act, 1999* (the Act) requires that no new substance be introduced into Canadian commerce without first being assessed to determine if it could pose a risk to Canadians or the environment. In 2004, Environment Canada and Health Canada conducted assessments of four new fluorotelomer-based substances after notifications were received from companies wishing to import these substances in Canada. The assessments concluded the four new fluorotelomer-based substances are sources of long chain PFCAs, and meet "toxic" criteria set out in Section 64 of the Canadian Environmental Protection Act (CEPA), 1999. The Ministers subjected these substances to a temporary prohibition and on June 17<sup>th</sup>, 2006, a proposed regulation to prohibit their import and manufacture was published. Considering there are substances similar to these four substances in Canadian commerce, Environment Canada and Health Canada will implement the measures of the Action Plan outlined below.

**Summary of Proposed Measures for the Assessment and Management of PFCAs and their Precursors**

1. Prevent the introduction into Canada of new substances which would contribute to the observed load of longer chain PFCAs in the environment:
  - maintain the prohibitions on the four new fluorotelomer-based substances by proposing a regulation to that effect; and

- based on the current understanding of the science and consistent with past actions, consider issuing Ministerial prohibitions on any new long chain PFCA precursor which is notified under the *New Substances Notification Regulations*.
2. Recognising that “residual” PFCA precursors are present in certain substances already in Canadian commerce, seek action from industry to significantly reduce these residuals, consistent with the current EPA global stewardship programme. Environment Canada and Health Canada will work with stakeholders to establish details for this action, including timelines and reduction targets and a reporting and accountability framework.
  3. Pursue further assessment of PFCAs and precursor substances already in Canadian commerce in order to guide further risk management actions, as needed.
  4. An assessment of PFOA is in preparation by Existing Substances programme of Environment Canada and Health Canada, and a State of the Science Report (Ecological) is expected to be released soon.
  5. Advance the understanding of issues and related solutions through the promotion of:
    - scientific research on PFCAs and their precursors, including additional work on sources, fate and effects, and better understanding of the contribution of PFCAs in the environment resulting from the breakdown of fluorotelomer-based substances; and
    - research and development of alternatives that are preferable for the protection of human health and the environment, for example substances with reduced persistence, bioaccumulation and toxic properties.
  6. Engage international partners in global action to reduce risk from longer chain PFCAs. As the industry is global in nature, and there is a long range transport dimension to PFCA pollution, cooperation with other regulators will seek actions to address this issue.

## Conclusion

This series of measures regarding PFCAs and their precursors, addressed through the Action Plan, will further protect the health of Canadians and the environment from exposure to these substances. New information may result in amendments to these measures as needed.

Please refer to the following website for additional detail:

[http://www.ec.gc.ca/TOXICS/EN/detail.cfm?par\\_substanceID=199&par\\_actn=s1](http://www.ec.gc.ca/TOXICS/EN/detail.cfm?par_substanceID=199&par_actn=s1).

**ANNEX 3:  
EU ACTIVITIES ON PFCA**

**Background Document for the OECD Workshop on PFCAs and Precursors  
20-22 November 2006, Stockholm, Sweden**

***Research***

Perfluorinated compounds (PFCs) are used in many consumer products today. These chemicals are highly stable, do not degrade easily in the environment and can accumulate in living organisms. To make a full risk assessment of the environmental impact of PFCs, accurate data on their physicochemical properties and new tools to assess the movement and distribution of PFCs are needed. The Commission has set out the PERFORCE research project, bringing together expert teams, including industry, to significantly boost our understanding of PFCs.

Work in the project is split between developing new chemical analytical methods, bioanalytical tools, physicochemical property and fate modelling, environmental modelling and validation of techniques. An important component of the project will be transfer of know-how from industry to the academic teams. The final exposure assessment will be based on both field data and modelling.

The project also links with other international initiatives, especially in North America and OECD projects, to provide calibration and comparison/standardisation of techniques to give a global dimension to this global problem.

PERFORCE selected some representative PFCs from the many that are manufactured or observed in the environment. The chemical analytical and quality assurance work packages showed that blank contamination is an item of paramount importance in the analysis. Analytical methods for four different matrices were developed and validated; these include water, sediment, air, and biota. For these matrices analytical protocols were developed that are deliverables of the project. The analytical methods developed showed good accuracies on the matrices included in the validation, demonstrating that these methods are fit-for-purpose. A worldwide inter-laboratory study was organised using a fish tissue, fish liver extract and a water sample. The results revealed large variations in the between-laboratory results, showing that participating laboratories were not yet able to generate comparable results. Specific bioassays were developed that were able to quantify individual compounds (PFOA and PFOS) but were less promising when applied to extracts from environmental matrices due to cytotoxic side effects. Perfluoralkyl compounds show distinct toxicological modes of action *in vitro* that include estrogen-like, mitogen-like properties, membrane and DNA interference, and oxidative stress.

