

# KEMI

Report  
Nr 7/06

A Report from the Swedish Chemicals Agency

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## Perfluorinated substances and their uses in Sweden

SWEDISH CHEMICALS AGENCY

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ISSN: 0284-1185  
Order No. 360 844  
Stockholm, November 2006  
Publisher: Swedish Chemicals Agency©  
Order address: Telefax +46 8 50 59 33 99, e-mail: kemi@cm.se



## **Preface**

A project was carried out at the Swedish Chemicals Agency (KemI) between autumn 2005 and spring 2006 with the aim of improving knowledge of the use of perfluorinated substances in different products.

This summary is a report on the project and our ambition is that it will constitute the basis for continued work in different forums on measures to decrease risks associated with these compounds.

The project was carried out at the Swedish Chemicals Agency's departments for Risk Reduction and Risk Assessment, and a number of people contributed to the report, including Lisa Anfält (Project leader), Inger Cederberg, Åsa Edell, Sten Flodström, Stefan Gabring, Inger Lindkvist, Bo Nyström and Ulf Rick.

Information was gathered from literature, from the KemI products register, through meetings and other contacts with interested parties for the product groups in question, and major producers of perfluorinated substances. In April and May 2006, KemI invited interested parties to a discussion on four different product groups: textiles, paper, fire fighting foam and cleaning agents. Participants at the meetings included representatives of chemicals producers and other industries that use perfluorinated substances in the manufacture of chemicals or other products, and companies that import such articles. Also present were representatives from environmental organisations, trade organisations and trade research institutes, other research institutes and other relevant authorities. See annex 2 for trade contacts.

The project may be extended into a second stage whose aim would be to determine which compounds and uses involve risks so large that measures should be taken, and to produce a strategy for the phasing-out or reduced use of these compounds.

Sundbyberg, September 2006

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## Summary

Perfluorinated substances have been produced and used since the 1950s for their special characteristics: they are thermally stable, water-repellent, dirt-repellent and grease-repellent, to give some examples. Perfluorinated substances are a group of organic compounds characterised by a carbon chain in which all hydrogen atoms have been replaced with fluorine atoms.

With the development of better analysis methods for perfluorinated substances, their dispersion in the environment and people has attracted an increasing amount of attention. Since it became known that perfluorooctane sulphonate (PFOS) has very serious effects on health and the environment, PFOS related substances are being phased out. To replace PFOS, several manufacturers have moved towards other fluorinated compounds that have the same desirable technical properties. Unfortunately, several of the replacement compounds have been shown to have similar negative effects on health and environment.

This report does not focus on PFOS, but on other perfluoroalkyl sulphonates (PFAS), perfluoroalkyl carboxylic acids (PFCA) and other substances which can degrade into these compounds, e.g. fluorotelomer alcohols. The aim is to increase our knowledge of which highly fluorinated compounds, in addition to PFOS, are found in the environment, which compounds degrade into perfluoroalkyl sulphonates (PFAS) and perfluoroalkyl carboxylic acids (PFCA), the use of these compounds, and possible alternatives.

The most commonly used perfluorinated substances used in products are fluorotelomers. They are used either as independent active ingredients (e.g. in fire fighting foam) or as a component in more complex structures (e.g. in impregnating agents). The main uses of fluorotelomers are in fire fighting foam, in water-repellent and dirt-repellent textiles and mats, in grease-repellent paper, and in surface treatments of tiles, flooring materials etc. The uses of PFCA are fewer. The main uses of PFOA are as process aid in the manufacture of various fluoropolymers, such as polytetrafluoroethylene (PTFE <sup>1</sup>).

As far as risks are concerned there are many uncertainties, including the effects, fate and exposure of humans as well as other vertebrates and organisms in the environment. It is, however, clear that perfluorinated substances are extremely persistent as a group can be transported over great distances, and that some are bioaccumulative and toxic. There are indications that levels in mammals in the Arctic are increasing. There is thus a risk of serious long-term problems if these stable compounds have hitherto unknown hazardous properties, especially as they are already so widely spread in the environment and, in addition, show tendencies towards increasing levels which may rise even further if the substances are increasingly widely used.

Information on the use of perfluorinated substances in Sweden has been obtained from the products register at KemI. There were just under 24 tons of PFAS, PFCA and related substances in the products register in 2004. The entire volume consisted essentially all of substances which could potentially degrade into PFCA, above all fluorotelomer based substances. Figures from the register do not include imports of finished articles which are treated with and which contain perfluorinated substances (e.g. furniture, clothes and

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<sup>1</sup> Teflon is a trade mark

packages). Such articles are assumed to account for the largest proportion of perfluorinated substances transported to Sweden.

The largest quantities of perfluorinated substances imported to Sweden in chemical products go to the textile industry, where they are used for the treatment of sun-blocking textiles, car textiles and work clothes. It is mainly telomer based polymers that are used. Imported articles which probably contain fluorinated compounds include work clothes, sports clothes, and furniture textiles. Analyses of textiles have shown that telomer alcohols are released from clothes and other textiles. Garments treated with fluorinated compounds are rather expensive, but in return they have many desirable functions: they are water-repellent, grease-repellent, dirt-repellent and they can “breathe”. There are alternative treatments and materials which will provide some of these functions, but no non-fluorinated alternatives can at present provide all these functions.

Fluorinated compounds can be used in packages for oily foodstuffs. They occur in paper product manufacturing in Sweden, but are probably more common in paper packages manufactured in central Europe, for example. It is difficult to estimate how common imported fluorinated foodstuffs packages are in Swedish shops. With regard to grease-repellent paper packages, there are alternative qualities of paper and barrier materials which function equally well in comparison with fluorinated paper. Foodstuffs packages may be assumed to constitute one source of direct exposure for humans, since fluorotelomers have been shown to migrate from packages into foodstuffs.

Fluorotelomers are used in fire fighting foam for their film forming properties and the ability to decrease fuel absorption. These foams are especially useful for major fires, e.g. chemical fires. The quantities in the foam are low, less than one per cent, but the foam is directly released into the environment. The largest use of fire fighting foam is in fire exercises, and then the foam used is no longer considered to be reliable for extinguishing fires. According to information received, the amount of foam past its use-by date which is destroyed is relatively small. This is probably true also of foam containing PFOS which still exists in public stocks. There are fluorine-free foams available today, but they are not as effective. However, research is being carried out, which in the long-term may provide effective fluorine free alternatives.

Fluorinated tensides are used in very low levels in a large number of cleaning products, e.g. polish, waxes, all-purpose cleaners, window cleaners etc. Their use is widespread and directly released into wastewater. The use of fluorinated tensides in products with cleaning functions does not comply with the EU Regulation (EC no. 648/2004) on detergents since they are not sufficiently biodegradable. In products such as polish, fluorinated compounds are not added primarily for their cleaning characteristics but because they provide good spreading properties and an even surface. According to information, there are no good alternatives to perfluorinated substances in polish, but silicones are seen as having potential for development.

In some countries measures have been taken to decrease the risks associated with perfluorinated substances. Canada has prohibited four telomer based compounds and is expected to continue work in decreasing risks associated with similar compounds. USA's environmental authority has acceded to a global voluntary agreement with a number of companies that have undertaken to drastically reduce emissions from production plants and levels of PFCA related compounds in their products.

Apart from PFOS, perfluorinated substances have not been discussed to the same extent in the EU. Negotiations are ongoing with the Council of Ministers and the European Parliament for a ban on PFOS within the framework of the limitation directive (76/769/EEC).

EU's new chemicals legislation REACH (Registration, Evaluation and Authorisation of Chemicals) has not yet been ratified, but is expected to come into force in 2007. The proposed legislation is expected to have the consequence that certain perfluorinated substances which occur in volumes less than one ton per manufacturer or importer will not be covered by the requirement for registration of the compounds' hazardous properties and use, or alternatively that the substances are first registered after more than 10 years.

Those perfluorinated substances which fulfil criteria for special health or environment hazards may fall into the category that require authorisation. The requirement for an authorisation will be applicable if the level of the hazardous substance in the product exceeds 0.1 per cent. In several products, e.g. fire fighting foam and polish, fluorinated compounds are used in concentrations of less than 0.1 per cent and would therefore seem to avoid the requirement for authorisation.

According to the proposal for new chemical legislation, an obligation will be introduced to report substances of very high concern which are used in articles if the amount of the substance exceeds 1 ton per year and manufacturer or importer, and if the concentration of the substance in the articles exceeds 0.1 per cent (w/w). The requirement is dependent on whether the concentration of 0.1 per cent will be calculated for the whole article or parts of it, and if the amount of the substance exceeds 1 ton per year and manufacturer or importer.

The proposal for new chemicals legislation also includes the obligation to provide information to the recipient regarding substances of very high concern contained in the articles at levels exceeding 0.1 per cent. This obligation is applicable whether or not the manufacturer or importer of articles is obliged to file a registration or report on the substance to the European Chemical Agency. The purpose of this is to ensure that the articles are handled in a safe way.

Perfluorinated substances will be discussed at an OECD conference in November 2006, for which Sweden is the host. The aim is to obtain an overall picture of the issue of perfluorinated substances and to discuss what further information is required to be able to make well-informed assessments and plan possible measures.

Conclusions which may be drawn include the fact that there is inadequate knowledge of the properties of many perfluorinated substances, which substances are used in products, how the substances are spread and how we are exposed to them. Pending further knowledge, it is important that continued emissions of perfluorinated substances are decreased in order that serious long-term problems do not occur. It is vital that perfluorinated substances do not further increase in humans and the environment.

Examples of measures that must be accelerated are that manufacturers of perfluorinated substances must investigate their effects on health and environment, and that emissions of these substances must be reduced during the manufacturing process. It is urgent that alternative substances with less hazardous properties are developed. Another example is that companies which manufacture products with perfluorinated substances, or which use such products in their activities to any large extent, request information on perfluorinated substances and reconsider the need for functions provided by such substances.



## Sammanfattning

Perfluorerade ämnen har producerats och använts sen femtiotalet för sina speciella egenskapers skull, t.ex. temperaturtålighet, vatten-, smuts- och fettavvisande egenskaper. Perfluorerade ämnen är en grupp av organiska ämnen som kännetecknas av att de innehåller en kolkedja där alla väteatomer bytts ut mot fluoratomer.

I takt med utvecklingen av bättre analysmetoder för perfluorerade ämnen har dess vida spridning i miljön och i människor blivit alltmer uppmärksam. Sedan det framkommit att perfluoroktansulfonat (PFOS) har mycket allvarliga effekter på hälsa och miljö så pågår en utfasning av PFOS-relaterade ämnen. För att ersätta PFOS har flera tillverkare gått över till andra fluorföreningar som har samma eftertraktade tekniska egenskaper. Dessvärre har även flera av ersättningsämnena visat sig ha liknande negativa effekter för hälsa och miljö.

Denna rapport fokuserar inte på PFOS utan på andra perfluoroalkylsulfonater (PFAS) och perfluoroalkylkarboxylsyror (PFCA) samt på ämnen som kan brytas ned till dessa, t.ex. fluortelomeralkoholer. Syftet har varit att öka kunskapen om vilka högfluorerade ämnen, utöver PFOS, som hittas i miljön, vilka ämnen som bryts ned till dessa perfluoroalkylsulfonater (PFAS) och perfluorkarboxylsyror (PFCA), och användning av dessa ämnen och eventuella alternativ.

De perfluorerade ämnen som förekommer mest i produkter är fluortelomerer. De används antingen som fristående aktiv ingrediens (t.ex. i brandsläckningsskum) eller som en komponent i mer komplexa strukturer (t.ex. i impregneringsmedel). De huvudsakliga användningarna av fluortelomerer är i brandsläckningsskum, i vatten- och smutstålånga textilier och mattor, i fettavstötande papper, i ytbehandlingar för kakel, golv m.m. Användningen av PFCA är mindre. Den huvudsakliga användningen av PFOA är som hjälpkemikalie vid tillverkningen av olika fluorpolymerer, t.ex. polytetrafluoretylen (PTFE<sup>2</sup>).

När det gäller riskerna finns det många osäkerheter bl.a. när det gäller effekter, spridningsvägar och exponering för såväl människan som ryggradsdjur och andra organismer i miljön. Det står dock klart att perfluorerade ämnen är en grupp mycket persistenta ämnen som kan transporteras långt samt att vissa är bioackumulerande och toxiska. Det finns bl.a. indikationer på att halterna i däggdjur i Arktis stiger. Det finns därför en risk för allvarliga långsiktiga problem om dessa stabila ämnen visar sig ha idag okända farliga egenskaper när de redan är så spridda i miljön och dessutom visar tendenser till stigande halter som kan tänkas tillta om ämnena får ökad användning.

Uppgifter om användningen av perfluorerade ämnen i Sverige har hämtats från Produktregistret på Kemikalieinspektionen. I produktregistret fanns knappt 24 ton PFAS och PFCA och relaterade ämnen registrerade år 2004. I stort sett hela volymen var ämnen som potentiellt bryts ned till PFCA, framförallt fluortelomerbaserade ämnen. Siffrorna från registret omfattar inte importen av färdiga varor som är behandlade med och innehåller perfluorerade ämnen (t.ex. möbler, kläder, förpackningar). Sådana varor antas stå för den största delen av tillförseln av perfluorerade ämnen till Sverige.

De största mängderna av de perfluorerade ämnen som importeras till Sverige i kemiska produkter går till textilindustrin, där de bl.a. används för behandling av solskyddstextilier,

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<sup>2</sup> Teflon är ett varumärke

textil i bilar och arbetskläder. Det är framförallt telomerbaserade polymerer som används. Importerade varor som troligen innehåller fluorföreningar är arbetskläder, sportkläder, möbeltextilier m.m. Analyser av textilier har visat att telomeralkoholer frigörs från kläder och andra textilier. Klädesplagg som behandlas med fluorföreningar är ganska dyra men har i gengäld många eftertraktade funktioner; de är vatten-, fett, och smutsavvisande och de kan andas. Det finns alternativa behandlingar och material som ger vissa av dessa funktioner, men inget icke-fluorerat alternativ kan idag ge alla funktionerna.

Fluorföreningar kan användas i livsmedelsförpackningar för feta livsmedel. De förekommer i pappersvarutillverkning i Sverige, men är troligen vanligare i pappersförpackningar tillverkade i t.ex. centraleuropa. Hur vanligt det är i svenska butiker med importerade fluorbehandlade livsmedelsförpackningar är svårt att uppskatta. När det gäller fettavstötande pappersförpackningar finns det alternativa papperskvaliteter och barriärmaterial som fungerar lika bra som fluorbehandlat papper. Livsmedelsförpackningar kan antas utgöra en källa till direktexponering av människor, då fluortelomerer har visat sig kunna migrera från förpackningar in i livsmedel.

Fluortelomerer används i brandsläckningsskum för dess filmbildande egenskaper och förmåga att minska bränsleupptag. Dessa skum är särskilt användbara vid svåra bränder, t.ex. kemikaliebränder. Halterna i skummen är låga, under en procent, men skummen genererar direkta utsläpp till miljön. Den största användningen av brandsläckningsskum sker vid brandövningar, och då används också skum som inte längre anses vara tillförlitligt vid brand. Enligt uppgift är det en relativt liten mängd skum av äldre datum som destrueras. Det gäller troligen också de PFOS-innehållande skum som finns kvar i lager i samhället. Det finns fluorfria skum idag men de är inte lika effektiva. Det pågår dock forskning som på sikt kan ge upphov till fungerande fluorfria alternativ.

Fluortensider används i mycket låga halter i ett stort antal rengöringsprodukter, t.ex. polish, vaxer, allrengöring, fönsterputs m.m. Det är en spridd användning med direkta utsläpp till avlopp. Användning av fluortensider i produkter med rengörande effekt är inte förenligt med detergentförordningen ((EG) nr 648/2004) eftersom de inte är tillräckligt nedbrytbara. I produkter som polish tillsätts fluorföreningar inte i första hand för sina rengörande egenskaper, utan snarare för att de ger bra utflytning och en jämn yta. Enligt uppgift saknas det väl fungerande alternativ till perfluorerade ämnen i polish, men silikoner ses som intressanta att utveckla.

