Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances

Part of the LOUS-review

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Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances

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Preface

Background and objectives
The Danish Environmental Protection Agency’s List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of specific concern due to the actual consumption in Denmark and for which the use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (DEPA, 2011) includes 40 chemical substances and groups of substances which have either been classified as dangerous or identified as problematic due to other concerns. The criteria employed by the Danish EPA for inclusion of substances on the list include:

- Properties of concern according to the EU ‘List of hazardous substances’;
- Properties of concern identified using computer-based model calculations outlined in the Danish EPA’s ‘Advisory list for self-classification of dangerous substances’ (the Self-classification list);
- PBT/vPvB substances as identified by the EU;
- Substances on the EU ‘Priority list of substances for further evaluation of their role in endocrine disruption’.

Furthermore a tonnage threshold has been used. Substances used in quantities exceeding 100 tons per year in Denmark and fulfilling any of the abovementioned criteria have been included in LOUS 2009. For substances which are the subject of special focus in Denmark, the tonnage threshold can however be different.

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure and information regarding ongoing activities under REACH among others.

The Danish EPA will on the basis of the surveys assess the need for any further regulation, substitution/phase out, classification and labelling, improved waste management, development of new knowledge or increased dissemination of information.

This survey concerns PFOA and PFOS-related compounds which constitute one of the 40 substances/substance groups, introduced on the List of Undesirable Substances (LOUS) of the Danish EPA in 2004. The entry in LOUS for these substances is “PFOA and PFOS compounds” and the group of substances is indicated to include at least 175 substances listed in a 2008 survey fluorinated substances in impregnated consumer products and impregnating agents (Jensen et al., 2008). The 175 substances referred to in this report are in the substances group “Perfluorooctane sulfonate (PFOS) and related compounds” from the 2006 OECD list (OECD, 2006). The reason for including the PFOA and PFOS compounds is that they are all potentially degradable to substances which have proven to be persistent and which have been measured in human and animal blood. Furthermore, the substances are indicated to be included in the lists because they are toxic to animals.

As mentioned above, the main objective of this study is to provide background for the Danish EPA’s consideration regarding the need for further management measures. The survey includes substances which may not be considered “PFOA and PFOS compounds”; one of the objectives is also to pro-
vide a background for a more specific description of the substance group with a clear definition of which substances are included in the group.

Organisation of the survey
The survey has been undertaken by COWI A/S in cooperation with NIPSECT and BIPRO from June to November 2012. The work has been followed by an advisory group consisting of:

- Louise Grave-Larsen, Lea Stine Tobiassen and Mikkel Aaman Sørensen, Danish EPA
- Ulla Hansen Telcs, Confederation of Danish Industry
- Nanna Rosted Vind, Danish Working Environment Authority
- Saoirse Eriksen, Danish Veterinary and Food Administration
- Allan Astrup Jensen, NIPSECT
- Carsten Lassen, COWI A/S

Data collection
The survey and review is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors.

During summer 2012 available literature, relevant legislation and regulatory activities in the pipeline, and statistics was searched using search strings or CAS numbers covering the different groups of perfluorinated and polyfluorinated substances. Data was mainly searched via the Internet on websites of relevant organisations and databases. The data search included (but was not limited to) the following:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA’s website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention.
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHAs website;
- Data on ecolabels from the Danish ecolabel secretariat (Nordic Swan and EU Flower) and the German Angel.
- Pre-registered and registered substances from ECHA’s website;
- Production and external trade statistics from Eurostat’s databases (Prodcom and Comext);
- Export of dangerous substances from the Edexim database;
- Data on production, import and export of substances in mixtures from the Danish Product Register (confidential data, not searched via the Internet);
- Date on production, import and export of substances from the Nordic Product Registers as registered in the SPIN database;
- Information from Circa on risk management options (confidential, for internal use only, not searched via the Internet)
- Monitoring data from the National Centre for Environment and Energy (DCE), the Geological Survey for Denmark and Greenland (GEUS), the Danish Veterinary and Food Administration, the European Food Safety Authority (EFSA) and the INIRIS database.
- Waste statistics from the Danish EPA;
- Chemical information from the ICIS database;
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of:
  - The Nordic Council of Ministers, ECHA, the EU Commission, OECD, IARC, IPCS, WHO, OSPAR, HELCOM, and the Basel Convention;
- Environmental authorities in Norway (Kliif), Sweden (Kemi and Naturvårdsverket), Germany (UBA), UK (DEFRA and Environment Agency), the Netherlands (VROM, RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature.
- US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada.
  - PubMed and Toxnet databases for identification of relevant scientific literature.