The physicochemical data collected in this work confirm that atmospheric transport may be important for certain PFCs, notably the fluorotelomer alcohols. In addition they showed that the two major representatives of the PFCs, vis. PFOA and PFOS, do not accumulate in sediments, and that sorption to sediment does not strongly affect water-mediated transport of these PFCs. Sediment is probably not a major sink for PFOS, PFOA and shorter chain homologues. Sorption does increase with carbon chain length, however, and thus becomes more important in the environmental fate of longer chain PFAS. Anaerobic and aerobic degradation of PFCs was tested and did not occur under the test conditions used.

The results of the sampling campaigns show that PFCs are ubiquitously present in the European environment. Sewage treatment plants probably serve as sources of PFAS both for the aquatic ecosystems (through effluent discharges) and the terrestrial environment (through application of sewage sludge in agriculture). Levels of PFOS in sediments have increased from 1990 to 2005, whereas for PFOSA an initial increase was followed by a possible decrease after 2000.

The annual loading to the European environment of PFHxA, PFHpA, and PFOA from rivers is estimated to be of the order of 10, 2, and 20 tonnes. The Danube and Rhine watersheds are particularly important source regions, whereby the Elbe and Po also make a significant contribution for PFHxA and PFHpA/PFOA, respectively. In European air, PFOA was often the predominant PFC found in the particulate phase, while 6:2 FTOH and 8:2 FTOH were the prevailing analytes found in the gas phase. Many other compounds were also present in air.

Spatial differences were observed particularly in biota. PFOS and PFOSA concentrations were higher in North Sea cod liver than in cod liver from the Kattegat and the Baltic. In marine mammals concentrations of PFOS are higher in species feeding close to the shore or in estuaries than in off shore feeders. A relationship appears to exist between concentrations of PFOS and trophic levels in marine mammals. In these mammals perfluorinated carboxylic acids are relatively low in all species and tissues analysed. PFOS, PFDA and PFUnA bioaccumulate in a simple estuarine food chain, PFOA accumulates significantly less.

More info: <http://www.science.uva.nl/perforce/>.

## **PFOS**

### ***Risk Assessment***

Perfluorooctane sulfonate (PFOS) is a fully fluorinated anion, the related compounds of which are members of the large family of perfluoroalkyl sulfonate substances (PFAS). The majority of PFOS related substances are polymers of high molecular weight in which PFOS is only a fraction of the polymer molecular weight. The term 'PFOS related substances' is used to represent any substance that can degrade to PFOS in the environment.

After the announcement of 3M in May 2000 that it would phase-out the use of PFOS voluntarily from 2001 onwards, several OECD countries agreed to informally work together to collect information on the physico-chemical and toxic properties of PFOS for the purpose of conducting a hazard assessment. The UK and the US agreed to take the lead. This hazard assessment concluded that the presence and persistence of PFOS in the environment, combined with its toxicity and bioaccumulation potential indicated a cause for concern to the environment and human health.

In response to these findings, the Environment Agency for England and Wales commissioned a study to review the environmental risks (RER) arising from uses of PFOS. The RER concluded that PFOS is a risk to the environment and that it meets the PBT criteria for concern outlined in the UK chemicals strategy and is therefore a priority for action. It has identified risks to the environment for all remaining uses of PFOS related substances. The calculated background concentrations have been found to be sufficiently high to indicate a risk for secondary poisoning without the local contributions from the specific use patterns.

More info:

[http://www.environment-agency.gov.uk/commondata/105385/pfos\\_rer\\_sept04\\_864557.pdf](http://www.environment-agency.gov.uk/commondata/105385/pfos_rer_sept04_864557.pdf).

## **Risk Reduction Measures**

### ***UK RRS and restrictions proposal***

The UK commissioned an environmental Risk Reduction Strategy (RRS) for PFOS and related substances, including an analysis of the advantages and drawbacks of potential risk reduction options. The RRS was developed in accordance with the EU Technical Guidance Document on development of RRS. They have analysed all risk reduction options and concluded that 'marketing and use restrictions on the use of PFOS related substance for all current uses, as well as former and potential future uses, will provide the only effective level of control'. In addition to prohibiting the use, they proposed also to prohibit storage of the substance. They also defined a few time limited derogations with the ban (i.e. full restrictions coming into force for a specified time).