I vissa länder har åtgärder för att minska riskerna med perfluorerade ämnen införts. Kanada har förbjudit fyra telomerbaserade ämnen och förväntas arbeta vidare med riskminskning av liknande ämnen. USA:s miljömyndighet har ingått en global frivillig överenskommelse med ett antal företag som åtar sig att drastiskt minska utsläpp från produktionsanläggningar och halter av PFCA-relaterade ämnen i produkter.

Inom EU har perfluorerade ämnen, förutom PFOS, inte diskuterats i samma utsträckning. Förhandlingar om ett förbud för PFOS inom ramen för Begränsningsdirektivet (76/769/EEG) pågår för närvarande i ministerrådet och i Europaparlamentet.

EU:s nya kemikalielagstiftning REACH (Registration, Evaluation and Authorisation of Chemicals) är ännu inte beslutad men förväntas träda ikraft under 2007. Den föreslagna förordningen väntas innebära att vissa perfluorerade ämnen, som förekommer i volymer under ett ton per tillverkare eller importör, inte kommer att omfattas av kravet på registrering av

ämnens farliga egenskaper och användning, alternativt att ämnena registreras först efter mer än 10 år.

De perfluorerade ämnen som uppfyller kriterierna för särskilt hälso- eller miljöfarlighet kan bli kandidater för tillståndsprövning. Kravet på tillstånd gäller om halten av det farliga ämnet överstiger 0,1 % i en produkt. I flera produkter, t.ex. brandsläckningsmedel och polish, används fluorföreningar i halter lägre än 0,1 procent och ser därför ut att undgå kravet på tillstånd.

Enligt förslaget till ny kemikalielagstiftning införs en anmälningsskyldighet för ämnen med särskilt farliga egenskaper, som används i en vara, om mängden av ämnet överstiger ett ton per år och tillverkare eller importör samt om ämnets koncentration i varan överstiger 0,1 procent (w/w). Kravet beror på om halten 0,1 procent ska beräknas på hela varan eller på delar av denna och om mängden av detta ämne överstiger ett ton per år och tillverkare eller importör.

Förslaget till ny kemikalielagstiftning innebär vidare en skyldighet att till mottagaren lämna information om särskilt farliga ämnen som ingår i varor över 0,1%. Denna skyldighet ska gälla oavsett om tillverkaren eller importören av en vara är skyldig att göra en registrering eller en anmälan av ämnet till kemikaliemyndigheten. Syftet är att varan ska kunna hanteras på ett säkert sätt.

Inom OECD diskuteras perfluorerade ämnen på en konferens i november 2006 som Sverige är värd för. Syftet är att få en samlad bild av problemen med perfluorerade ämnen samt diskutera vilken ytterligare information som behövs för att kunna göra välavvägda bedömningar och möjliga åtgärder.

Slutsatser som kan dras är att det råder brist på kunskap om egenskaperna hos många av de ämnen som ingår i gruppen perfluorerade ämnen, om vilka ämnen som används i produkterna, om hur ämnena sprids och hur vi exponeras för dem. I avvaktan på mer kunskap är det angeläget att fortsatta utsläpp av perfluorerade ämnen minskar så att allvarliga långsiktiga problem inte uppstår. Det är av största vikt att perfluorerade ämnen inte ökar ytterligare i människor och i miljön.

Exempel på insatser som redan nu måste påskyndas är att tillverkare av perfluorerade utreder ämnenas effekter för hälsa och miljö, samt att utsläppen av ämnena minskar vid tillverkning. Det är också angeläget att alternativa ämnen med mindre farliga egenskaper utvecklas. Ett annat exempel är att företag som tillverkar produkter med perfluorerade ämnen eller använder sådana produkter i sin verksamhet i större utsträckning begär information om perfluorerade ämnen och överväger behovet av de funktioner som ämnena tillför.

# 1 Introduction

## 1.1 Background

Perfluorinated substances have been produced and used since the 1950s for their special characteristics: they are thermally stable, water-repellent, dirt-repellent and grease-repellent. Perfluorinated substances are sometimes referred to as “new environmental toxins”, and the reason for this is probably that they have only become measurable in humans and in the environment during the last few years. Earlier analysis methods were inadequate. Several of the compounds, e.g. fluorotelomer alcohols, are still very difficult to analyse.

Perfluorooctane sulphonate (PFOS) and PFOS related compounds have been the subject of much attention since 2000, when the 3M company announced that they had decided to cease production of these compounds. The associated risks have been assessed by a number of bodies, and PFOS has been shown to be persistent, bioaccumulative and toxic. Measures to reduce risks are on the way in many countries, in the EU and globally. As a result, the production and use of PFOS has decreased drastically in recent years.

In order to replace PFOS, many manufacturers have started to use other fluorinated compounds with the same desirable technical properties. Unfortunately, many of the replacement compounds have been shown to have similar negative effects on health and environment.

The natural step to take to follow up the phasing-out of PFOS is to investigate other highly fluorinated compounds. Perfluorooctane acid (PFOA) is the substance which has received most attention after PFOS. The group of highly fluorinated compounds is extremely large and complex. Knowledge of the distribution and effects of the replacement compounds is still limited, even though intensive research is being carried out in the area at the moment.

The KemI's work to increase knowledge of perfluorinated substances is shown in this report. As a first step, the aim is to increase our knowledge of

- which highly fluorinated compounds, apart from PFOS, have been found in the environment,
- which compounds degrade into these perfluoroalkyl sulphonates (PFAS) and perfluorocarboxylic acids (PFCA),
- the use of these compounds and possible alternatives.

## 1.2 Terms of reference

Since KemI has already investigated PFOS and presented a strategy (Kemikalieinspektionen 2004) for its phasing-out to the government, PFOS is not included in this project other than in a comparative context and in the description of trends in use of such compounds. The focus of the project has been on a number of other highly fluorinated compounds, namely other perfluoroalkyl sulphonates (PFBS, PFHxS, PFDS) and perfluoroalkyl carboxylic acids (PFHxA, PFHpA, PFOA, PFNA, PFDA, PFA, PFDa, PFTrA, PFTA, PFPeA), as well as compounds which can degrade into these categories. Sulphonamides are included since they can degrade to give PFAS.

Polytetrafluoroethylene (PTFE, e.g. Teflon<sup>®</sup>) is a stable fluorinated polymer and is not included in the group which is in focus here, i.e. compounds which can degrade into PFAS and PFCA.

### 1.3 Abbreviations

<b>PFOS:</b>	Perfluorooctane sulphonate
<b>PFAS:</b>	Perfluoroalkyl sulphonates, one example being PFOS
<b>PFOA:</b>	Perfluorooctane acid
<b>PFCA:</b>	Perfluorocarboxylic acids, one example being PFOA
<b>FTOH:</b>	Fluorotelomer alcohols, components in trade products which can degrade into PFCA
<b>PFOS related compounds:</b>	All compounds which can degrade into PFOS
<b>PFOA related compounds:</b>	All compounds which can degrade into PFOA
<b>PFBS:</b>	Perfluorobutane sulphonate
<b>PFHxS:</b>	Perfluorohexane sulphonate
<b>PFDS:</b>	Perfluorodecane sulphonate
<b>PFHxA:</b>	Perfluorohexane acid
<b>PFHpA:</b>	Perfluoroheptane acid
<b>PFOA:</b>	Perfluorooctane acid
<b>PFNA:</b>	Perfluorononane acid
<b>PFDA:</b>	Perfluorodecane acid
<b>PFUnA:</b>	Perfluoroundecane acid
<b>PFDoA:</b>	Perfluorododecane acid
<b>PFTrA:</b>	Perfluorotridecane acid
<b>PFTA:</b>	Perfluorotetradecane acid
<b>PFPeA:</b>	Perfluoropentadecane acid
<b>PFOSA:</b>	Perfluorooctane sulphonamide
<b>PTFE:</b>	Polytetrafluoroethylene

## 2 Groups of compounds, manufacture and use

Perfluorinated substances are a complex group of compounds. What makes the issue especially complicated is that it is seldom the compounds that are the focus of most attention and which are the greatest reason for worries, such as PFOS and PFOA, which are actually used in articles. Instead there is a large group of other compounds, including telomers, which are used in articles and which, when released into the environment, degrade to PFOA, among other compounds.

### 2.1 Presentation of compound groups

Perfluorinated substances are a group of organic compounds characterised by a carbon chain in which all hydrogen atoms have been replaced by fluorine atoms (Kissa 2001). The bonds between carbon and fluorine are extremely strong chemical bonds, making perfluorinated substances very persistent and non-degradable.

#### 2.1.1 PFAS

Perfluoroalkyl sulphonates (PFAS) are a group of perfluorinated substances in which one sulphonate group is bonded to the perfluorinated carbon chain. Perfluorooctane sulphonate (PFOS) belongs to this group of compounds. PFAS may also be included in other chemical compounds, e.g. sulphonamides, and polymers, e.g. acrylate polymers, and may be formed when these compounds degrade. PFOS, for example, is a degradation product from different types of PFOS derivatives (PFOS related compounds), of which approximately 100-200 have been identified.

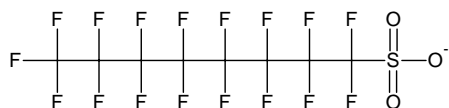


Figure 1. Diagrammatic chemical structure of perfluorooctane sulphonate, PFOS.

#### 2.1.2 PFCA

Perfluorocarboxylic acids (PFCA) are perfluorinated carboxylic acids, of which perfluorooctane acid (PFOA) has been given the most attention due to its toxic and eco-toxic properties. Other PFCA are called, for example, perfluorononane acid (PFNA), perfluorodecane acid (PFDA) and so on depending on the length of the perfluorinated carbon chain.

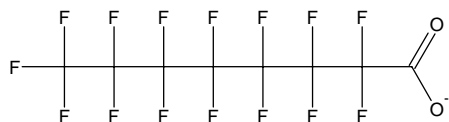


Figure 2. Diagrammatic chemical structure of perfluorooctane acid, PFOA, here shown as an anion.

#### 2.1.3 Fluorotelomers

Telomers are a group of perfluorinated substances that are produced through a process known as telomerising. Telomers are not completely perfluorinated, but have one remaining hydrocarbon group consisting of two carbon atoms, which is why the distinction is often made between telomers and PFAS for example, which is completely perfluorinated.

One notable group of compounds is the fluorinated telomer alcohols (FTOH) and their derivatives and polymers, since they can degrade into perfluorinated carboxylic acids, e.g. PFOA. Telomer alcohols are often used as reactants in the manufacture of certain polymer dispersions. Carbon chains of telomers are then built into the polymers and contribute to the desirable grease-repellent, water-repellent and dirt-repellent properties.

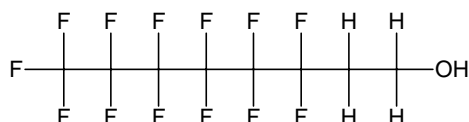


Figure 3. Diagrammatic chemical structure of 6:2 fluorotelomer alcohol.

OECD has compiled a list of approximately 850 compounds which, it may be assumed, can degrade into PFAS and PFCA (OECD 2005). The use of all these compounds can therefore be reckoned as potentially problematic.

Polytetrafluoroethylene (PTFE, e.g. Teflon<sup>®</sup>) is regarded as a stable fluoropolymer and is not included in the group in focus here, i.e. compounds which can degrade into PFAS and PFCA. In the manufacture of fluoropolymers, including Teflon<sup>®</sup>, PFCA is used as a process aid and residual quantities may remain in the polymers produced (Prevedouros *et al.* 2006).

## 2.2 Manufacture

### 2.2.1 Manufacturing processes

Perfluorinated substances are manufactured using two main methods: direct fluorination (electrochemical fluorination, ECF) and telomerising (Prevedouros *et al.* 2006). The perfluorinated substances produced may then react further, giving different derivatives and polymers (Kissa 2001).

In the process of direct fluorination, the organic compounds to be fluorinated are dissolved or dispersed in liquid hydrogen fluoride and an electrical current is passed through the solution. All hydrogen atoms in the organic compounds are then replaced with fluorine atoms and perfluorinated organic compounds are produced. The reaction is extremely vigorous and mixtures of perfluorinated substances are produced with varying lengths of carbon chains, with both even and odd numbers of carbon atoms. Branched chains may also occur.

Telomerising is a process in which the perfluorinated molecule, called a telogen, reacts with an unsaturated molecule called a taxogen. The compound formed through this reaction is called telomer and has given its name to a group of compounds, telomers. Fluorinated telomers are characterised by the molecule containing a perfluorinated carbon chain bonded to a short carbon chain, usually two carbon atoms with hydrogen atoms. Fluorinated telomers always have straight carbon chains with an even number of carbon atoms, as distinct from perfluorinated compounds produced by direct fluorination.

Telomers are produced and used commercially as mixtures, in which the typical span of chains is between four and eighteen carbon atoms; chains shorter than eight carbon atoms are approximately two per cent by weight, eight carbon atoms approximately 30 per cent by weight, and longer than eight carbon atoms approximately 68 per cent by weight (DuPont 2006).

Perfluorinated compounds in the form of fluorinated telomers and PFAS, for example, can be further reacted and will then occur in other chemical compounds, e.g. acrylate polymers. This means that perfluorinated compounds and fluorinated telomers may occur in a large number of different chemical compounds. OECD has compiled a list of approximately 850 perfluorinated substances, of which 367 contain fluorinated telomers and 203 contain PFAS (OECD 2005).

### 2.2.2 Global production/quantities

The largest manufacturers of fluorotelomers are DuPont de Nemours, Daikin, Clariant Corporation and Asahi Glass. In 2004 estimated quantities of products sold were 72 000 tons, containing between 11 250 and 13 500 tons of active fluorotelomer ingredients (NERA 2006). Another source claims that the production of fluorotelomer alcohol (FTOH) is 12 000 tons per year (Wallington *et al.* 2006).

In 2005 there were four producers of APFO (the ammonium salt of PFOA); Miteni (Italy), DuPont (USA), Daikin (Japan) and one Chinese producer. Between 1995 and 2002 the annual production of APFO was estimated at 200-300 tons (Prevedouros *et al.* 2006).

Perfluorobutane sulphonate (PFBS) related compounds have been produced by 3M since 2002 (3M 2006).

There are no further estimates to be found of the annual production of PFCA and PFAS related compounds.

## 2.3 Areas of use

Perfluorinated substances are used in many types of products which utilise their properties of creating smooth, water-repellent, grease-repellent and dirt-repellent surfaces.

Fluorotelomers are the compounds most widely used in products. They are used either as independent active ingredients (e.g. in fire fighting foam) or as a component in more complex structures (e.g. impregnating agents). The main areas of use of fluorotelomers are fire fighting foam, water-resistant and dirt-resistant textiles and mats, in grease-repellent paper, and surface treatments for tiles, flooring materials etc. (NERA 2006).

Uses for PFCA are fewer. The main uses of PFOA are as process aids in the manufacture of different fluoropolymers, e.g. polytetrafluoroethylene (PTFE, Teflon is a trademark) and fluoroethylene propylene (FEP). For this reason, PFOA is sometimes called a “Teflon chemical” by the media.

Another PFCA, perfluorononane acid (PFNA) is also used in a similar way in the production of fluoropolymers, primarily polyvinylidene fluoride (PVDF) (Prevedouros *et al.* 2006). The production and consumption of fluoropolymers has continually increased with the use of PFOA. Fluoropolymers are used, for example, in frying pans, electronics, textiles, cables, semiconductors, space materials etc.

Historically, PFCA has been used in many different products. As early as 1966, the following areas of use were described in literature: metal cleaning, electrolytic surface treatment, floor polish, cement, fire fighting materials, paints, lubricants, petrol, and for the treatment of paper, leather and textiles (Prevedouros *et al.* 2006).



Further uses which are found among patents in recent years are in copying machines, toner, magnetic recording media, electronics and semiconductor manufacture, cleaning products, hair products, inhalers, fuel additives and air fresheners. To what extent these patents have become real products is not known (Prevedouros *et al.* 2006).