Besides, direct enquiries were sent to Danish and European trade organisations and a few key market actors in Denmark.
Summary and conclusion

Over the period 2012-2015, all 40 substances and substance groups on The Danish Environmental Protection Agency’s List of Undesirable Substances (LOUS) will be surveyed and reviewed and the Danish EPA will assess the need for any further regulation on the basis of the results, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and related compounds, which were introduced in LOUS in 2004. The entry in LOUS for these substances is “PFOA and PFOS compounds” and the group of substances is indicated to include at least 175 substances listed as “perfluorooctane sulfonate (PFOS) and related compounds” in the first list of perfluorinated and polyfluorinated compounds published by the OECD. This survey addresses all perfluoroalkylated substances and substances that may degrade into perfluoroalkylated substances i.e. substances beyond what is considered “PFOA and PFOS compounds”.

The survey addresses three groups of substances:

- perfluoroalkyl substances with a chain of fully fluorinated carbon atoms (= perfluorinated);
- fluorotelomers and other polyfluoroalkyl substances where the carbon chain is not fully fluorinated, but the substances still contain a perfluorinated moiety (part of the molecule), and
- side-chain-fluorinated polymers with side-chains that contain a perfluorinated moiety.

The substances will collectively be referred to as PFCs, but should not be confused with the fluorocarbon greenhouse gases with the same abbreviation. The side-chain-fluorinated polymers differ from fluoropolymers such as polytetrafluoroethylene (e.g. Teflon®) which have fluorine directly attached to the carbon backbone and are beyond the scope of this survey.

The substance group is highly diverse; more than 600 substances from this group are pre-registered under REACH. Many side-chain-fluorinated polymers are not pre-registered because they are exempt from registration under REACH. The substances differ as to the length of the perfluorinated moiety and the functional groups attached to the carbon chain having influence on the fate of the substances in the environment and the potential health and environmental effects of the substances and their degradation products. The substances are partly degraded into the basic perfluoroalkyl acids in the environment, and the substances have been grouped by the OECD into categories based on the substances that they can degrade into; e.g. one group consists of substances that may degrade into perfluorooctane sulfonic acid (PFOS).

A distinction is made between long-chain perfluorinated compounds and short-chain perfluorinated compounds, based on the toxicity and bioaccumulation differences between the two groups. According to the OECD “Long-chain perfluorinated compounds” refers to:

- perfluorocarboxylic acids with carbon chain lengths C8 (with eight carbons in the chain) and higher, including PFOA;
- perfluoroalkyl sulfonates with carbon chain lengths C6 and higher, including PFOS and perfluorohexane sulfonic acid (PFHxS), and
- precursors of these substances that may be produced intentionally or are present as impurities in products.
PFOS and other long-chain perfluoroalkyl sulfonates

PFOS and substances that can degrade into PFOS have traditionally been the substances of most concern. Until 2000, PFOS and derivatives were the main PFCs produced, but from 2000 to 2003 the production of these substances dropped dramatically; currently, global production stands at a fraction of the peak production in 2000. PFOS is, however, still the PFC found in the highest concentration in municipal waste water, in environmental samples of surface water, sediments and biota, in food, and in human blood and breast milk. The concentration in blood and milk has decreased significantly since 2000. The fact that PFOS is still present in high concentrations in the environment reflects partly that the substance is persistent, partly that significant quantities are still accumulated in articles in use in society.

The main dietary intake of PFOS is in fish whereas it for other PFC is more even distributed among food groups. The European Food Safety Authority (EFSA) concluded in 2012 that the intake with food is well below the tolerable daily intake (TDI). EFSA notes that the uncertainty on the assessment is particular high for children younger than 1 year, due to a lack of dietary surveys reporting consumption data for this age group. Sources other than food may contribute significantly to the total human exposure, but reviews of total intake indicate that for adult in the general population the total intake is still well below the TDI. The same is indicated for children, but in this case there are some reservations because the exposure situation of children is not well understood. The TDI is based on animal studies and is under debate.