More info:

<http://www.defra.gov.uk/environment/chemicals/pdf/pfos-riskstrategy.pdf>.

<http://www.defra.gov.uk/corporate/consult/pfos/ria.pdf>.

The work of the UK on the risk assessment and the development of the RRS was discussed with Member States and stakeholders in technical meetings on risk assessment and on risk reduction. The Scientific Committee on Health and Environmental Risks (SCHER) adopted on 18 March 2005 an opinion on the UK report on 'Perfluorooctane Sulphonates Risk reduction strategy and analysis of drawbacks and advantages'. The SCHER opinion was critical about the UK report, but agreed that:

- PFOS is a (v)P(v)BT.
- PFOS fulfills the POP criteria.
- Re-occurrence of former uses must not be allowed.
- Significant new uses must not be allowed in future.
- Use in plating industry should be restricted.
- Ongoing uses in aviation, semiconductor and photographic applications do not pose a significant risk, if releases to environment and workplace are minimised.

More info: [http://ec.europa.eu/health/ph\\_risk/committees/04\\_scher/docs/scher\\_o\\_014.pdf](http://ec.europa.eu/health/ph_risk/committees/04_scher/docs/scher_o_014.pdf).

### ***EU restrictions proposal***

The European Commission proposed marketing and use restrictions under Directive 76/769/EEC in December 2005.

More info: [http://eur-lex.europa.eu/LexUriServ/site/en/com/2005/com2005\\_0618en01.pdf](http://eur-lex.europa.eu/LexUriServ/site/en/com/2005/com2005_0618en01.pdf).

The Council and Parliament have subsequently discussed the proposal and have recently reached an agreement on the basis of which the Commission will now proceed. The contents of the agreed restrictions will be presented.

## POPs

### *Stockholm Convention*

PFOS has been proposed by Sweden to be included in the Stockholm convention. The Swedish proposal has been discussed during the first meeting of POP review Committee (Geneva, 7–11 November 2005). The Committee adopted the following decision:

"Decision POPRC-1/7: Perfluorooctane sulfonate

The Persistent Organic Pollutants Review Committee,

Having examined the proposal by Sweden, which is a Party to the Stockholm Convention on Persistent Organic Pollutants, to list perfluorooctane sulfonate and ninety-six potential perfluorooctane sulfonate precursors in Annex A to the Convention and having applied the screening criteria specified in Annex D to the Convention, Noting that the perfluorooctane sulfonate anion does not have a Chemical Abstracts Service number and does not appear as an anion in the environment, but that the perfluorooctane sulfonate acid and its salts listed in the proposal have the following Chemical Abstracts Service numbers:

- Acid 1763-23-1
- Potassium 2795-39-3
- Lithium 29457-72-5
- Ammonium 29081-56-9
- Diethanolamine salt 70225-14-8

1. *Decides*, in accordance with paragraph 4 (a) of Article 8 of the Convention, that it is satisfied that the screening criteria have been fulfilled for perfluorooctane sulfonate, as set out in the evaluation contained in the annex to the present decision;
2. *Decides also*, in accordance with paragraph 6 of Article 8 of the Convention and paragraph 29 of decision SC-1/7 of the Conference of the Parties to the Stockholm Convention, to establish an ad hoc working group to review the proposal further and to prepare a draft risk profile in accordance with Annex E to the Convention;
3. *Decides further* that issues related to the inclusion of potential perfluorooctane sulfonate precursors should be dealt with in developing the draft risk profile;
4. *Invites*, in accordance with paragraph 4 (a) of Article 8 of the Convention, Parties and observers to submit to the Secretariat the information specified in Annex E before 27 January 2006."

The POP review Committee will discuss the PFOS risk profile at its second meeting (2-6 November 2006).

### *UNECE POP-Protocol*

PFOS has been proposed by the European Community to be included in the UNECE POP Protocol. The proposal has been discussed in 2005 and the parties, at the Executive body meeting in

December 2005, to the protocol took note of the conclusions on the technical content of the dossier on PFOS and agreed that it should be considered as POPs as defined under the Protocol, and requested that the Task Force on POPs continue to explore management strategies for PFOS. The discussions on management strategies could be finalised in 2007 and the Protocol amended later on taking into account the outcome on the discussions.

## **PFOA**

### ***Risk Assessment***

The OECD hazard assessment on PFOA by Germany and the US is nearly finished.

Germany will continue to develop a risk assessment on PFOA.