PFBS related compounds are used above all for impregnating textiles and carpeting, but also in the semiconductor and electronics industry, and in paints (3M 2006).

### **3 Preliminary risk assessment**

#### **3.1 Hazard and exposure assessment**

##### *3.1.1 Chemical and physical properties*

Perfluorinated substances do not occur naturally in the environment, but are produced by man. One characteristic property of perfluorinated substances is that they are extremely stable due to the strong chemical bonds between carbon and fluorine. They are not degraded by strong acids or alkalis, and resist both reduction and oxidation even at high temperatures (Kissa 2001). They cannot be degraded by UV light or photolysis (von Stedingk and Bergman 2004).

The solubility of perfluorinated compounds in different solvents is influenced by the carbon-fluorine bonds and other functional groups in the structure, e.g. sulphonate or carboxylic acid groups. The solubility of perfluorinated compounds is in general low, both in water and in organic solvents. These compounds have hydrophilic and hydrophobic parts, which means that they have a tendency to collect at an interface, e.g. between water and an organic solvent or between a liquid and solid surface. The distribution, for example, between octanol and water,  $K_{ow}$ , is difficult to determine for this group of compounds (Kissa 2001).

##### *3.1.2 Sources, environmental fate and exposure*

The difficulties involved in analysing perfluorinated substances have meant that it has only recently been possible to measure their levels in the environment and in people. Reliable and accurate methods of analysis are necessary to carry out different types of studies of perfluorinated substances. One of the greatest problems is to obtain access to extremely pure individual perfluorinated compounds for use as analytical standards in chemical analyses (Martin *et al.* 2004).

#### **Sources**

Emissions from manufacturing plants and other point sources have gradually decreased in significance, but are still one source of perfluorinated substances in the environment. The manufacture of fluoropolymers has, at least historically, been a large source of PFCA emissions.

The more recent use of telomer based compounds in different products may be a significant source of PFCA found in the environment. Telomer alcohols have been shown to give rise to PFCA, both through biological and atmospheric degradation. Studies from purification plants with active sludge have shown that the levels of PFCA are often higher in the output water than the input water (Sinclair and Kannan 2006).

The higher levels of linear isomers of PCFA in blood in comparison with branched isomers indicate that the telomer process is an important source (De Silva and Mabury 2006).

PFCA precursors may originate in fluorotelomer based compounds in two ways (Government of Canada 2006):

- They are residual compounds, e.g. unreacted monomers in compounds which are relatively easily released
- They are released during the degradation of fluorotelomer based compounds. How much this source contributes to levels of PFCA in the environment is uncertain, since there are many remaining unknown factors concerning degradation mechanisms and degradation rates.

Those PFCAs that are produced from fluorotelomer based compounds have chain lengths equivalent to the telomer's perfluorinated chain length.

Studies of indoor air have shown that PFCA precursors are bound to dust particles, which would indicate sources such as carpets and textiles. Analyses of textiles have also been made, and it has been found that telomer alcohols, and smaller quantities of PFCA and PFAS, are released from clothes and other textiles (Swedish Society for Nature Conservation 2006). In another investigation, the analyzed textiles samples contained up to 10.7 mg/m<sup>2</sup> FTOH (SFT, Norwegian Pollution Control Authority, 2006).

PFCA precursors were measured at levels up to 3.8 per cent in one study in which several products with fluorotelomer based compounds, such as carpet impregnating agents, cleaning agents and windscreen cleaning agents, were studied (Government of Canada 2006).

### **Environmental fate**

Many and varied sources can explain the higher levels of perfluorinated substances found in urban environments, e.g. emissions from industrial and municipal waste, training areas for fire fighting (military bases and aerodromes) and leachate from landfill.

Exactly how perfluorinated substances are transported to remote areas is less clear. Certain PFCA precursors, e.g. fluorotelomer alcohols, are volatile and can be transported high into the atmosphere (Ellis *et al.* 2004). Preliminary data indicate that this may be an explanation of the rapidly rising levels of PFCA in the Antarctic (Renner 2006b). It is possible that PFCA is also transported over long distances by ocean currents (Prevedouros *et al.* 2006).

### **Exposure**

It has been proved that fish are a source of human exposure (Falandysz *et al.* 2006), but in general the occurrence of perfluorinated substances follows different patterns in animals and in people, which would indicate that fish and other foodstuffs are not the primary source of human exposure. However, certain groups of people may have considerable exposure through foodstuffs since certain food packages, e.g. those for microwave popcorn, can contain fluorotelomer based compounds which can migrate from the packaging to the food and be metabolised in the body to PFOA (Begley *et al.* 2005).

Other exposure may originate from the use of perfluorinated substances in different articles. Indoor air and dust, for example, have been proposed as a significant source of exposure to certain perfluorinated substances (Shoeib *et al.* 2005). Direct exposure may also occur through various hygiene and cleansing products, to name some examples.

### 3.1.3 Occurrence in the environment and in humans

Measurements showed that low concentrations of PFCA with between eight and 15 carbon atoms are widespread in the Arctic environment. High concentrations have been found in animals at the top of the food chain (e.g. polar bears and seals) which would indicate biomagnification. The concentration of PFNA and PFDA in the livers of polar bears doubles every five to eight years, which indicates increasing exposure in the environment.

The following description of the occurrence in the environment is mainly based on a paper by Houde *et al.* (2006). The levels of PFOA are remarkably similar in different geographical areas, even far away from the sources of emission and densely populated areas, whereas the measured levels of other perfluorinated substances in different organisms tend to be higher the closer they are to industrialised areas.

Perfluorinated substances occur in all groups of organisms and trophic levels, but quantities are generally higher in the upper levels of food chains. There is strong evidence that PFOS, PFHxS, and PFCA with between eight and twelve carbon atoms may bioaccumulate and biomagnify in food chains, but there is no clear pattern and the variation between species and different species' choice of food appears to play a large role.

Among mammals, for example, the highest levels have been measured in such varied species as bottle-nosed dolphins in North America and polar bears in the Arctic. Bottle-nosed dolphins often live close to industrialised areas, and have a relatively rapid metabolism of these compounds in their blood. As with people, age does not appear to be a significant factor in the blood concentration of these substances. The high levels in polar bears, on the other hand, may probably be explained by their special diet, the main part of which is the skin and internal organs of seals. Seals and polar bears in the Arctic show similar patterns in the occurrence of different perfluorinated substances, but the correlation with concentrations in the surrounding water is low.

One further indication of the relative complexity of causal links is that comparisons between different time series of measurements on animals and humans do not always correlate. Concentrations of PFOS and PFCA in different organisms have, according to measurements, increased continually during the 1990s, but there is no equivalent trend in humans. The significance of the use of perfluorinated substances in different articles is probably larger for the exposure to humans, which possibly masks the long-term increase in the compounds in the environment.

Levels in human blood often lie between 2-20 µg/l both in the northern and southern hemispheres. Investigations show that the newly-born are exposed primarily through the placenta, but also through breast milk (Renner 2006a). Concentrations in the blood have not yet reached directly toxic levels, but these levels are on the increase and the half life of these substances in people seems to be several years. As for other mammals, the reasons for the accumulation are largely unknown, but it has been shown that perfluorinated substances can recirculate in the liver and blood. In the latter case, the explanation is that these compounds are released when albumin is broken down and subsequently re-adsorbed to new blood plasma protein. In this way, a high level in the blood is maintained despite the carrier, albumin, being continually metabolised.

The levels of certain perfluorinated substances in the Nordic environment have also been investigated, and findings show that they are ubiquitous. High levels were found in waste

water sludge and leach water from landfills, and in top-predators such as the grey seal (Kallenborn *et al.* 2004).

Studies of emissions from the normal use of fluoropolymer coated kitchen utensils (e.g. frying pans) have not indicated any detectable quantities of PFOA however (Powley *et al.* 2005).

### 3.1.4 Persistence

There is a lack of knowledge of the properties of many of the characteristics of perfluorinated substances, but one thing is certain: they are extremely stable compounds as a group. This may be explained by the bond between carbon and fluorine being one of the strongest chemical bonds that exists. Some perfluorinated substances are completely unaffected by chemical or biological degradation, or degrade extremely slowly. Others, e.g. telomer alcohols, degrade in the environment to give persistent substances .

### 3.1.5 Bioaccumulation

Certain perfluorinated substances are extremely bioaccumulative, but since perfluorinated substances are fat-repellent and water-repellent they are not stored in fatty tissues, as are many other bioaccumulative substances. Instead they bind to proteins and are stored in the liver and in the blood. The differences are also large between different species in terms of the potential for bioaccumulation. The half life of PFOA in serum has been measured in humans as 4.4 years (Burris *et al.* 2002) while the half life varies between three hours and nine days in rats, depending on the individual and its gender. Due to the unusual chemical properties of these compounds, traditional tests for bioaccumulation are sometimes considered to give insufficient information. However, many of the facts indicate that the longer the perfluorinated carbon chain, the higher is the potential for bioaccumulation, at least up to a certain chain length. Based on estimates of bioconcentration factors and the results of environmental monitoring, PFCA with more than eight carbon atoms in the chain is considered to be bioaccumulative (Government of Canada 2006).

As a comparison, it may be mentioned that perfluorinated butyl sulphonate, PFBS, has in recent years been launched as a replacement for PFOS, and there are studies of PFBS that indicate a lower tendency to bioaccumulate.

### 3.1.6 Toxicity

The American environment authority US EPA is carrying out an overall risk assessment of PFOA (US EPA 2006a). The OECD high volume program (SIDS) is also making an evaluation. PFOA is probably disruptive to reproduction and causes prenatal and postnatal damage to mice and rats. Concerning its carcinogenic properties, it is more difficult to make statements with certainty. US EPA has decided that animal studies indicate PFOA and its salts are possible human carcinogens (suggestive evidence). According to an independent scientific committee which audits and advises US EPA, PFOA should be seen as a likely human carcinogen, which within the EU would be equivalent to being classified in category 2.

In the EU classification work, Norway submitted a proposal for classification of PFOA in spring 2006, but as yet there is no final classification proposal.

According to available studies it appears that PFBS is less toxic than PFOS and PFOA. The Australian authorities have, however, taken a restrictive approach to PFBS and any use which

may cause widespread dispersion will require advance application and permission (Australian Government 2005).

With the exception of PFOS, PFBS and PFOA there is very little data on the health and environmental effects of other perfluorinated substances. In spite of this, it may be assumed that long-chain PFCA (more than eight carbon atoms) will cause more serious effects than PFOA since it is proved that they have longer secretion times and higher potential for bioaccumulation. This indicates that long-chain PFCA could fulfil the criteria for POPs (Persistent Organic Pollutants) since it is both persistent and bioaccumulative. Based on data for PFOA (Environment Canada and Health Canada 2006) it is also probable that these substances have toxic effects on laboratory animals. Many of the substances will probably have the potential for long-range transport since measurements show that they already exist in the Arctic environment.

Fluorotelomers in themselves do not appear to have such harmful properties, but PFCA often occurs as uncombined residuals in telomer products. In addition, fluorotelomers are converted to PFCA in the environment, in mammals, and probably also in humans. Repeated exposure to telomer products could therefore result in the same effects as exposure to PFCA.

### **3.2 Risk characterisation**

There is insufficient evidence to make a well-founded assessment of the risks for most perfluorinated substances at present. Many uncertainties remain, including their effects, fate and exposure for humans, other vertebrates and other organisms in the environment.

However, it is clear that perfluorinated substances are extremely persistent and that some of them are bioaccumulative and toxic. In addition there are indications that their levels in mammals in the Arctic are rising, which indicates a potential for long-range transport. There is therefore a risk of serious long-term problems. Should it be the case in the future that the risks are greater than so far believed, it may be difficult to rectify the problem quickly if these stable compounds increase in use and dispersion.

## 4 Use in Sweden

The information in this chapter is based on literature, data from the products register at KemI and contacts with experts. See annex 2 for trade contacts.

KemI has held separate meetings for the following product groups: textiles, paper articles, fire fighting foam and cleaning agents/polish. Discussions at the meetings had the following points of departure:

- Are PFOS related substances still used in the products?
- To what extent are other perfluorinated substances found in the products? In what type of function/products? Which substances are used?
- Are short-chain fluorinated compounds used?
- Is it possible to use the only fluorine-free alternatives? Which? In what type of functions/products? Advantages and disadvantages of these?
- How long would it take to phase in fluorine-free alternatives?

### 4.1 Products register data

The products register is a national register kept by KemI. Companies that manufacture or import them into products to Sweden must register the product at KemI. This requirement applies to chemical products over 100 kg, and all substances contained in the product that exceed five per cent must be stated. Hazardous substances must be stated in lower concentrations.

In the products register at KemI up there were 23.77 tons of PFAS and PFCA and related substances (excluding PFOS related substances) registered. This volume was divided among 40 different substances in 110 different products which were marketed in 2004. A further 16 substances were registered in active products on the Swedish market, but no volumes of these were imported in 2004. The names, CAS numbers and chain length of these substances are in annex 1.

PFAS, PFAS related compounds, PFOA or only PFOA related substances accounted for only approximately 25 kg. Almost the whole volume was therefore substances which could potentially degrade into PFCA (including PFOA, often stated as a range of chain lengths, e.g. C6-12).

Of those substances found which can degrade into PFCA, approximately 22 tons were fluorotelomers and less than two tons were other perfluorinated substances (e.g. perfluoro phosphonates and phosphinates). Perfluorophosphonates and phosphinates (together just under two tons) are used primarily as anti-foaming agents in the textile industry, in pesticides and in lubricants. Fluorotelomers account for the major use and are spread over many different areas of use, the largest volumes going to the textile industry, however. The total distribution of the areas of use is summarised in figure 4.

The small quantity of PFOA that is imported is used as a raw material in the manufacture of plastics. It is included in fluoropolymers in small quantities, which in Sweden are used to coat various surfaces. The PFAS related substances, with chain lengths from four to eight, are used in impregnating agents for textiles, paints and varnishes, hydraulic oil, flooring materials, surface treatment agents, wax and window cleaning agents.

Approximately 41 kg of the substances found are components in products available to consumers, mostly in leather polishes (shoe polish) and impregnating agents for textiles, but also in different types of wax, finishing, polishing and cleaning agents.

It is difficult to see any clear pattern of use of individual substances in extracts from the products register since many substances have several areas of use. One conclusion which is possible to draw, however, is that polymers are most frequently used for impregnating textiles, while compounds with tenside properties dominate other areas of use. The quantities of perfluorinated constituent parts are higher in products for textile impregnation than in other products and that is why the largest quantities may be attributed to textile impregnation. However, there are some exceptions to this, e.g. anti-foaming agents, which also occur in large quantities. In terms of the number of products, there are many more used as cleaning, polishing and waxing agents, while there are fewer products for impregnating textiles.

### Use of perfluorinated substances in Sweden 2004 (PFOS excluded) total 23.77 ton

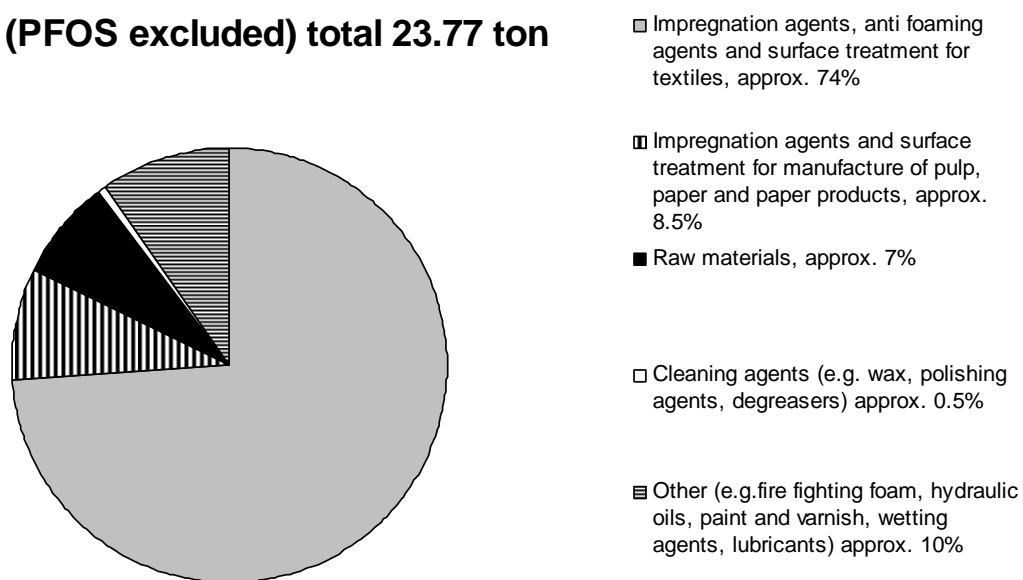


Figure 4. Perfluorinated substances divided into areas of use, source: KemI Products register 2004.