Population studies have discovered positive associations between serum levels of perfluoroalkylated acids (PFAA) and uric acid levels, thyroid disease, overweight, insulin- and leptin levels, and Chronic Kidney Disease (CKD), which is a major public health problem with increased prevalence. An investigation of children from Faroe Island in the Atlantic showed that commonly prevalent exposures to PFAAs were associated with lower antibody responses to childhood immunizations (vaccinations). The immune system seems to be highly sensitive to PFAAs, and various immune parameters were affected at levels which are found in exposed human populations.

PFOS and four derivatives have a harmonised classification as carcinogenic, toxic to reproduction and acutely toxic.

PFOS and derivatives are included in the list of restricted substances under the Stockholm Convention on persistent organic pollutants with some specific exemptions and acceptable purposes and are in the EU restricted via Annex XVII of REACH with a few specific exemptions. As part of their revised implementation plans for the Stockholm Convention from 2012, both Denmark and the European Commission have prepared an action plan for reduction of the remaining uses and emissions of PFOS.

The current uses of PFOS and derivatives for exempt application in the EU and Denmark are well described. Data from the Danish Product Register show that six of the registered substances are included in the OECD category of substances that may degrade to PFOS. The total registered production and import was 0.52 t/y. The known consumption for exempt applications, process chemical in hard chromium plating, is only about 0.02 t/y. The data from the Product Register indicates significant consumption of PFOS for applications which are most likely restricted, but it is unclear to what extent it is due to inadequate update of the notifications to the register.

One of the main issues regarding PFOS in Denmark is the presence of PFOS in articles still in use in society. The waste situation for PFOS is well described both at EU-level and in Denmark. The majority of the solid waste containing PFOS and other PFCs in Denmark is disposed of to municipal solid waste incinerators, but it is not known to what extent the substances are destroyed at the temperatures used these waste incinerators. Limited data are available on the destruction efficiency.
under the actual conditions in the incinerators. More studies are needed to clarify whether it would be necessary to dispose of PFOS-containing waste to hazardous waste incinerators in order to comply with the requirements of the Stockholm Convention.

PFOS derivatives were used in fire-fighting foam before restrictions were put in place, and cases have been observed of soil, surface water and groundwater having been contaminated with PFOS, PFOA and other PFCs at fire drill sites. The extent of the soil contamination with PFOS and PFOA in Denmark is not known; it is planned that an investigation will be launched under the Danish technology programme to examine soil and groundwater contamination. A study of releases of PFOS and PFOA to the Baltic Sea estimated that the majority of the PFOS releases were a consequence of the former use of fire-fighting foam.

A recent Danish risk evaluation of perfluorinated compounds in sewage sludge concludes that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystems where the sludge is applied and that more information on the fate and effects of PFCs in soil is needed.

Perfluorohexane sulfonate (PFHxS) is the PFOS homologue with a 6-carbon chain. Due to its toxicological profile it is considered among the long-chain perfluoroalkane sulfonates. The substance has been detected in waste water, environmental samples, food, human blood and breast milk, but in lower concentrations than PFOS. No information on its use in the EU has been identified, and the substance is not registered in the Danish Product Register. The sources and pathways of PFHxS in the environment are not known. The substance is not regulated or addressed in the registry of intentions under REACH.

**PFOA and other long-chain perfluoroalkyl carboxylic acids**

The uses of PFOA and other long-chain perfluoroalkyl carboxylates and their precursors, fluoroteflomers, are not restricted in the EU. These substances do not have a harmonised classification in the EU. A proposal for identifying PFOA and its salt APFO as Substances of Very High Concern (SVHC) under REACH due to CMR properties is under way and a harmonised classification of two other substances have been proposed. Furthermore, Annex XV dossiers proposing four other long-chain perfluoroalkyl carboxylic acids as SVHCs due to PBT properties have been submitted, and for two other long-chain perfluoroalkyl carboxylic acids, a harmonised classification as toxic to reproduction is in the pipeline. PFOA and other long-chain perfluorinated carboxylic acids and their salts are all extremely persistent in the environment and they bioaccumulate in particular in mammals and birds.