### ***Risk Reduction Measures***

Within the context of the PFOS marketing and use restrictions it has been agreed that the Commission shall keep under review the ongoing risk assessment activities and the availability of safer alternative substances or technologies related to the use of perfluorooctanoic acid (PFOA) and related substances and propose all necessary measures to reduce identified risks, including restrictions of marketing and use, in particular when safer alternative substances or technologies, that are technically and economically feasible, are available.

### ***Classification & Labelling***

EU Technical Committee on Classification and Labelling of Dangerous Substances (TC C&L) has agreed that PFOA should be classified as follows (Summary Record of the Technical Committee Meeting of 3rd October 2006): Carc. Cat. 3; R40, Repr. Cat 2; R61, NC Repr. Cat. 3; R62, T; R48/23, Xn; R20/22, Xn; R48/22, Xi; R36. More details are provided in the Box below.

<p><b>N002</b></p> <p><b>Perfluorooctanic acid (PFOA) [1]</b>  <b>Ammonium pentadecafluorooctanoate (APFO) [2]</b>  <b>Sodium pentadecafluorooctanoate [3]</b>  <b>Potassium perfluorooctanoate [4]</b>  <b>Silver(1+) perfluorooctanoate [5]</b>  <b>Pentadecafluorooctyl fluoride [6]</b>  <b>Methyl perfluorooctanoate [7]</b>  <b>Ethyl perfluorooctanoate [8]</b></p> <p><b>Not listed in Annex I</b>  <b>EC No:</b> 206-397-9 [1]  223-320-4 [2]  206-404-5 [3]  219-248-8 [4]  206-402-4 [5]  206-396-3 [6]  206-808-1 [7]  221-468-4 [8]  <b>CAS No:</b> 335-67-1 [1]  3825-26-1 [2]  335-95-5 [3]  2395-00-8 [4]  335-93-3 [5]  335-66-0 [6]  376-27-2 [7]  3108-24-5 [8]</p>	<p><i>In March 2006</i> the first discussion of the TC C&amp;L was based on the N classification proposal (ECBI/18/06).</p> <p>It was pointed out that almost all data was derived from the ammonium salt (which also was the salt of most commercial interest) and as the acid was a strong acid, it could be reasonable to separate the acid from the salt(s) in different Annex I entries. In the first round of discussion all end-points for classification, were therefore focusing on the ammonium salt [2].</p> <p>During the Follow-up period of March 2006 N and/or IND should provide the TC C&amp;L with an overview on which data was on the acid and which on the salts for the acute toxicity end-points. In addition IND should provide the TC C&amp;L on further information on the linear and branched molecules of PFOA.</p> <p>Further in March 2006 carcinogenicity was recognised as a borderline case between category 2 and 3. N had changed their proposal from Cat. 3 to Cat. 2.</p> <p>Reproductive toxicity, developmental effects should be further discussed at the next meeting. In preparation for the October 2006 meeting, N sent a scientific paper on the effects of PFOA during pregnancy in the Mouse in ECBI/18/06 Add. 3.</p> <p>N also provided a revised C&amp;L proposal (ECBI/18/06 Rev. 1). IND commented on the revised C&amp;L proposal with document ECBI/18/06 Add. 4</p> <p><i>In October 2006</i> the TC C&amp;L agreed that the acid and the nominated salts and esters should be equally classified. It was pointed out that the acid itself [1] as well as the fluoride acid of PFOA [6] could be different from the other compounds with respect to the acute toxicity and irritancy end-points but there was no data available to support this, and until such data would be reported they should be all classified equally as a group.</p> <p><b><u>Carcinogenicity</u></b>  TC C&amp;L agreed that this was a borderline case but they agreed not to support the N proposal for Category 2 based a weak evidence and classification in Category 3 was the final recommendation.</p> <p><b><u>Reproductive toxicity, developmental effects</u></b>  TC C&amp;L agreed to classify with Repr., Cat. 2; R61 for developmental effects.</p> <p><b><u>Reproductive toxicity, fertility effects</u></b>  It was noted that there might be some concern but based on very weak evidence and the N proposal, the TC C&amp;L confirmed their recommendation from March 2006 not to classify for this end-point.</p> <p><b><u>Acute toxicity</u></b>  Xn; R20/21 agreed for all substances listed in the draft entry.</p> <p><b><u>Irritancy</u></b>  Xi; R36 agreed for all substances listed in the draft entry.</p> <p><b><u>Repeated dose toxicity</u></b>  The provisional classifications with T; R48/23 and Xn; R48/22 from March 2006 were confirmed.</p> <p>→ Final classification proposal agreed by TC C&amp;L</p>																
<p><b><u>Classification</u></b></p> <table> <tr><td>Carc. Cat. 3; R40</td><td><i>Agreed 1006</i></td></tr> <tr><td>Repr. Cat 2; R61</td><td><i>Agreed 1006</i></td></tr> <tr><td>NC Repr. Cat. 3; R62</td><td><i>Agreed 0306</i></td></tr> <tr><td>T; R48/23</td><td><i>Agreed 1006</i></td></tr> <tr><td>Xn; R20/22</td><td><i>Agreed 0306</i></td></tr> <tr><td>Xn; R48/22</td><td><i>Agreed 1006</i></td></tr> <tr><td>Xi; R36</td><td><i>Agreed 0306</i></td></tr> <tr><td>NC for ENV</td><td><i>Agreed 0406</i></td></tr> </table> <p><b><u>Labelling:</u></b>  T  R: 61-20/22-36-40-48/22-48/23  S: 53-45</p>	Carc. Cat. 3; R40	<i>Agreed 1006</i>	Repr. Cat 2; R61	<i>Agreed 1006</i>	NC Repr. Cat. 3; R62	<i>Agreed 0306</i>	T; R48/23	<i>Agreed 1006</i>	Xn; R20/22	<i>Agreed 0306</i>	Xn; R48/22	<i>Agreed 1006</i>	Xi; R36	<i>Agreed 0306</i>	NC for ENV	<i>Agreed 0406</i>	
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NC for ENV	<i>Agreed 0406</i>																