These data do not constitute a complete picture of the use of these substances in Sweden, and should be interpreted with caution.

Substances included in chemical products manufactured in or imported to Sweden must be reported to the products register if they constitute more than five per cent of the product. The product need only be reported if the company imports more than 100 kg per year. In many products where perfluorinated substances are used for their film forming properties, they are only included in the product in very low concentrations (less than one per cent), e.g. in fire fighting foam, polish and other cleaning agents. Most of these substances are not found in the products register since such low quantities of perfluorinated substances do not need to be reported. Even though the concentrations in the products are low, the total volume may be considerable since some of the products are used in large quantities.

Naturally, figures from the registry do not reflect the import of complete articles that are treated with and contain perfluorinated substances (e.g. furniture, clothes, and packages). Imported articles must be assumed to constitute by far the largest proportion of incoming perfluorinated substances to Sweden.

Searches in the products register were based on lists of PFAS, PFCA and related compounds compiled by OECD in 2005 through questionnaires sent to all OECD countries (OECD 2005). The list contains a total of 853 substances, of which 138 are PFOS related, 203 PFAS related, 28 PFOA related and 484 PFCA related. 38 of the substances on the OECD list have no CAS number and have not been searched for in the products register.

The OECD list was compared with other lists of perfluorinated substances, e.g. the US Environmental Protection Agency SNUR list from 2002 (US EPA 2002), OSPAR list in the background document for PFOS (OSPAR 2005) and lists in other Nordic investigations, and was supplemented by only one substance from the OSPAR list, perfluorononane acid, which has the CAS number 375-95-1. In 2006 a further 183 PFAS related substances have been proposed for inclusion under SNUR (Significant New Use Rules) (US EPA 2006b); 72 of these were not included on the OECD list and have not been searched for in the products register.

A search for a further substances was made in the KemI's substance register which contains approximately 130 000 chemical compounds which are used or have been used in chemical products in Europe and USA. In this search, a further nine substances were found containing "perfluoro", "gamma" and "omega" in the substance name. (Fluorotelomers have "gamma" and "omega" in the substance name). It was found that these substances alone constituted more than half of the volumes in the products register.

Polymers that are only used for special applications are seldom given a CAS number. This is partly because patents are seldom applied for such polymers and they are seldom described in literature. The products register at KemI seldom receives complete information (complete compound names) for polymers which are included in products registered, and thus cannot register the polymers. Since many of the products of interest with respect to perfluorinated substances contain polymers with perfluorinated carbon chain tails, there is a risk that these are missed in searches made in the products register. In those cases when the products register is given sufficient information about the polymers without a CAS number, specific identification numbers are created and entered in the register. Five such polymers are included in the volumes reported here.



### 4.1.1 Trends

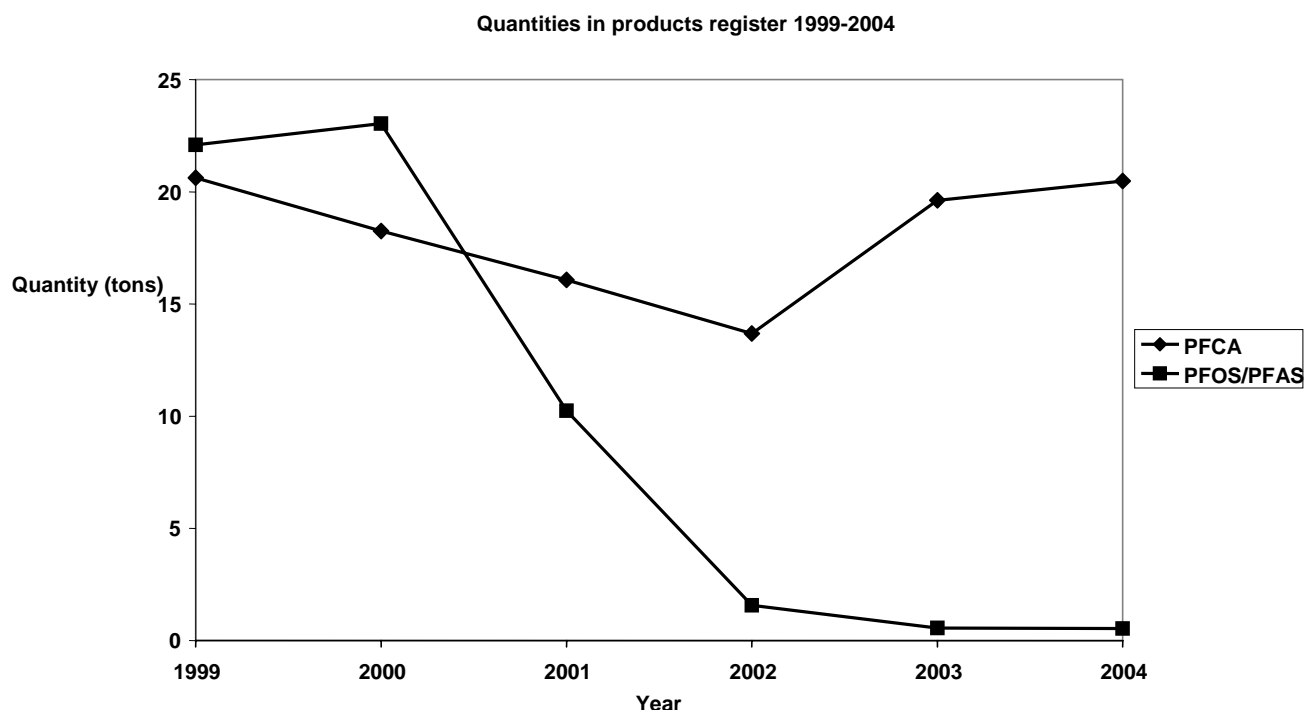


Figure 5. Total quantities of PFCA and PFOS/PFAS related substances in the products register 1999-2004.

Figure 5 shows a clear fall in the use of PFOS and PFAS related substances in Sweden in recent years, from just over 23 tons in 2000 (when 3M decided to phase out production of PFOS related substances) to just under 700 kg in 2004.

No clear trends are discernible in the use of PFCA related substances, however.

In 2004 there were seven PFOS related and 13 PFAS related substances registered in 77 products. The total quantity was 684 kg. The remaining uses of PFOS were mostly as manufacturing raw materials for the surface treatment industry, in metal coatings, cleaning agents, printing inks, developers, leather tanning, flooring materials, paints and varnishes.

## 4.2 Textiles

### 4.2.1 Use and function

Textile and leather impregnation is the largest area of use for fluorotelomers. Fluorotelomer based compounds are used for dirt-repellent and water-repellent surfaces on textiles, e.g. for rain clothes, tents, shoes, carpets, upholstered furniture, awnings etc. Water-repellent and dirt-repellent textiles may consist of woven materials of Teflon, polyester, polyamide etc. which are impregnated with a dispersion polymer with "telomer tails". Much evidence indicates that these carbon chain tails can be released from polymers and/or that the impregnating agent contains uncombined residual telomers. The Swedish Society for Nature Conservation has analysed a number of rain jackets and found primarily uncombined FTOH, but also PFCA and PFOS related substances in all of them (Swedish Society for Nature Conservation 2006).

Despite the textile manufacturing industry in Sweden being rather small nowadays, the largest proportion of perfluorinated substances imported to Sweden through chemical products, or approximately 75 per cent, goes to the textile industry. The remaining textile industry is in

many cases specialised in more expensive niche products which are still profitable to produce in Sweden, e.g. multifunctional textiles treated with fluorinated substances.

In all probability, however, it is imported textiles which account for the largest quantities of perfluorinated substances brought in to Sweden. As a comparison, it may be mentioned that over 9000 tons of outdoor clothes were imported to Sweden in 2005 (Statistics Sweden 2006). What proportion of these is impregnated with fluorinated substances is unknown.

These days fluorotelomers can be bound to textile fibers at the molecular level, which means that the treated textiles are soft instead of stiff. Polymer structures adhere to the textile weave, whereas fluorotelomer groups stick out at right angles to it.

Perfluorinated substances in the textile industry are found in the products register under their functions: impregnating agents, wetting agents, and antifoaming agents.

Examples of known uses in Sweden are in textiles which for safety reasons are used in car engine compartments, interior sun visors (roller blinds and similar, for easily-wiped surfaces), in uniforms and working clothes for, among other groups, policemen and firemen (for increased comfort).

With regards to sports clothes and rain clothes, it is generally more expensive garments that contain fluorinated substances. PVC and polyurethanes are more often used in cheaper garments. Fluorocarbons are generally used in leisure clothes for their breathable and water-repellent functions rather than dirt repellency.

There is a great need for more knowledge at companies which import textile garments. Almost every trademark, whether profiled towards the sports market or the fashion market, has outer garments, jackets and often trousers, which use materials that very probably contain perfluorinated substances. Media attention in recent years on the use of these substances in textiles has caused many consumers to put questions to retailers and importers.

Companies that import clothes seldom know what chemical substances they contain. To support its member companies, the Swedish trade association *Textile Importers* has produced a purchasing guide which includes requirements on chemicals used. PFOS is included in the list, but none of the other less well-known perfluorinated substances such as, for example, PFOA and telomers, are included. Many importers ask suppliers about those substances which are included on the list of chemicals, and in certain cases carry out control analyses for these substances, but seldom have sufficient knowledge to ask about or analyse less well-known substances. Some larger companies have their own lists of chemicals.

Just how widespread the use of fluorinated substances is in impregnated furniture fabrics is not clear. IKEA no longer uses fluorocarbons in its furniture, and instead has removable and washable furniture fabrics.

Most fluorotelomers that are used for treating textiles have six or more carbon atoms in the chain.

## 4.2.2 Trends

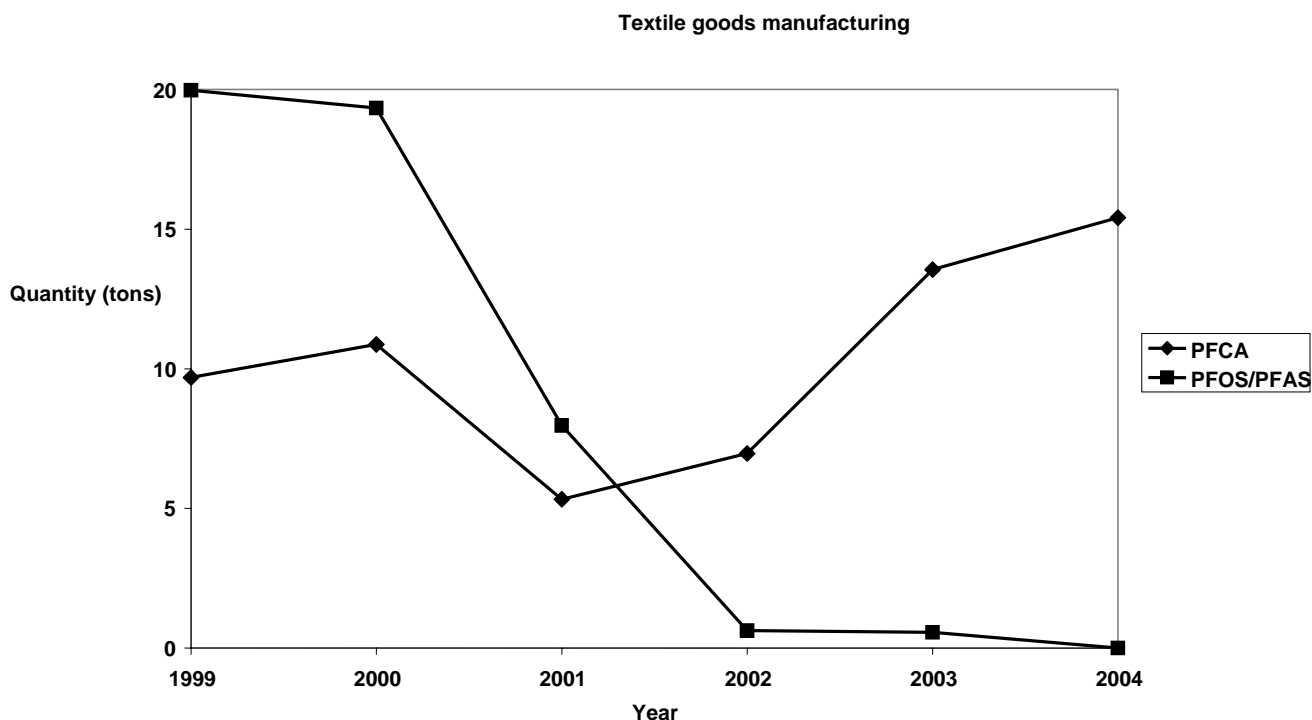


Figure 6. Import of PFCA and PFOS/PFAS related compounds for use in the textile industry, 1999-2004.

Data from the products register shows a clear fall in the use of PFOS related compounds in the Swedish textile industry (see figure 6). Fluorotelomers have been produced since the 1970s and have been used in the textile industry among others. The above curve can be interpreted as an increase in the use of fluorotelomers in the Swedish textile industry as a result of the phasing out of PFOS related compounds.

The general impression at a meeting with the trade was that PFOS is no longer found in textiles in Sweden. The Textile Importers Association in Sweden demands that imported textiles are free from PFOS.

Tests of outdoor jackets have been carried out and traces of PFOS and PFOS derivatives have been measured (Swedish Nature Conservation Society 2006). The concentrations were so low that they could not fulfil any functions in the garments. They were probably not intentionally used, but were contaminants in other products that were added.

The largest manufacturer, 3M, has phased out its production of PFOS. There are, however, other producers of PFOS related compounds in Italy and Russia, and maybe also in Asia, but it is not clear which companies are involved.

The use of fluorotelomers in different types of clothes is on the increase globally and clothes treated with these chemicals are sold in many clothes chains in Europe and USA. Fluorotelomers are even used in “normal” clothes, for example shirts and trousers in cotton or synthetic materials (e.g. polyester). According to trade experts, approximately 10 to 20 per cent of all khaki trousers are treated with fluorotelomers to make them dirt repellent (NERA 2006).

One Swedish chemicals supplier claims that demand from the textile industry for fluorinated compounds is decreasing. It is often demands from customers for a certain function, e.g. surfaces which can be wiped clean, which make textile companies use fluorocarbons if the function cannot be achieved by other means.

#### *4.2.3 Emissions from textiles*

According to a Canadian report, as much as 73 of fluorinated compounds in garments treated with impregnating spray for consumer use disappear in washing during the lifetime of the garment (Environment Canada 2004). How much disappears through washing of commercially treated textiles is not clear.

A Swedish textile company tested one of its products which was treated with fluorinated compounds and found that the full effect remained even after 100 washes. However, no analyses were carried out on what disappeared with the washing water.

According to tests at IFP Research, a treated textile retains its functions over a long time period despite a worn surface. Telomer chains on the polymer can be reactivated through ironing (150 C°).

Analyses at the Norwegian Institute for Air Research (NILU) show that there are many residuals from telomer based polymers. Many of these probably released into the air.

It is difficult to analyse fluorocarbon emissions from surfaces, but the Swedish National Testing and Research Institute (SP) has a new method that can measure surfaces at the molecular level.

Norwegian analyses of indoor air indicate high levels of perfluorinated substances. It is probable that these levels or not only caused by clothes, but also furniture etc. Telomer alcohols are volatile and should therefore occur in gaseous phases rather than in dust or other particles. The levels are approximately 100 times higher in indoor air than in outdoor air. Other possible indoor sources are wallpaper, carpets, curtains and other interior textiles.

How to dispose of old outdoor garments is a problem. Burning them at high temperatures destroys perfluorinated substances. According to some municipal refuse collection departments, it is not good to burn old jackets. Perfluorinated substances are converted into hydrogen fluoride when they are burned, which is extremely corrosive. Fluorinate compounds with short chains are also formed, which are extremely potent greenhouse gases. If the clothes are left on the local landfill, the fluorinated compounds are released into the environment sooner or later.

#### *4.2.4 Alternatives*

Short chain sulphonates with four carbon atoms have been developed by 3M as an alternative to PFOS, among other compounds. These compounds are also extremely persistent, but not bioaccumulative or toxic. When the company was searching for a replacement for PFOS, fluorinated and non-fluorinated alternatives were investigated, including silicones, but tests showed that only fluorinated compounds provided the desired combination of water repellency and dirt repellency as well as being easily wiped clean.

Design and function are often first priorities in the choice of chemicals for clothes. With respect to completely fluorine-free alternatives, it is necessary to check what functions are to

be replaced, since there is not one alternative but several. Waterproof functions can be replaced by using impermeable materials such as fabrics coated with PVC, polyurethane or polyacrylates, but these do not breathe. Tightly woven and mangled fabrics are relatively waterproof in themselves. Certain fabrics, e.g. polyester and nylon, are more naturally dirt-repellent than others, such as cotton. For materials that need to breathe, paraffin wax emulsions or silicones can be used, but they are not dirt-repellent or oil-repellent. Water repellency and washing durability are worse for paraffin wax emulsions than for fluorocarbons. Other environmental and health problems may arise if alternatives are used, e.g. softeners in PVC. Fluorinated compounds' strongest advantage compared with fluorine-free alternatives is that they are dirt-repellent.

It is important to use chemicals for the function which is required and not for all fabrics. Products for normal consumption, such as children's clothes and fashion clothes for everyday use, do not perhaps require all the functions which fluorinated compounds can provide. Sometimes it may be sufficient to use fabrics that are only water repellent, sometimes waterproof and breathable, in which case there are alternative compounds and materials which can be used.

Various nanoproducts are being launched on the market, but it is unclear exactly what they contain. In certain cases they contain fluorocarbon based nano products (e.g. fluorocarbon silanes, which give a nano surface).

There is currently a large interest in waterproof garments which breathe, and consumers will probably not go back to totally impermeable garments. The appearance of garments is also important. Fluorinated membranes are on the inside of the fabric and are discrete. It would probably be easier to find good alternatives if they could be on the outside of the fabric.

Just how quickly a transition to fluorine free alternatives can take place is difficult to estimate. Legislation against the use of fluorocarbons would be a strong incentive for the development of fluorine free alternatives.

## **4.3 Paper**

### *4.3.1 Use and function*

Paper can be treated with impregnating agents which contain fluorotelomer derivatives (e.g. phosphate esters) or fluorotelomer dispersions (polymers with telomer chains). These are primarily found in foodstuffs packages where their properties for repelling fats are desirable.

STFI/Packforsk has a database of chemical compounds and products which are used by their member companies. There is only one active product with a perfluorinated substance currently in the database. Previously there were about 10 perfluorinated substances registered, but these are now deleted since the industry has phased out their use. The product safety group for the forest industry asked Swedish paper mills last autumn whether they used fluorinated compounds. No paper mill answered in the affirmative.

However, the KemI's product registry contains approximately 2 tons of perfluorinated substances registered under the functions of impregnating or surface treatment for paper. These may well be used by so-called converters rather than paper mills. Converters are companies which purchase paper products and then may treat these with fluorinated chemicals in order to produce certain fat-repellent properties for packages, often for

foodstuffs. These companies are more difficult to contact since they are often small companies who do not have their own trade associations.

According to one chemicals supplier, fluorinated chemicals are used in Sweden for niche products which are manufactured for a short period of time or only used in one special product. Fluorinated compounds may be added to the crush, as a coating or in a size press, depending on what function is to be achieved. This use is almost exclusively for paper used in foodstuffs packages which must be fat repellent.

There are regional differences in the use of fluorinated chemicals between the Nordic countries and the rest of Europe which can be traced back to the size of paper mills. There are large paper mills in the Nordic countries which can produce bulk paper cheaply. Other European countries have paper mills with smaller machines and more often produce niche products in smaller runs, and probably use more fluorinated chemicals than in the Nordic countries.

There may well be perfluorinated substances in imported paper products, for example foodstuffs packages. One large Swedish retail chain stated that they place demands required by law on materials in contact with foodstuffs, but not much more than that.

It is possible that paper is imported which is already treated with fluorinated chemicals and which is cut in Sweden, printed with company names and so on, to be used by fast food chains and others.

Imported recycled paper may also contain perfluorinated substances. There are approximately 700 000 tons of recycled paper imported to Sweden each year. There are no measurements of perfluorinated substances in this recycled paper at present.

EFSA, the European authority for foodstuff security, makes recommendations for paper and cardboard in contact with foodstuffs, and also a list of compounds which are used in foodstuffs packages. The latest version of this list contains very few fluorinated compounds.

Examples of products which contain or have contained fluorinated compounds are:

- wallpaper may contain fluorinated chemicals in non-woven materials, in order to avoid the paste permeating the wallpaper or to make it wipe-clean, but it is doubtful whether this is still done.
- Paper in packages for animal food may be treated with fluorinated chemicals (they were previously). An alternative is to use plastic instead.
- Fluorinated compounds were used in baking paper earlier in the Nordic countries. The paper is now coated with silicone emulsion instead.
- Imported disposable plates and tablecloths may be impregnated with fluorinated chemicals.
- Fluorinated chemicals occur in food packages for use in microwave ovens, e.g. popcorn. Ciba does not recommend its products for this use.

Swan-marked fat-repellent baking paper and food paper (baking plate paper, cake forms) must not be coated with fluorinated compounds.

### 4.3.2 Trends

Data from the products register show that PFOS related compounds have not been used in the Swedish paper industry since 1999.

The manufacture of paper products with fluorinated substances has, according to the paper and pulp industry, decreased in Sweden and Norway. Data from the products register also seem to indicate this. In Sweden, fluorinated compounds were previously used in the manufacture of packages for animal foods, wallpaper and baking paper, amongst other products. This has probably been discontinued.

Several years ago, some foodstuffs manufacturers decided that they did not want fluorinated compounds in their packages. Mc Donald's in Sweden state that they do not use perfluorinated substances in their packages.

Those perfluorinated substances which are used have carbon chains containing about eight carbon atoms; between six and 10 carbon atoms is a common range. The trend, however, is towards shorter carbon chains containing between four and six carbon atoms. There are manufacturers that can guarantee carbon chains of eight atoms do not occur, and that the majority contain about six carbon atoms. One large fast food chain in USA is said to have changed from using eight to six carbon atom compounds in their packages.

### 4.3.3 Emissions from paper products

The American Food and Drug Administration have determined that fluorotelomer alcohols can migrate from food packages to foodstuffs. Packages for microwave popcorn for example can contain 25 mg of fluorotelomers per dm<sup>2</sup> of paper (Begley *et al.* 2005). A significant amount of fluorotelomers are transferred into the oil around the popcorn and may constitute a significant amount of the total quantities of PFCA/PFOA that are found in human blood through the metabolism of fluorotelomer alcohols into PFCA in the body.

In the Nordic countries most foodstuffs packages are burned, whereas in many other countries they are dumped on landfills.

### 4.3.4 Alternatives

There are working alternatives to fluorinated chemicals in the form of special quality papers or alternative materials which produce a fat barrier in foodstuffs packages.

Greaseproof is an extremely dense quality of paper which works well as an alternative to paper treated with fluorinated compounds. Current production capacity of greaseproof paper could cover demand from the Nordic countries, but not global demands. It is a completely different method of manufacturing paper. The sulphite mass is milled much more than usual, which increases energy consumption. Larger quantities of water are also consumed in production and its removal requires more energy. The overall result is that the paper is much more expensive to produce than other qualities of paper. Completely different paper machines with very high purchasing costs are also required. Only one of these machines exists in Sweden. The cost of greaseproof paper is between 10-30 per cent higher than for paper treated with fluorinated chemicals.

Vegetable parchment is another alternative which has almost disappeared from the market and which is even more expensive than greaseproof paper.

New chemicals are expensive to develop. It is the cost for consumers that govern product development and if paper products are too expensive people choose plastic or metal instead. Plastics (e.g. polyethylene) and metals are seen as the most conceivable fluorine free alternatives. If paper is coated with plastic or metal, it makes recycling problematic since they must be separated. Foodstuff paper packages are not generally recycled though, as a result of residual food products on the paper.

Fluorine free alternatives could include composite materials for impregnation or biotechnically modified fibres, but they would probably not tolerate higher temperatures as well as products impregnated with fluorinated chemicals. Research at Chalmers and other institutes is being carried out on various modifications of fibers, e.g. acetylation. Some carbohydrates, like sugar molecules such as chitosan, could be possible alternatives.

One Swedish wallpaper manufacturer uses micro-wax as a moisture repellent in its wallpapers. There are also PVC coated wallpapers which do not need any further moisture repellents.

## **4.4 Fire fighting foam**

### *4.4.1 Use and function*

Fire fighting foam is extremely useful when volatile or flammable liquids are to be extinguished. It covers the fire and forms a barrier between the burning fuel and oxygen in the air. Examples of incidents when foam liquids can be used include spillages from crashed tanker trucks, minor spillage fires, car fires, fires in tanks, large scale fires involving articles in stores, securing spillage surfaces etc. Fire fighting foam is produced by mixing water, foam concentrate and air in suitable proportions.

The mechanism for the function of fluorotelomers is not fully known, but probably the capacity to resist mixing with the fuel is vital for its effectiveness, and probably also its property as a film former, which takes place when a thin film of water is produced between the foam and the fuel.

Fluorotelomers are used in different types of foam, e.g. AFFF (Aqueous film-forming foam), fluoroprotein foam, and FFFP (film-forming fluoroprotein foam). In global terms, its use in fire fighting foam accounts for less than two per cent of the total use of fluorinated chemicals (Danish Ministry of Environment 2005).

Fluorotelomers are used in very low concentrations (less than one per cent) in fire fighting foam, which means that it is not possible to find imported quantities in the products register. When people talk about one per cent, three per cent, or six per cent foam, it is not the concentration of fluorotelomers referred to but the concentration of the product to be mixed with water for use.

There are 12 companies which manufacture fire fighting foam in Europe. Calculations have been made which show that approximately 13000 tons of foam per year is used on the European market. (NERA 2006).

It is primarily fluorotelomers with six perfluorinated carbon atoms which are used, in certain cases eight. Shorter carbon chains are not considered to be sufficiently stable, according to



one foam manufacturer. Foam manufacturers feel that they obtain more information from raw materials suppliers today about the constituent compounds than they did some years ago. New fuels such as E85 which use mixtures of ethanol complicate matters and are significant when using fire fighting foam. Fires involving E85 require the use of alcohol resistant film forming foam, and fluorotelomers are included.

Hand-held foam fire extinguishers always use fluorotelomers.

The largest consumption of foam is during exercises. Fire departments try to run fire exercises using water or cheap foam due to poor finances. For exercises, foam which is passed its best before date is sometimes used since it is cheaper. This may contain PFOS. The useful life of foam is approximately 20 years.

The National Rescue Services Agency does not use foam which contains fluorinated chemicals for exercises or training.

#### *4.4.2 Trends*

There may still be foam containing PFOS with end-users, but not at manufacturers. There is probably none left at the fire prevention services since they do not keep large stocks. Our estimation is that current figures are probably the same as in 2003 concerning quantities of foam in stock at different end-users. At that time it was calculated that approximately 1000 m<sup>3</sup> of concentrated extinguisher foam was stored in Sweden (Kemikalieinspektionen 2004). It is not clear how much of the foam contains PFOS but at a meeting with trade representatives, the estimate was that probably less than one quarter is of that type today.

PFOA was used in AFFF until around 1975. Telomer sulphonates have replaced PFOS in fire fighting foam, in general 6:2 fluorotelomer sulphonate from DuPont.

#### *4.4.3 Emissions from fire fighting foam*

The use of foam containing perfluorinated substances for incidents and exercises produces direct emissions of perfluorinated substances into the environment.

3M has now discontinued certain applications in which perfluorinated substances would be directly dispersed into the environment, e.g. fire fighting foam.

Destruction of foam takes place at Ragnsells, Högbytorp, or at Sakab. At Högbytorp there is a flocculating plant where solids are precipitated, ultra-composted and finally put in landfills. Fluorinated compounds are probably not broken down by this treatment. The aqueous phase goes to a repository. Sakab has another process in which the foam is burned. There were plans to build an osmosis plant, but they were never realised. Prices for destruction at SAKAB are approximately 7-10 kr/litre depending on the calorific value of the foam. Customers have to pay approximately 50 kr/hand-held fire extinguisher for destruction when hand-held extinguishers are replaced. Relatively small amounts of foam are destroyed, however.

#### *4.4.4 Alternatives*

Some manufacturers have fluorine free foam, but they have a lower capacity than AFFF according to ICAO norms (aviation testing methods), and they are classed at a lower quality level A, instead of B for AFFF.

SP have carried out a preliminary study of fluorine free class A foam for fires in fibrous materials. Results indicate that larger quantities of foam are used for extinguishing. The

development of CAFS (compressed air foam system) would produce better foam and better control of the foam for extinguishing. It is an old technique which may work as an alternative to film forming foam with fluorotensides. CAFS can also be effective for petroleum fires.

Fluorotensides decrease the absorption of fuel into the foam. They decrease surface tension and are thermally stable. Fluorotensides are unique in their good film forming properties, but the mechanisms are not entirely clear and neither is it clear how important this property is for performance of the foam in comparison with, for example, the ability to reduce fuel absorption in the foam. In order to develop alternatives it is necessary first to acquire fundamental knowledge of exactly what gives foam its performance. It is also possible to develop extinguishing techniques, nozzles etc.

Foam manufacturers have shown interest in research and development of fluorine free alternatives, but also caution in cooperation due to problems with secrecy. It is important to be able to work together with raw materials manufacturers, which are in possession of most of the relevant information.

The Institute of Surface Chemistry (YKI) has a lot of expertise on tensides and foam, and is planning a cooperation project with SP.

The fluorine free alternatives which are available today have poorer extinguishing qualities than AFFF, which means that more foam must be used and extinguishing times are increased. The result is increased quantities of extinguishing water, i.e. foam liquid together with toxic residuals from the fire, which also has an impact on the environment. Extinguishing water is not treated to any great extent, and most of it is released directly into the environment. Oil storage depots often have protective embankments.

The largest current areas of use for fluorine free foam are exercises. Examples of manufacturers of fluorine free foam are Sohlberg, Angus and BIO-EX.

Exactly which tensides are used in fluorine free foams is unclear. According to the Institute for Surface Chemistry (YKI) several new tensides have been developed in recent years, but they are company secrets. One way to find out what alternatives exist is to look among new patents.

There are still no P marked fluorine free foams. P marking is a voluntary quality marking which is carried out by SP (Swedish National Testing and Research Institute) and there may be fluorine free foams which would come up to P marking standards.

So far, development has moved towards decreasing the quantities of fluorotensides with retained effect, and the content of fluorinated compounds in products has decreased drastically in the last ten years. If the mechanism behind film formation could be clarified together with knowledge of the role played by fluorotensides in this mechanism, new alternatives may be developed. More fundamental research is required into these mechanisms.

Rules would provide incentives for alternatives, but the Swedish market is far too small for products to be specially adapted to it. Standards and norms that must be complied with are international.

”PFOA Stewardship Program”, which was initiated by US EPA, contains no incentives for development alternatives since it is primarily carbon chains with fewer than eight carbon atoms which are used in fire fighting foam.

## **4.5 Polishes, waxes and other cleaning agents**

### *4.5.1 Use and function*

Perfluorinated substances are used in low concentrations in cleaning agents such as floor polish, waxes, window cleaning agents, and car care products. Typical concentrations in products are below one per cent.