**ANNEX 4:  
BIODEGRADATION AND BIO-CONCENTRATION OF PFOA AND ITS HIGHER  
HOMOLOGUES**

**METI's contribution to OECD PFCA Workshop, November 20-22, 2006, Stockholm, Sweden**

Chemicals (CAS No.)	Chemical Structure	Mw	METI No. (K-No)	Biodegradation (%) (OECD TG 301C)	Judgment By CSC (Year)	log Pow	LC50 mg/l (himedaka)	Bio-concentration (BCFss) OECD TG304	Judgment By CSC (Year)
Perfluorooctane Sulfonate Potassium salt (2795-39-3)	$\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{K}$	538.22	2-2810 (K-1520)	Standard Method 4 weeks. Tested in the year 2000. BOD 0, 0, 1 (0) TOC 8, 4, 4 (6) LC-MS 8, 0, 0 (3)	Not Bio- degradable (2000)	4.13* 1	89.1 (96hr)	Tested in the year 2001. 20µg/L : 720 2µg/L : 200~1500*3 Fat ratio Start 3.87% End 3.08%	Not Highly Bio accumulative (2001)
Perfluorooctanoic Acid (335-67-1)	$\text{CF}_3(\text{CF}_2)_7\text{COOH}$	414.07	2-2659 (K-1519)	Standard Method 4 weeks. Tested in the year 2000 BOD 10, 0, 4 (5) TOC 2, 4, 2 (3) HPLC 0, 0, 0 (0)	Not Bio- degradable (2000)	6.30* 1	100 (96hr)	Tested in the year 2000. 50µg/L : 3.1 5µg/L : <5.1~9.4*3 Fat ratio Start 3.10% End 2.82%	Not Highly Bio accumulative (2001)
Perfluoroundecanoic Acid (2058-94-8))	$\text{CF}_3(\text{CF}_2)_8\text{COOH}$	564.09	2-1182 2-2659 (K-1733)	Expert Judgment using data of analogues may be applicable.		4.0 (pH2) (HPL C)	>0.500 (96hr)	Tested in the year 2004 1 µg/L : 2300 0.1µg/L : 3700 Fat ratio Start 3.10% End 3.95%	
Perfluorododecanoic Acid (307-55-1)	$\text{CF}_3(\text{CF}_2)_9\text{COOH}$	614.10	2-2658 2-2659 (K-1750)	Standard Method 4 weeks. Tested in the year 2006. BOD -11,-16,-16 (0)*2 HPLC 2, 1, 2 (2)		10.16 *1	>0.500 (96hr)	Tested in the year 2005. 1 µg/L : 16000 0.1µg/L : 10000 Fat ratio Start 3.63% End 5.03%	
Perfluorotetradecanoic Acid (376-06-7)	$\text{CF}_3(\text{CF}_2)_{11}\text{COOH}$	714.11	2-2658 (K-1734)	Standard Method 4 weeks. Tested in the year 2005. BOD -23,-22,-24 (0)*2 LC-MS -1, 0, 0 (0)*2		5.1 (pH2) (HPL C)	>0.290 (96hr)	Tested in the year 2004. 1 µg/L : 16000 0.1µg/L : 17000 Fat ratio Start 3.06% End 5.12%	
Perfluorohexadecanoic Acid (67905-19-5)	$\text{CF}_3(\text{CF}_2)_{13}\text{COOH}$	814.13	2-2658 (K-1789)	Expert Judgment using data of analogues may be applicable.		14.03 *1	>0.150 (96hr)	Tested in the year 2006. 1 µg/L : 4800 0.1µg/L : 4700 Fat ratio Start 3.61% End 5.29%	
Perfluorooctadecanoic Acid (16517-11-6)	$\text{CF}_3(\text{CF}_2)_{15}\text{COOH}$	914.14	2-2658 (K-1749)	Expert Judgment using data of analogues may be applicable		15.96 *1	>0.04 (96hr)	Tested in the year 2005. 1 µg/L : 430 0.1µg/L : 320 Fat ratio Start 3.74% End 5.46%	