Film forming products, for example polishes, contain fluorinated chemicals at present. These products were developed in the late 1960s, and before that time different types of natural products were used, for example waxes and shellack (a secretion from scale insects).

Polish makes floors easier to clean and increases the life of the floor, which in itself is good from the environmental point of view.

Polish can be divided into hard and soft types, the hard types being more like varnishes and the soft types containing more waxes. The soft types are worn off more quickly and replaced more often. Both types contain fluorinated chemicals primarily to give them good flow properties.

Surface improvement agents (spray polish/products for spray polishing) are used after polish has been applied, and these may also contain fluorinated chemicals. There are also mops which are impregnated with fluorinated chemicals which are used to improve the polish film.

Fluorinated chemicals are used in waxes, but not in all types of wax, e.g. not in soap wash waxes. Products that maintain hard wax surfaces, and also have a cleaning effect, may contain fluorinated compounds however.

The Detergent Regulation<sup>3</sup> requires that tensides in cleaning agents must be easily degradable or primarily degradable. Fluorotensides do not comply with these requirements and may therefore not be used in cleaning agents. This requirement only applies to products which have a cleaning effect and thus does not include polishes which only condition surfaces without actually cleaning them. A polish remover that both cleans/removes and applies new polish would be covered by this directive.

Polish is more comparable with varnish and paint than cleaning agents.

In the Kemi's products register there is a large number of products registered under the function of cleaning agents which contain fluorinated compounds.

### *4.5.2 Trends*

The trade association *Industrial and Institutional Hygiene* (IIH) has asked its member companies if they use any of the compounds which are included in Sweden's proposal for the banning of PFOS, and has recently updated its records. The results show that none of the compounds appears to be used. No investigation has been carried out into the larger group of perfluorinated substances which are now relevant. It is difficult to obtain information from suppliers of fluorinated chemicals about their content.

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<sup>3</sup> (EC) no. 648/2004

It appears that a new generation of polishes containing fluorotensides with shorter carbon chains of between four and six carbon atoms is in the pipeline.

#### *4.5.3 Emissions from polish etc.*

Cleaning products, polishes and so on are widely used and are directly released into wastewater and water purification plants, where degradation to more persistent compounds is often accelerated. In spite of the low concentrations used in products, emissions to the environment can be significant.

Polish can remain on flooring materials for three to four years, and during that time the floor may be polished or cleaned and a new layer of polish applied. This works for a number of years and then all the polish is removed and new polish applied. When the film of polish is removed, the perfluorinated substances end up in wastewater. Some of the film is worn away and forms particles which may be deposited in washing water, mop materials, vacuum cleaners etc. The fact that paths are sanded in winter in the Nordic countries may mean that polish is more rapidly worn away in these countries.

It is also possible that perfluorinated substances migrate through the film and are released into the air.

#### *4.5.4 Alternatives*

Polish and cleaning agents constitute a small market in comparison with paint, varnish and paper, and there is probably no large-scale product development for these applications at chemical companies.

One basic property of polish is good flow characteristics so that an even and thin film can be applied. At present there are no alternatives to fluorinated chemicals which are equally effective in providing good flow at such low concentrations. Fluorine free compounds (polymers and waxes) are used for film formation, however.

Silicones provide one alternative and also have good flow characteristics, but do not fasten as easily on the surface and provide poorer fat repellency. Silicones, too, are questionable from the environmental viewpoint.

The functional requirements for cleaning products are not as stringent as for polish. It is easier to accept slightly “worse” products, e.g. increasing the quantity used or using more mechanical processing. It should therefore be easier to find fluorine free alternatives for cleaning agents than for polishes. Soft polish in the form of soap wash wax need not contain fluorinated chemicals for its function.

The development of fluorine free alternatives will take a long time. Chemicals companies must first develop the chemicals, and then polish manufacturers must formulate new products. Testing to ensure that polish products fulfil all technical function requirements is very time consuming since tests must be carried out at different temperatures, humidity and “traffic” conditions. The formulation of a polish product can take between three and five years from the time when the raw material was ready.

The Swedish Standards Institute (SIS) environmental marking is at the moment revising its Swan criteria for film forming floor products and has seen from circulation responses that it is difficult to replace fluorinated chemicals and at the same time retains the functions of a product. For this reason the criteria will probably allow the use of fluorinated chemicals but

the limits for concentration have not yet been determined. It is hoped that development will move towards fluorine free alternatives and that the next revision of criteria will include stricter demands for the use of fluorine free products.

#### **4.6 Other areas of use**

The products register also includes minor areas of use, for example:

- In pesticides, e.g. in a fungicide intended to prevent the occurrence of leaf fungus in potatoes. The use of small concentrations of fluorinated compounds as anti-foam additives is, according to one producer, relatively common in pest control agents.
- In products for graphics processing, e.g. in agents used for the production of templates for screen printing
- In floor paints

Products such as paints, varnishes and glue are known to contain fluorinated compounds. They may well constitute hidden statistics since they contain low concentrations of fluorinated compounds which are not required to be reported to the product registry.

Other areas which could be interesting to examine more closely are their possible use in the electronics and semiconductor industry and the impregnation of floor tiles, for example.

## **5 Activities and measures in other countries**

### **5.1 EU**

Apart from PFOS, perfluorinated substances have not been discussed within the EU to the same extent as in North America. Negotiations on a ban on PFOS within the framework of the Limitation Directive (76/769/EEC) are taking place at present in the Council of Ministers and in the European Parliament, and are expected to be completed in autumn 2006. The proposal which the commission has formulated exempts in principle current use of this substance.

The EU Detergent Regulation ((EC) nr 648/2004), which came into force in autumn 2005, means that there are certain limitations on the use of perfluorinated substances in cleaning agents. The directive requires that tensides in cleaning agents must be easily degradable or primarily degradable. Fluorotensides do not comply with these requirements and thus may not be used in cleaning agents. The requirements only apply to products which have a cleaning effect and so polish, which only conditions a surface without cleaning it, is not covered. A polish remover, which cleans/removes and applies new polish, is covered though.

In the products register at KemI there is a large number of products which contain fluorinated compounds registered under the function of cleaning agents.

EFSA, the European authority for foodstuff security, is evaluating the impact on health of PFOS and PFOA at the moment.

EU has a research programme on perfluorinated substances called PERFORCE, with researchers from Sweden, Norway, Holland, Belgium, and DuPont.

### **5.2 USA**

In January 2006 the US Environmental Protection Agency (EPA) offered manufacturers of telomers and fluoropolymers the opportunity to participate in a global "PFOA Stewardship Program". The purpose is that companies will undertake to drastically decrease emissions from the production and product contents of PFOA and PFOA related compounds by 95 per cent before the year 2010, and to eliminate them completely by the year 2015. Compounds which can degrade into longer PFCA are also included in this phase-out. All companies that were requested, which together probably constitute virtually the entire world market, accepted the offer to participate. Those companies contacted by the US EPA 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 Program" is a voluntary undertaking and companies are not obliged to fulfil any undertakings under any law. Several of the companies have already, completely or almost completely, achieved the goal for the year 2010 through the recent development of new and better techniques for reducing residual levels in products and have said that they are willing to share this knowledge with other manufacturers.

US EPA includes in its Significant New Use Rules (SNUR) an obligation to report for 88 listed PFAS related compounds (US EPA 2002). According to the rules, manufacturers and importers are obliged to report new areas of use for these compounds within 90 days in advance of manufacture or importation. During this reporting time, the US EPA has the opportunity of evaluating the area of use and, if judged necessary, to ban or limit the proposed

use before it commences. The obligation to report has been applicable since 2003, after which date there have been some reports of new areas of use submitted, none of which have been approved.

In March 2006, US EPA proposed the introduction of a further 183 PFAS under SNUR (US EPA 2006b). Of these newly added compounds, 72 were not on the 2005 OECD list.

### **5.3 Canada**

In 2004, Environment Canada prohibited the importation and manufacture of four fluorotelomer based compounds. The temporary ban was based on risk assessments made within the Canadian system for notification of new compounds. These rules are still valid and on 16 July 2006 Environment Canada published a proposal for a permanent ban on these four compounds (Government of Canada 2006). The proposed rules prohibit all manufacture, use, sales and imports of these compounds in Canada. They will not include the compounds if they are included in certain imported articles.

The plan is to handle future applications for launching new compounds on the market which can degrade into PFCA in the same way, by banning them. Environment Canada has also drawn up an action plan for all PFCA compounds longer than eight carbon atoms and PFCA related compounds. The plans include risk assessments of several compounds and risk reduction measures of various types.

The four compounds which are temporarily banned in Canada have no CAS number, but have the following compound names in English:

- 2-propenoic acid, 2-methyl-, hexadecyl ester, polymers with 2-hydroxyethyl methacrylate, gamma-omega-perfluoro-C10-16-alkyl acrylate and stearyl methacrylate
- Hexane, 1,6-diisocyanato-, homopolymer, reaction products with alpha-fluoro-omega-2-hydroxyethylpoly (difluoromethylene), C16-20-branched alcohols and 1-octadecanol
- 2-Propenoic acid, 2-methyl-, 2-methylpropyl ester, polymer with butyl 2-propenoate and 2,5-furandione, gamma-omega-perfluoro-C8-14-alkyl esters, tert-Bu benzenecarboxyate-initiated
- 2-propen-1-ol, reaction products with pentafluoroiodoethane tetrafluoroethylene telomer, dehydroiodinated, reaction products with epichlorohydrin and triethylenetetramine

The first of these four compounds above was registered in 2004 in the KemI products register (see Chapter 4.1).

### **5.4 Australia**

Australia has a system for reporting and assessing chemicals, NICNAS (National Industrial Chemicals Notification and Assessment Scheme). NICNAS has carried out a risk assessment for PFBS. As a result of this, it was determined that any use which results in emissions into aquatic environments is inappropriate. All planned dispersive use of PFBS and PFBS based chemicals must be reported in advance to NICNAS for assessment and possible approval.

## **5.5 OECD work**

In 2004, OECD carried out a questionnaire survey regarding the production and use of PFOS, PFAS, PFOA and related compounds in its member countries. On the basis of responses received, a list was drawn up of perfluorinated substances (OECD 2005). A new questionnaire survey is being carried out at the moment and in this year's version, compounds which can degrade into PFCA are included.

Perfluorinated substances in the OECD will be discussed at a conference in November 2006, for which Sweden is the host. The aim is to gain an overall picture of the issue of perfluorinated substances and to discuss what further information is required in order to make well-considered assessments and see possible ways forward.



## **6 Perfluorinated substances and REACH**

REACH stands for Registration, Evaluation and Authorisation of Chemicals and is the new EU chemicals legislation. Negotiations are ongoing at present, autumn 2006, in the Commission and in Parliament. The decision on legislation is expected around the end of 2006 or the beginning of 2007. This means that the legislation can come into force at the earliest during the spring of 2007. At the time of writing, the proposed bill has not been passed and some parts of it may be changed. This chapter must therefore be seen as a preliminary evaluation of what implications REACH may have for perfluorinated substances.

### **6.1 Registration**

#### *6.1.1 Chemical products*

According to the proposed bill for new chemicals legislation, any company that manufactures or imports more than one ton of a substance per year, either as a pure substance or in a preparation, must submit a registration for that substance to the EU chemicals agency. Perfluorinated substances are low volume compounds and as such are often included in very low concentrations in chemical products that are ready for use (e.g. in fire fighting foam and cleaning agents). It is therefore probable that the volume of one ton of pure substance or in a preparation set as a limit for registration will not apply to a number of perfluorinated substances. It is the substance itself which is manufactured or imported, and not the degradation products of the substance such as PFOS or PFOA, that must be registered if certain requirements are fulfilled.

#### *6.1.2 Polymers*

Polymers are generally exempted from the requirement for registration. They need only be registered if a previously unregistered monomer is used in the manufacture and constitutes more than two per cent of the polymer backbone. In the present bill proposal it is stated that the rules for the registration of polymers need to be reviewed as soon as possible after REACH has entered into force.

#### *6.1.3 Time plan for registration*

The time plan for when registration must be completed runs over a period of 11 years. The completion date for registration is linked to the annual volume of the substance. Assuming that the new chemicals legislation comes into force in 2007, the registration of low volume substances, i.e. substances which are manufactured or imported in volumes over one ton but less than 10 tons per year, will not be completed until the year 2018. For the most hazardous substances and substances which are manufactured or imported in volumes over 1000 tons per year, registration must have taken place by the year 2010. In those cases where the volume per manufacturer/importer of highly fluorinated compounds does not exceed one ton, the registration will thus not be fully completed until the year 2018.

### **6.2 Authorisation and restrictions on use**

One of the cornerstones of the REACH legislation is the requirement for authorisation to introduce products containing the most hazardous substances (carcinogenic, mutagenic, toxic to reproduction, persistent, bioaccumulative and toxic, or substances which cause an equivalent level of concern) on the market or to use them. According to the proposed bill for new chemicals legislation, the requirement for an authorisation will be valid if the concentration of the substance in the chemical product exceeds 0.1 per cent. In several products, e.g. fire fighting foam and polish, fluorinated compounds are used at concentrations

of less than 0.1 per cent and in consequence are exempted from the requirement for authorisation.

According to the proposed bill for new chemicals legislation, the requirement for authorisation for the most hazardous substances will be introduced successively as they are decided to require authorisation. The first recommendations for which substances and uses of them that requires authorisation must be ready two years after the REACH directive enter into force; at the earliest, that is, in 2009.

Another possible method of limiting the use of a substance that may introduce an unacceptable risk is by drawing up a proposal for a restriction of the substance, i.e. limiting how the substance is released onto the market, or how it is used. This procedure in the new chemicals legislation will replace the directive 76/769/EEC, the so-called Limitation Directive. Substances which are not covered by authorisation requirement may also come under the restriction rules.

Under the new chemicals legislation, a substance with uses that requires authorisation cannot at the same time be further restricted with reference to the characteristics which have led to the authorisation requirement. Among highly fluorinated substances, there are those that fulfil the requirement for so-called PBT or vPvB substances and those that do not fulfil these criteria. Some of these could possibly be described as producing equivalent concern since they degrade into PBT or vPvB substances which fulfil the criteria for substances requiring authorisation.

### **6.3 Chemical safety report**

Registration must, in addition to describing all areas of use, also include information on the properties of a substance and guidelines for its safe use, among other things. Documentation must be summarised in a chemical safety report for substances that are manufactured or imported in quantities of at least 10 tons per year. For substances which are classified as hazardous to health or environment, or which are judged to be PBT and vPvB substances, the registration application must also include relevant exposure scenarios, including risk management measures for all the areas of use of the substance. The purpose is to ensure safe handling of the substance.

In general terms, highly fluorinated substances fulfil criteria for classification as hazardous to health or environment and some of them, primarily those with more than eight carbon atoms in the chain, can probably be assessed as PBT compounds. On the other hand, the quantity which an individual manufacturer or importer puts onto the market per year seldom exceeds 10 tons. A comprehensive chemical safety report will not be required in such cases.

### **6.4 Substances contained in articles**

For those who manufacture or import articles, the requirement for registration of substances contained in the articles applies if the total amount of a substance exceeds 1 ton per year in all articles in the company's range, and if the substance is intended to be released under normal and predictable conditions.

In some of the areas of use now known, such as the treatment of articles to give them water repellent and dirt repellent characteristics, the highly fluorinated substances which are used are not intended to be released during the lifetime of the articles, even if there is a certain loss as a result of wear and washing. In such cases, these highly fluorinated substances will probably not fall under the requirement to be registered.

For substances of very high concern which are used in a product, an obligation to report will be introduced if the quantity of the substance exceeds 1 ton per year and manufacturer or importer, and if the concentration of the substance exceeds 0.1 per cent (w/w). Some of the highly fluorinated substances which have extremely hazardous properties may be included in this category, but that depends on whether the concentration of 0.1 per cent is calculated for the whole product or parts of it, and if the quantity of this substance exceeds one ton per year and manufacturer or importer.