\*1 Estimated values by Kowwin v 1.67. \*2 Entered "0" since average value is below 0. \*3 Bio-concentration factor during exposure period

**ANNEX 5:  
OECD HAZARD ASSESSMENT OF PERFLUOROOCCTANOIC ACID (PFOA)**

**Background Document for the OECD Workshop on PFCAs and Precursors,  
November 20-22, 2006, Stockholm, Sweden**

At the OECD Joint Meeting in autumn 2004, it was agreed to prepare a hazard assessment of PFOA as a joint project between the US EPA and German UBA. The first draft SIAR (Initial Assessment Report) was submitted in January 2006 for discussion at SIAM 22. According to the comments received, the documents needed to be revised including more recent findings and other additional information available in the member countries.

At SIAM 22 in April 2006, it was agreed that the case of PFOA (CAS. 335-67-1) was not dealt with as a normal SIDS (Screening Information Dataset Dossier) case, as these are non-HPV Chemicals of international interest. Clarification was sought from the Sponsor Countries (Germany and the US) as to whether comments made by member countries would be dealt with to revise the SIAR and SIAP (Initial Assessment Profile). The conclusion of the discussion was that the Sponsor Countries will review comments made, and will submit a proposal to SIDS Contact Points regarding the further procedure for these chemicals.

The response document on the environmental part of the draft was posted on the SIAM CDG on April, 6, 2006.

On September 19, 2006, the OECD Secretariat posted on the SIAM CDG the following message: "Attached you will find a document submitted by the US to the OECD Secretariat containing responses (human health part) to comments made at SIAM 22 on the SIDS documents presented in relation to the PFOA.

The Sponsor countries (Germany and the US) also agreed to include more recent information from the US in the environmental part. The revised SIAP and SIAR (human health part), and also a proposal for amending the environmental part to include the recent findings, have been sent to Germany for finalisation in mid-September 2006. The draft is nearly completed, but still needs to be approved by both Sponsor countries.

These revised SIDS documents will be posted on the SIAM CDG (no timeline provided) for agreement via the written procedure, unless it turns out that a face-to-face discussion is needed.

The US also indicated that Dr. Jennifer Seed will be participating in the OECD workshop on PFCA in Stockholm in November 2006. It is possible that some of the SIDS/SIAM participants may be attending this workshop and thus there will be an opportunity to clarify lingering issues. Dr. Felix Endres and Dr. Christoph Schulte who are coordinating the activities in Germany are also participating in the workshop. In addition, Dr. Watze de Wolf, who is in charge for the support of the work at DuPont for the environmental part, will attend.

SIAM 23 took place in Korea on October 17-20, 2006. Germany confirmed that the revised documents will be submitted to the SIAM CDG as soon as the draft is approved by the Sponsor countries.

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The revised documents (SIAR, SIAP, SIDS) will then be finalised in 2007 via the written procedure on the SIAM CDG.

**ANNEX 6:**  
**FINAL AGENDA OF THE OECD WORKSHOP ON PERFLUOROCARBOXYLIC ACIDS**  
**(PFCAs) AND PRECURSORS**  
**20-22 NOVEMBER 2006, STOCKHOLM, SWEDEN**

### **Context**

The widespread occurrence of certain perfluorinated compounds in the environment, in certain animal species, as well as in humans, has attracted great attention. Perfluorinated compounds are known to be persistent. Some of these compounds are bioaccumulating, in particular those with long carbon chains, and some have been reported to cause toxic effects in laboratory animals.

PFOS was the first among the perfluorinated compounds to be found in significant levels in various environmental media. The major US producer of precursors to PFOS ceased the manufacture of these compounds a number of years ago. PFOS has been regulated within the US, is reviewed for risk reduction measures within the EU and is under discussion as a candidate substance for the Stockholm Convention, and for the LRTAP POPs Protocol. PFOS belongs to the PFAS-group of chemicals.