#### *6.4.1 Information on highly toxic compounds in articles*

The proposal for the REACH regulation that has been put forward will mean in all probability an obligation to provide information to recipients of substances of very high concern that are included in articles at concentrations above 0.1 per cent. This obligation applies whether or not a manufacturer or importer of articles is obliged to make a registration or report of the substance to the chemicals authority. The purpose is to ensure safe handling of the articles.

#### **Authorisation and restrictions**

Highly fluorinated substances which fulfil criteria for PBT or vPvB compounds, or are considered to produce equivalent concern, may be candidates for authorisation applications when they are used within the EU, either for manufacture of preparations or of articles. Authorisation applications will not be processed before 2009.

With regard to imported articles, there is no possibility of regulating the import of extremely hazardous compounds in articles through authorisation applications. Imported articles that contain compounds requiring authorisation may, on the other hand, be subject to equivalent investigation through the procedure for restrictions after the date when the substance may no longer be used subsequent to its rejection in the authorisation application.

## **7 Discussion and conclusions**

### **7.1 Complex group of substances**

The group of fluorinated substances is a large and complex group which contains several hundred known compounds and contains many subgroups. New perfluorinated substances are continually emerging and it is difficult to gain an overall picture. Companies seldom state exactly which substances are in their products.

One educational problem when discussing the group of substances or giving information on them is that it is seldom the substances which have been most in focus, perfluorooctane sulphonate (PFOS) and perfluorooctane acid (PFOA), which are actually used in chemical products and articles. There is a large group of other substances, e.g. fluorotelomers, which are used and when they are released in the environment they degrade to PFOA, for example.

### **7.2 Uses and alternatives**

Two companies which have historically been large producers of perfluorinated substances on the world market, DuPont and 3M, have attempted to find different solutions to replace PFOS. There are primarily two types of substance which have replaced PFOS related substances, namely fluorotelomers and short PFAS related substances, e.g. PFBS.

No perfluorinated substances are manufactured in Sweden. However, a conservative estimate of imports is about 24 tons through chemical products and a large quantity is probably imported in the form of articles. Even though it is difficult to make estimates of the quantities of perfluorinated substances that come into the country through imported articles, it is highly probable that these account for the largest quantities. Examples of such articles are clothes, textiles, furniture and foodstuffs packages. According to DuPont, textile treatment is the largest area of use of fluorotelomers in global terms.

Fluorotelomers have been manufactured since the 1970s, and have also been used parallel with PFOS. They make up the larger part of registered volumes in the KemI products register (see Chapter 4.1), mostly in the form of telomer based polymers which are used in the textile industry. Since fluorotelomers can degrade to give PFCA, telomers, or at least long-chain telomers, are not a suitable alternative to PFOS.

PFBS related compounds have only been manufactured for some years and their use in Sweden is so far very limited, according to the KemI products register. But several companies are now developing products with shorter fluorinated carbon chains, with fewer than eight carbon atoms. These appear to be less toxic and have less potential for bioaccumulation than longer perfluorinated substances, but they are still extremely persistent. As yet there is no assessment of whether these can be seen as acceptable alternatives.

There are fluorine free alternatives with varying performances for the four product groups that have been more closely investigated. Fluorinated compounds do have very special properties however, and in many cases it appears difficult to find alternatives which are as good. Some of the alternatives which are currently or which may become relevant have not been completely evaluated in terms of their health and environment characteristics and should be more closely investigated. Examples of these are certain silicones and nano materials.

### *7.2.1 Textiles*

The largest quantities of perfluorinated substances imported to Sweden in chemical products go to the textiles industry, where they are used for treatment of sun-blocking textiles, car textiles and working clothes. It is primarily telomer based polymers which are used. Imported articles in which fluorinated compounds may be found are working clothes, sports clothes, furniture textiles etc.

Analyses of textiles have shown that telomer alcohols, and also small quantities of PFCA and PFAS, are released from clothes and other textiles. Garments and other articles treated with fluorinated compounds are rather expensive but in return they have many desirable functions: they are water-repellent, grease-repellent, dirt-repellent and they can breathe. There are alternative treatments and materials which will provide some of these functions, but no non-fluorinated alternatives can at present provide all these functions. In the final analysis it is often a question of what level of comfort the consumer or end-user desires. It should be possible to adapt the use of chemicals to the intended use of the articles more than is done today. Maybe fashion clothes do not need to be highly grease-repellent; maybe children's clothes do not need to be breathable; maybe furniture fabrics can be made washable instead of wipe-clean.

### *7.2.2 Paper*

Fluorinated compounds can be used in packages for oily foodstuffs. They occur in paper product manufacturing in Sweden, but are probably more common in paper packages manufactured in central Europe, for example. It is difficult to estimate how common imported

fluorinated foodstuffs packages are in Swedish shops. With regard to grease-repellent paper packages, there are alternative qualities of paper and barrier materials which function equally well in comparison with fluorinated paper. Foodstuffs packages may be assumed to constitute a source of direct exposure for people, since fluorotelomers have been shown to migrate from packages into foodstuffs.

### *7.2.3 Fire fighting foam*

Fluorotelomers, especially with six perfluorinated carbon atoms in the chain, are used in fire fighting foam for their film forming properties and the ability to decrease fuel absorption. These foams are especially useful for severe fires, e.g. chemical fires. The quantities in the foam are low, less than one per cent, but the foam is directly released into the environment. According to information received, the amount of foam past its use-by date which is destroyed is relatively small. This foam is used for training instead of fighting real fires. The same is probably true for foam containing PFOS which still exists in public stocks. There are fluorine free foams available today, but they are not equally effective. Research is being carried out which in the long term may produce effective fluorine free alternatives.

### *7.2.4. Cleaning agents*

Fluorinated tensides are used in very low levels in a large number of cleaning products, e.g. polish, waxes, all-purpose cleaners, window cleaning agents etc. Their use is widespread and directly released into wastewater. The use of fluorinated tensides in products with cleaning effects does not comply with the Detergent Regulation<sup>3</sup> since they are not sufficiently biodegradable. In products such as polish, fluorinated compounds are not added primarily for their cleaning characteristics but because they provide good spreading properties and an even surface. According to information, there are no good alternatives to perfluorinated substances in polish, but silicones are seen as interesting for development.

With respect to chemical products such as cleaning agents and fire fighting foam, the volumes are perhaps not large but it is their widespread use with direct release into the environment or to water purification plants which accelerates their degradation into persistent compounds.

## **7.3 Unclear risk picture**

There is a shortage of knowledge about the properties of many perfluorinated substances, of which substances are used in products, of how the substances are spread and how people are exposed to them. What can be stated with certainty is that perfluorinated substances are extremely stable as a group. Some compounds are broken down slowly or not at all, others are converted to persistent compounds in the environment. Some of them are bioaccumulative and there are indications that concentrations in animals in the Arctic are rising. There is therefore the risk of a serious long-term problem if these stable compounds do in fact have hazardous properties, now that they are already spread in the environment. Pending further knowledge in the area, it is a matter of urgency that emissions of perfluorinated substances are reduced so that serious long-term problems do not occur.

Thus, there are many pieces missing in the puzzle before the problems associated with perfluorinated substances are sufficiently understood. Some issues which need further investigation are presented below.

### *7.3.1 Long range transport*

There are different theories regarding how perfluorinated substances reach isolated and remote areas such as the Arctic. Some claim that a large proportion of perfluorinated substances found there originate from old sins, such as industrial emissions from

fluoropolymer production and other local emissions, and have been transported in surface water and ocean currents. Others say that it is the more recent use of telomer based compounds that is behind much of the perfluorinated substances in the Arctic, since telomer alcohols are volatile and can be transported over great distances in the atmosphere and degrade to give PFCA. What exactly is the main source is very significant for attitudes towards the current use of perfluorinated substances in articles.

### *7.3.2 Residuals in products or degradation of polymers*

It is generally accepted that residual levels of telomer alcohols in fluorotelomer based polymers can constitute a source of exposure for people and environment, and chemicals suppliers are making efforts to reduce these residual levels. To what extent perfluorinated carbon chain tails of polymers break loose during the life cycle of different products, which seems likely from a purely chemical point of view, may also be a key issue and should be examined more closely. In USA the chemicals industry has undertaken to compile data on the emissions of PFCA precursors from ageing articles and US EPA is carrying out studies with the purpose of determining how much PFCA is produced from fluorotelomer based polymers.

Difficulties in finding effective methods of analysis for all perfluorinated substances may hamper the measurement of their occurrence in people and the environment.

### *7.3.3 Assessment of bioaccumulating properties*

One problem area is that traditional test methods for bioaccumulation do not appear to be suitable for perfluorinated substances, which makes difficult the assessment of environmental hazards posed by these substances in accordance with standard criteria. Furthermore, the effects of different PFCAs (in addition to PFOA) need to be studied in more depth.

## **7.4 Possible measures**

The main purpose of this study is to increase knowledge of the occurrence and use of perfluorinated substances. Further information is required to assess the risks and propose measures to decrease those risks. Potential measures should be analysed in terms of their effectiveness, costs, feasibility and the possibility of following them up. This report may hopefully constitute the basis for continued work in decreasing the above risks. Some possible areas for continued work are introduced below.

### *7.4.1 Legislation*

Perfluorinated substances are complicated to manage within existing legislation since the compounds used in products are not monitored in the environment and have hazardous properties. For example, even if PFOA and its salts are classified as CMR, it is doubtful whether that classification would also apply to compounds which can degrade into PFOA, as do certain telomers. Due to the complex chemistry of these compounds, it is not easy to state exactly which compounds should be covered by rules, and it can be difficult to draw the line between different compounds since there is often a mixture of chain lengths in the manufacture. Enforcement in this area is hampered by the fact that the analysis of certain perfluorinated substances is problematic.

There is a risk that many perfluorinated substances will not be covered by the requirement for registration in REACH since they are manufactured or imported in volumes of less than one ton. Thus, much information about this group of substances will be missing. One possibility is to compile information and propose prohibition or limitations on their use through the procedure in REACH which will replace the directive 76/769/EEC (the so-called Limitation Directive). See Chapter 6 on REACH and perfluorinated substances.

With the introduction of REACH, the chances of introducing national restriction rules for chemical compounds will decrease. The effects of introducing national bans on the use of perfluorinated substances would also be limited for several reasons. It is clear that these compounds can be transported over great distances and constitutes a global environmental problem. Banning them in products in Sweden would not mean that they would be absent from the Swedish environment.

#### *7.4.2 International conventions*

The advantage of conventions is that many countries are included in measures decided upon. This is important, not least for controlling the use of substances in articles. Conventions may be needed as a complement to EU regulations when considering extensive global trade.

PFOS has been nominated as the POP candidate during the LRTAP and Stockholm conventions. It is doubtful how many and which other perfluorinated substances could fulfil the POP criteria. It is important that those compounds nominated in the POP conventions clearly fulfil the criteria and that sufficient data exist to support this. The EU PBT group, under the TCNES (Technical Committee for New and Existing Compounds), assesses which substances are PBT according to EU criteria, but also have the mandate to assess which fulfil the POP criteria. No single EU member state can nominate compounds for the POP conventions if there is no agreement within the EU circle on the nomination. The normal path taken is that compounds are first regulated in the EU and are subsequently nominated by the commission in a POP convention. The convention process often takes at least three years from nomination to decision on measures.

It should also be considered whether measures can be introduced in stages; for example, to first manage PFOS, then PFOA, followed by long PFCA and so on, or to manage a larger group at one time. The tendency appears to be that companies move from one fluorinated compound to another. The long-chain perfluorocarboxylic acids are judged to be worse than the short-chain acids, but it can be difficult to draw the limits between different compounds since there is often a mixture of chain lengths at the production stage.

#### **7.5 Continued work with risk reduction**

The large group of perfluorinated substances should be given more attention in the EU and efforts to reduce risks associated with perfluorinated substances should be increased. In addition, compounds that can degrade to give PFCA should be taken up on the EU agenda for restriction of chemical risks.

Sweden has initiated an OECD workshop in which authorities and other interested parties will meet in Stockholm in November 2006 to gain an overall picture of the problems surrounding perfluorinated substances and to discuss what further information is required in order to make well-founded assessments and see possible ways forward.

#### **7.6 Contributions that companies and consumers can make now**

### 7.6.1 Companies

The regulation of perfluorinated substances has been initiated in a number of regions in the world and players on the market should be prepared for the phasing-out of a number of these compounds within the next few years.

**Chemicals industry:** manufacturers of perfluorinated substances are obliged to investigate the effects of these substances on health and the environment, and to decrease emissions of the compounds during manufacture. It is a matter of urgency that alternative substances with less hazardous properties are developed.

**Companies that manufacture products using perfluorinated substances:** request information on the health and environmental properties of perfluorinated substances and consider the need for using these substances in products. Reduce emissions via products, for example, by minimising residues of uncombined perfluorinated substances in products.

**Companies that use or trade products containing perfluorinated substances:** request information on the contents of products, put forward demands for products with less hazardous compounds. Make demands for decreased residues of uncombined perfluorinated substances in products.

### 7.6.2 Consumers

At present there is no information that indicates perfluorinated substances constitute an acute threat to health. There is therefore no reason for private people to dispose of products which may contain such substances; for example, all-weather jackets. Consumers can contribute to a decrease in the use of perfluorinated substances by asking whether they are used in the products they buy, and by demanding less hazardous alternatives.



## Perfluorinated substances on the Swedish market

## Annex 1

Perfluorinated substances in KemI's products register in year 2004.

CAS No	Chemical name	Number of fluorinated carbon	Compound (OECD 2005)
115592-83-1	2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorododecyl ester, polymer with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorododecyl 2-propenoate, hexadecyl 2-propenoate, N-(hydroxymethyl)-2-propenamide, octadecyl 2-prop	6-12	Fluoro ester
118102-37-7	Alcohols, C8-14, g-w-perfluoro, reaction products with epichlorohydrin, polyethylene glycol monomethyl ether and N,N',2-tris(6-isocyanatohexyl)imidodicarbonic diamide (AICS)	6-12	Fluoro urethane
118102-38-8	Alcohols, C8-14, g-w-perfluoro, reaction products with epichlorohydrin, tetrahydrofuran homopolymer and N,N',2-tris(6-isocyanatohexyl)imidodicarbonic diamide (AICS)	6-12	Fluoro urethane
135228-60-3	Hexane, 1,6-diisocyanato-, homopolymer, g-w-perfluoro-C6-20-alc.-blocked (TSCA, NDSL, AICS)Homopolymere du 1,6-diisocyanatohexane, bloque avec le groupe g-w-perfluoro-C6-20-alcools (French) (NDSL)	4-18	Fluoro urethane
148878-17-5	2-Propenoic acid, 2-methyl-, C2-18-alkyl esters, polymers with a-fluoro-w-[2-[(1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene) and vinylidene chloride (DSL)	n	Fluoro ester
150135-57-2	2-Propenoic acid, 2-methyl-, 2-(dimethylamino)ethyl ester, polymers with Bu acrylate, g-w-perfluoro-C8-14-alkyl acrylate and polyethylene glycol monomethacrylate, 2,2'-azobis[2,4-dimethylpentanenitrile]-initiated (TSCA, NDSL)	6-12	Fluoro ester
17527-29-6	2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester (TSCA, DSL, ENCS)Acrylate de 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyle (French) (DSL, EINECS)3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate (EINECS)3,3,4,4,5,5,6,6,7,7,8,8,8-T	6	Fluoro ester
1996-88-9	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorododecyl ester (TSCA, DSL, AICS)Methacrylate de 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorododecyle (French) (DSL, EINECS)3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafl	8	Fluoro ester
	2-Propenoic acid, .gamma.-.omega.-perfluoro-C8-14-alkyl esters, polymer with Glycidylmethacrylate, N-(Butoxymethyl)-methacrylamide, N-Hydroxymethylmethacrylamide and Stearylacrylate		
203743-03-7	2-Propenoic acid, 2-methyl-, hexadecyl ester, polymers with 2-hydroxyethyl methacrylate, .gamma.-.omega.-perfluoro-C10-16-alkyl acrylate and stearyl methacrylate		
	2-Propenoic acid, .gamma.-.omega.-perfluoro-C8-14-alkyl esters, polymer with 2-ethylhexyl-acrylate, N-hydroxymethylmethacrylamide and stearylacrylate		
2144-53-8	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester (TSCA, DSL, ENCS, AICS)Methacrylate de 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyle (French) (DSL,	6	Fluoro ester