Another group of perfluorinated substances, perfluorocarboxylic acids, has recently been reported to increase over time in the environment, in particular in the Arctic. The occurrence of these substances in animal species and in man has been reported in many countries.

One source of the wide occurrence of PFCAs in the environment has been reported to be releases of PFCA-precursors such as fluorotelomer alcohols from products. The PFCA-precursors are present in the products either as residuals or can possibly be formed through degradation of fluorotelomer-based substances. Another source that has been identified is releases of PFCAs from the manufacture of fluoropolymers, such as polytetrafluoroethylene (PTFE).

In Canada, the Ministers for Health and Environment have imposed a temporary prohibition of four fluorotelomer-based polymers. Environment Canada and Health Canada have recently proposed an action plan for assessment and management of PFCAs and precursors.

In the United States, the Environmental Protection Agency (EPA) has launched a global stewardship programme inviting companies to reduce facility emissions and product content levels of perfluorooctanoic acid (PFOA), PFOA-precursors and higher homologue chemicals. All eight companies that were contacted have committed to participate in this programme. EPA has also entered into Enforceable Consent Agreements and Memoranda of Understanding with industry to generate certain data, including studies on incineration of fluoropolymers and fluorotelomer-based polymers, and environmental sampling and monitoring in the vicinity of fluoropolymer manufacturing facilities. PFOS, PFOA, and related chemicals have been included in the US national human biomonitoring programme. PFOA belongs to the PFCA group of chemicals

In EU, PFOA is currently prioritised for hazard classification concerning health and environmental effects. Several research programmes regarding sources, exposure and effects of these substances are ongoing in Canada, USA and in other countries. In EU a research programme (PERFORCE) is aiming at the European exposure assessment based on field data and modelling.

## Objectives

The purpose of the workshop is to:

1. Exchange information on on-going activities in OECD member countries regarding research, environmental monitoring, risk assessment and risk reduction related to PFCAs and precursors;
2. Identify gaps in knowledge and assessment needs for both long and short-chain PFCA and precursors;
3. Discuss which circumstances contribute to our concerns and how they could be mitigated; and
4. Develop recommendations for future activities. However, risk management recommendations are outside the scope of the workshop.

## Focus

The focus of the workshop is on perfluorocarboxylic acids (PFCAs) and their precursors. Session 1 of the workshop (Day 1, a.m.) will consist of 7 *scientific and technical reviews* with invited speakers. Session 2 (Day 1, p.m.) will entail *ongoing risk mitigation activities*. Session 3 (Day 2) will consist of *breakout group discussions* and the day will end with Session 4 on the *outcomes of breakout group discussions*. Session 5 (Day 3) will consist of discussions on the *conclusions and recommendations of the workshop*.

## AGENDA

**Monday, 20 November 2006**

***Registration from 08:30 to 09:30***

- 09:30-09:40 Welcome by Mrs. Ethel Forsberg, Director General of the Swedish Chemicals Inspectorate (KemI).
- 09:40-09:50 Welcome and logistics by the OECD Secretariat.
- 09:50-10:00 Objectives and Organisation of the Workshop by the Chair (Dr. Vibeke Bernson, Swedish Chemicals Inspectorate, KemI).

### Session 1: Setting the Scene

- 10:00-10:45 OECD 2006 survey on the manufacture, import and use of PFOS, PFAS, PFOA, PFCA and their related substances and products/mixtures containing these substances (Dr. Sneha Satya, NICNAS, Australia).
- Presentation 30 min, question period 15 min.
- 10:45-11:15 Coffee
- 11:15-12:15 Environmental monitoring, including biomonitoring (Ass. Prof. Pim de Voogt, Institute of Biodiversity and Ecosystem Dynamics (IBED), University of Amsterdam and Dr. Urs Berger, Stockholm Univ., Institute for Applied Environmental Science (ITM).
- Presentation 50 min, question period 10 min.
- 12:15-13:15 Environmental long range transport and fate, including environmental chemistry (Prof. Scott Mabury, University of Toronto, Canada).
- Presentation 50 min, question period 10 min.
- 13:15-14:45 Lunch
- 14:45-15:25 Health implications (Dr. Jennifer Seed, US EPA).
- Presentation 30 min, question period 10 min.
- 15:25-16:05 Environmental implications (Ass. Prof. Jonathan Martin, University of Alberta, Canada).
- Presentation 30 min, question period 10 min.
- 16:05-16:35 Coffee

- 16:35-17:15 Review of uses, sources and societal value of the perfluorinated chemistry (Dr. Robert C. Buck, DuPont, USA).
- 17:15-17:45 Environmental NGO viewpoint (Dr. Mariann Lloyd-Smith, Senior Advisor, National Toxics Network Inc., CoChair, International POPs Elimination Network).
- 17:45-18:15 General Discussion
- 18:15 END OF THE FIRST DAY
- 18:30 Reception hosted by the Swedish Chemicals Inspectorate (KemI) in Restaurant OXEN at ground floor of the workshop venue.