	EINECS)3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate (EINECS)3,		
221455-72-7	2-Propenoic acid, 2-methyl-, 2-hydroxyethyl ester, reaction products with 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane and Me Etketone oxime, polymers with 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate and .gamma.-.omega.-perfluoro-C8-20a		
335-36-4	Furan, 2,2,3,3,4,4,5-heptafluorotetrahydro-5-(nonafluorobutyl)- (TSCA, NDSL, ENCS, AICS)2,2,3,3,4,4,5-Heptafluorotetrahydro-5-(nonafluorobutyl)furane (French) (NDSL)2,2,3,3,4,4,5-heptafluorotetrahydro-5-(nonafluorobutyl)furan (EINECS, )2,2,3,3,4,4,5-hepta	8	Perfluoro ether
34454-97-2	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-N-(2-hydroxyethyl)-N-methyl- (TSCA, DSL, AICS)1,1,2,2,3,3,4,4,4-Nonafluoro-N-(2-hydroxyethyl)-N-methylbutane-1-sulfonamide (French) (DSL, EINECS)1,1,2,2,3,3,4,4,4-nonafluoro-N-(2-hydroxyethyl)-N-methylbuta	4	PFAS
34455-29-3	1-Propanaminium, N-(carboxymethyl)-N,N-dimethyl-3-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-, inner salt (TSCA)1-Propanaminium, N-(carboxymethyl)-N,N-dimethyl-3-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-, hydrox	6	Fluoro sulfonate/ sulfonamide/ sulfonyl
3825-26-1	Octanoic acid, pentadecafluoro-, ammonium salt (TSCA, DSL, AICS)Pentadecafluorooctanoate d'ammonium (French) (DSL, EINECS)ammonium pentadecafluorooctanoate (EINECS)Ammoniumpentadecafluorooctanoat (German) (EINECS)pentadecafluorooctanoato de amonio (Spanish	7	PFOA
479029-28-2	2-Propenoic acid, 2-methyl-, 2-(dimethylamino)ethyl ester, polymers with.gamma.-.omega.-perfluoro-C8-14-alkyl acrylate, acetates, N-oxides		
54950-05-9	Butanedioic acid, sulfo-, 1,4-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) ester, sodium salt (TSCA, NDSL, AICS)Sulfonatosuccinate de 1,4-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyle), sel sodique (French) (NDSL)sodium 1,4-bis(3,3,4,4,5,5,6,6,7,	6	Fluoro ester
6014-75-1	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentacosafuorotetradecyl ester (TSCA, DSL, ENCS)Methacrylate de 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentacosafuorotetradecyle (French) (DS	12	Fluoro ester
65530-59-8	Poly(difluoromethylene), a-fluoro-w-(2-hydroxyethyl)-, 2-hydroxy-1,2,3-propanetricarboxylate (3:1) (TSCA, DSL, AICS)a-Fluoro-w-(2-hydroxyethyle)poly(difluoromethylene), 2-hydroxypropane-1,2,3-tricarboxylate (3:1) (French) (DSL)	n	Fluoro ester
65530-63-4	Ethanol, 2,2'-iminobis-, compd. With a-fluoro-w-[2-(phosphonooxy)ethyl]poly(difluoromethylene) (2:1) (TSCA, DSL)2,2'-Iminodiethanol, compose (2:1) avec le a-fluoro-w-[2-(phosphonooxy)ethyl]poly(difluoromethylene) (French) (DSL)Ethanol, 2,2'-iminobis-, com	n	Fluoro phosphate
65530-64-5	Ethanol, 2,2'-iminobis-, compd. With a,a'-[phosphinicobis(oxy-2,1-ethanediy)]bis[w-fluoropoly(difluoromethylene)] (1:1) (TSCA, DSL)2,2'-Iminodiethanol, compose (1:1) avec l'a,a'-[phosphinicobis(oxyethylene)]bis[w-fluoropoly(difluoromethylene)] (French) (	n	Fluoro phosphate
65530-66-7	Poly(difluoromethylene), a-fluoro-w-[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]- (TSCA, DSL)a-Fluoro-w-[2-(methacryloyloxy)ethyl]poly(difluoromethylene) (French)	n	Fluoro ester

	(DSL)		
65530-69-0	Poly(difluoromethylene), a-[2-[(2-carboxyethyl)thio]ethyl]- w-fluoro-, lithium salt (TSCA, DSL, AICS)a-[2-[(2-Carboxyethyl)thio]ethyl]- w-fluoropoly(difluoromethylene), sel de lithium (French) (DSL)	n	Fluoro thioether
65530-70-3	Poly(difluoromethylene), a,a'-[phosphinicobis(oxy-2,1-ethanediyl)]bis[w-fluoro-, ammonium salt (TSCA, DSL)a,a'-[Phosphinicobis(oxyethylene)]bis[w-fluoropoly(difluoromethylene)], sel d'ammonium (French) (DSL)	n	Fluoro phosphate
65530-71-4	Poly(difluoromethylene), a-fluoro-w-[2-(phosphonooxy)ethyl]-, monoammonium salt (TSCA, DSL)a-Fluoro-w-[2-(phosphonooxy)ethyl]poly(difluoromethylene), sel de monoammonium (French) (DSL)	n	Fluoro phosphate
65530-72-5	Poly(difluoromethylene), a-fluoro-w-[2-(phosphonooxy)ethyl]-, diammonium salt (TSCA, DSL)a-Fluoro-w-[2-(phosphonooxy)ethyl]poly(difluoromethylene), sel de diammonium (French) (DSL)	n	Fluoro phosphate
65530-74-7	Ethanol, 2,2'-iminobis-, compd. With a-fluoro-w-[2-(phosphonooxy)ethyl]poly(difluoromethylene) (1:1) (TSCA, DSL)2,2'-Iminodiethanol, compose (1:1) avec l'a-fluoro-w-[2-(phosphonooxy)ethyl]poly(difluoromethylene) (French) (DSL)Ethanol, 2,2'-iminobis-, comp	n	Fluoro phosphate
65530-83-8	Poly(difluoromethylene), a-[2-[(2-carboxyethyl)thio]ethyl]- w-fluoro- (TSCA, DSL, AICS)a-[2-[(2-Carboxyethyl)thio]ethyl]- w-fluoropoly(difluoromethylene) (French) (DSL)	n	Fluoro thioether
65545-80-4	Poly(oxy-1,2-ethanediyl), a-hydro-w-hydroxy-, ether with a-fluoro-w-(2-hydroxyethyl)poly(difluoromethylene) (1:1) (TSCA, DSL, AICS)a-Hydro-w-hydroxypoly(oxyethylene), ether (1:1) avec l'a-fluoro-w-(2-hydroxyethyl)poly(difluoromethylene) (French) (DSL)	n	Fluoro ether
67584-42-3	Cyclohexanesulfonic acid, decafluoro(pentafluoroethyl)-, potassium salt (TSCA, DSL, AICS)Decafluoro(pentafluoroethyl)cyclohexanesulfonate de potassium (French) (DSL, EINECS)potassium decafluoro(pentafluoroethyl)cyclohexanesulphonate (EINECS)Kaliumdecafluoro	8	PFAS
67584-51-4	Glycine, N-ethyl-N-[(nonafluorobutyl)sulfonyl]-, potassium salt (TSCA, DSL, AICS)N-Ethyl-N-[(nonafluorobutyl)sulfonyl]glycinate de potassium (French) (DSL, EINECS)potassium N-ethyl-N-[(nonafluorobutyl)sulphonyl]glycinate (EINECS)Kalium-N-ethyl-N-[(nonafluoro	4	PFAS
67584-52-5	Glycine, N-ethyl-N-[(undecafluoropentyl)sulfonyl]-, potassium salt (TSCA, DSL, AICS)N-Ethyl-N-[(undecafluoropentyl)sulfonyl]glycinate de potassium (French) (DSL, EINECS)potassium N-ethyl-N-[(undecafluoropentyl)sulphonyl]glycinate (EINECS)Kalium-N-ethyl-N-	4	PFAS
67584-53-6	Glycine, N-ethyl-N-[(tridecafluorohexyl)sulfonyl]-, potassium salt (TSCA, DSL, ENCS, AICS)N-Ethyl-N-[(tridecafluorohexyl)sulfonyl]glycinate de potassium (French) (DSL, EINECS)potassium N-ethyl-N-[(tridecafluorohexyl)sulphonyl]glycinate (EINECS)Kalium-N-et	6	PFAS
67584-62-7	Glycine, N-ethyl-N-[(pentadecafluoroheptyl)sulfonyl]-, potassium salt (TSCA, DSL, ENCS, AICS)N-Ethyl-N-[(pentadecafluoroheptyl)sulfonyl]glycinate de potassium (French) (DSL, EINECS)potassium N-ethyl-N-[(pentadecafluoroheptyl)sulphonyl]glycinate (EINECS)Ka	7	PFAS

68187-47-3	1-Propanesulfonic acid, 2-methyl-, 2-[[1-oxo-3-[(g-w-perfluoro-C4-16-alkyl)thio]propyl]amino] erives., sodium salts (TSCA, DSL, EINECS)Acide 2-methylpropane-1-sulfonique, derives 2-[[[(g-w-perluoroalkyl)thio]propionamides}, sel de sodium (French) (DSL)aci	2-14	Fluoro phosphate
68298-62-4	2-Propenoic acid, 2-[butyl[(heptadecafluorooctyl)sulfonyl]amino]ethyl ester, telomer with 2-[butyl[(pentadecafluoroheptyl)sulfonyl]amino]ethyl 2-propenoate, methyloxirane polymer with oxirane di-2-propenoate, methyloxirane polymer with oxirane mono-2-prop	7-8	PFOS & PFAS
68391-08-2	Alcohols, C8-14, g-w-perfluoro (TSCA, DSL, EINECS, AICS)Alcools en C8-14, g-w-perfluoro (French) (DSL, EINECS)Alkohole, C8-14-, g-w-Perfluor- (German) (EINECS)alcohols, C8-14, g-w-perfluoro (Spanish) (EINECS)	6-12	Fluoro alcohol
68391-09-3	Sulfonic acids, C6-12-alkane, perfluoro, potassium salts (TSCA, NDSL, EINECS)Acides sulfoniques, alcanes en C6-12, perfluoro, sels de potassium (French) (NDSL, EINECS)Sulfonsauren, C6-12-Alkan-, Perfluor-, Kaliumsalze (German) (EINECS)acidos sulfonicos, C	6-12	PFOS & PFAS
68412-68-0	Phosphonic acid, perfluoro-C6-12-alkyl lumini. (TSCA, DSL, EINECS)Acide phosphonique, derives perfluoro-alkyles en C6-12 (French) (DSL, EINECS)Phosphonsaure, Perfluor-C6-12-alkylderivate (German) (EINECS)acido fosfonico, perfluoro-C6-12-alquil derivados	6-12	Perfluoro phosphonic/ phosphinic
68412-69-1	Phosphinic acid, bis(perfluoro-C6-12-alkyl) lumini. (TSCA, DSL, EINECS)Acide phosphinique, derives bis(perfluoroalkyle en C6-12) (French) (DSL)acide phosphinique, derives bis(perfluoro-alkyl en C6-12) (French) (EINECS)Phosphinsaure, Bis(perfluor-C6-12-al	6-12	Perfluoro phosphonic/ phosphinic
68555-74-8	1-Pentanesulfonamide, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-N-(2-hydroxyethyl)-N-methyl- (TSCA, DSL, AICS)1,1,2,2,3,3,4,4,5,5,5-Undecafluoro-N-(2-hydroxyethyl)-N-methylpentane-1-sulfonamide (French) (DSL, EINECS)1,1,2,2,3,3,4,4,5,5,5-undecafluoro-N-(2-hydrox	5	PFAS
68555-75-9	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N-(2-hydroxyethyl)-N-methyl- (TSCA, DSL, AICS)Tridecafluoro-N-(2-hydroxyethyl)-N-methylhexanesulfonamide (French) (DSL, EINECS)tridecafluoro-N-(2-hydroxyethyl)-N-methylhexanesulphonamide (EINECS)	6	PFAS
68555-76-0	1-Heptanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-N-(2-hydroxyethyl)-N-methyl- (TSCA, DSL, AICS)1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-Pentadecafluoro-N-(2-hydroxyethyl)-N-methylheptane-1-sulfonamide (French) (DSL, EINECS)1,1,2,2,3,3,4,4,5,5,6,6,	7	PFAS
68555-92-0	2-Propenoic acid, 2-methyl-, 2-[[[(heptadecafluorooctyl)sulfonyl]methylamino]ethyl ester, polymer with 2-[methyl[(nonafluorobutyl)sulfonyl]amino]ethyl 2-methyl-2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulfonyl]amino]ethyl 2-methyl-2-propenoate, 2-[me	4-8	PFOS & PFAS
68608-14-0	Sulfonamides, C4-8-alkane, perfluoro, N-ethyl-N-(hydroxyethyl), reaction products with 1,1'-methylenebis[4-isocyanatobenzene] (TSCA, DSL, EINECS)C4-8-(Perfluoro-alkane)sulfonamides N-ethyl-N-(hydroxyethyles), produits de reaction avec le diisocyanate de 4	4-8	PFOS & PFAS

68867-62-9	2-Propenoic acid, 2-methyl-, 2-[ethyl[(heptadecafluorooctyl)sulfonyl]amino]ethyl ester, telomer with 2-[ethyl[(nonafluorobutyl)sulfonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(pentadecafluoroheptyl)sulfonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl	4-8	PFOS & PFAS
70969-47-0	Thiols, C8-20, g-w-perfluoro, telomers with acrylamide (TSCA, DSL, AICS, )g-w-Perfluorothiols en C8-20 telomerises avec l'acrylamide (French) (DSL)	6-18	Fluoro amine
74499-44-8	Phosphoric acid, g-w-perfluoro-C8-16-alkyl esters, compds. With diethanolamine (TSCA, NDSL)Phosphates de g-w-perfluoro-C8-16-alkyle, composes prepares avec le 2,2'-iminodiethanol (French) (NDSL)Phosphoric acid, g-w-perfluoro-C8-16-alkyl esters, compounds	6-14	Fluoro phosphate
85631-54-5	2-Propenoic acid, g-w-perfluoro-C8-14-alkyl esters (DSL, EINECS, AICS)Acide propene-2 oique, esters de g-w-perfluoro-alkyles en C8-14 (French) (DSL, EINECS)2-Propensaure, g-w-Perfluor-C8-14-alkylester (German) (EINECS)acido 2-propenoico, g-w-perfluoro-C8-	6-12	Fluoro urethane
86508-42-1	Perfluoro compounds, C5-18 (TSCA, DSL, AICS)Composes perfluores en C5-C18 (French) (DSL)DEFINITION:An inert fluid composed of a complex combination of organic compounds resulting from the distillation of electrochemically fluorinated organic compounds. I Telomer B-blocked isocyanat polymer Telomer B acrylate polymer Telomer B acrylate polymer	5-18	Partial perfluoro and miscellaneous perfluoro

## Contacts

## Annex 2

These personal contacts have contributed with useful information on meetings, on telephone or e-mail.

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## Word list

AFFF	Aqueous film-forming foam
CAS nummer	Number series from Chemical Abstract Service
CMR	Carcinogenic, Mutagenic, toxic for Reproduction
LRTAP	Long-Range Transboundary Air Pollution convention
OECD	Organisation for Economic Cooperation and Development
OSPAR	Oslo-Paris convention
PBT	Persistent, Bioaccumulative, Toxic
POPs	Persistent Organic Pollutants
REACH	Registration, Evaluation and Authorisation of Chemicals
SNUR	Significant New Use Rule
US EPA	Environmental Protection Agency, USA
vPvB	very Persistent very Bioaccumulative



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