**Tuesday, 21 November 2006**

**Session 2: Ongoing Activities**

09:00-10:30 Ongoing activities:

- OECD (Dr. Henrik Harjula, OECD, 5 min)
- The United States (Mr. Jim Willis , US EPA, 20 min, presented by Jennifer Seed)
- Canada (Mr. Bernard Madé, Environment Canada, 20 min)
- European Union (Mr. Peter van der Zandt, European Commission, DG Environment, 20 min)
- Japanese intervention on biodegradation and bio-concentration of PFOA and its higher homologues (Mr. Takashi Fukushima, METI, 5 min)
- General Discussion (20 min)

**Session 3: Breakout Group Discussions**

10:30-11:00 Introduction of breakout group themes by the Chair.

11:00-16:30 PARALLEL BREAKOUT GROUP DISCUSSIONS

**Group 1: Assessment and research needs: Monitoring, emissions, environmental fate and transport**

Chair: Dr. Watze de Wolf (DuPont)

Rapporteur: Mr. Greg Hammond (Environment Canada)

The aim of the discussion is to identify needs for monitoring and research that would reduce uncertainties and support further assessment.

General discussion, answers to questions and formulation of recommendations.

**Group 2: Assessment and research needs: Effects**

Chair: Dr. Christoph Schulte (UBA, Germany)

Rapporteur: Ms. Anita Miettunen (Environment Canada)

The aim of the discussion is to identify needs for monitoring and research that would reduce uncertainties and support further assessment.

General discussion, answers to questions and formulation of recommendations.

**Group 3: Risk reduction approaches**

Chair: Dr. Mike Santoro (3M)

Rapporteur: Dr. Sneha Satya (NICNAS, Australia)

The aim is to discuss ways to mitigate the concerns. The group will identify risk reduction measures or approaches that could be considered and list their advantages and disadvantages. However, the workshop will not result in risk reduction recommendations.

General discussion and answers to questions.

**Group 4: Uses, trends and alternative chemistries**

Chair: Mr. Eric van Wely (DuPont)

Rapporteur: Mr. Kristan Markey (Environmental Working Group, USA)

The aim is to discuss the larger group of perfluorinated substances (including PFAS), their current uses, trends in use, the suitability of short-chain PFCs and possible non-fluorinated alternatives. The aim is to identify difficulties and possibilities/opportunities for substitution of long-chain PFCs for specific uses.

General discussion, answers to questions and formulation of recommendations.

Coffee 11:00-11:30

Lunch 13:00-14:30

Coffee 16:00-16:30

**Session 4: Outcome of Breakout Group Discussions**

16:30-18:00 Outcome of breakout group discussions by chairs and/or rapporteurs (20 min each)

18:00 END OF THE SECOND DAY

**Wednesday, 22 November 2006**

8:30 Outcome reports of breakout group discussions will be available outside the conference room.

**Session 5: Conclusions and Recommendations**

09:30-11:00 Discussion on the conclusions and recommendations of the workshop.

11:00-11:30 Coffee

11:30-13:00 Adoption of the workshop conclusions and recommendations.

13:00 END OF THE WORKSHOP

**ANNEX 7:  
LIST OF WORKSHOP PARTICIPANTS**

**OECD member states or permanent delegations**

<b>Australia</b>	<p>Dr. Sneha SATYA Team Leader Review &amp; Treaties National Industrial Chemicals Notification and Assessment Scheme (NICNAS) Department of Health and Ageing 334-336 Illawarra Road 2204 Marrickville Australia</p>	<p>Tel: +61-2-8577 8880 Fax: +61-2-8577 8888</p>
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<b>Canada</b>	<p>Mr. Greg HAMMOND Head, New Chemicals Evaluation Section Environment Canada PVM, 351 St-Joseph Blvd. K1A 0H3 Gatineau Canada</p>	<p>Tel: +1-819-956 9278 Fax: +1-819-953 7155</p>
	<p>Dr. Scott MABURY Professor of Environmental Chemistry University of Toronto ON M5S 3H6 Toronto Canada</p>	<p>Tel: +1-416-978 3566 Fax: +1-416-978 1631</p>
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