PFOA, like PFOS, is found in measureable concentrations in municipal waste water, in environmental samples of sediments and biota, in food and in human blood and human milk. The concentrations are in general lower than the concentrations of PFOS (typically 2-5 times lower). According to a HELCOM assessment, the risks of PFOA on the Baltic marine environment are currently difficult to assess due to the lack of ecotoxicological information; and consequently the predicted no effect concentration (PNEC) has not been comprehensively assessed.

EFSA concludes in the 2012 assessment that the total intake of PFOA with food for all age classes and for both average- and high-intake consumers is far below the tolerable daily intake (TDI). Reviews of total exposure from all sources indicate that intake with house dust may be of the same magnitude as the intake with food, but the total intake is still well below the TDI. Studies from several countries have demonstrated a decrease in the concentrations of both PFOS and PFOA in blood and breast milk for the period 2000-2010 while some studies have demonstrated a concurrent increase in the levels of other perfluoroalkyl substances such as PFBS, PFHxS, PFNA and PFDA.

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1 CMR: Carcinogenic, mutagenic or toxic to reproduction (human health effects). PBT: Persistent, bioaccumulative and toxic to organisms in the environment (environmental effects)
PFOA and PFNA (with one carbon more than PFOA) are mainly used as polymerisation aids in the manufacture of fluoropolymers such as polytetrafluoroethylene. Concerns is related to emissions from production processes and residual content of PFOA in the final articles. In the USA, the US EPA has initiated the PFOA Stewardship Program with the eight major companies in the industry (including some European companies) which target PFOA, precursor chemicals and higher homologue chemicals. The industry has committed voluntarily to reduce global facility emissions and product content on a global basis by 95 percent no later than 2010, and to work toward eliminating emissions and product content of these chemicals by 2015. The main alternatives are C6-fluorotelomers.

The use of PFOA in the EU and the emissions from its use are well described. The substance is mainly used in the EU for manufacture of fluoropolymers. In the Danish Product Register the total registered consumption of PFOA and substances that may degrade to PFOA was 1 kg/y. Virtually no information is available on the use of other long-chain perfluoroalkyl carboxylic acids at EU level. The Annex XV dossiers for long-chain PFCAs recently submitted concludes that the substances may be used to some extent on the basis of data demonstrating that the substances can be found in the environment. The current registrations under REACH provides very limited information on the actual consumed volumes of the PFCs as most substances are manufactured or imported in tonnages below 1,000 tonnes an consequently not registered yet.

A number of substances may serve as precursors for PFOA in the environment and for human exposure to PFOA by transformation, degradation or metabolism. Examples of those precursors are long-chain fluorotelomer alcohols (e.g. 8:2 FTOH), perfluorinated phosphonic acids and fluorotelomer-based side-chain fluorinated polymers (further described in the following). These precursors may be present in a wide range of consumer products, such as impregnated clothing and carpets. On the basis of reviews of the literature it has been concluded that FTOHs represented only a negligible contribution (<1%) to the PFOA exposure of adults. An assessment of sources of PFOA to the Baltic Sea estimated with high uncertainty that 30% of the releases were due to transformation of fluorotelomers. If this estimate is correct, the precursors may contribute significantly to the intake of PFOA with food. None of the fluorotelomers or side-chained fluorinated polymers has been proposed as Substances of Very High Concern under REACH. However, a proposal for a harmonised classification of 8:2 FTOH as toxic to reproduction has been submitted.

The French Food Safety Agency and the Norwegian Institute of Public Health have evaluated the potential human health risks related to the residual presence of PFOA in non-stick coatings for cookware and concluded that the consumer health risk is negligible. According to the German Federal Institute for Risk Assessment, it has not been shown that consumers are significantly exposed to PFOA and FTOH from clothing fabrics. However, some authors conclude that given the present state of knowledge, it is not possible to say whether the use of nonstick-coated cooking utensils or packaging materials with PFC-based coating lead to a significant increase in dietary PFC intake.

The pathways and substance flows that lead to the presence of PFOA in the environment and human exposure is still not fully understood. The missing information on the actual consumption with consumer products and the fate of the precursors through use and disposal of the articles hinder more certain modelling of the flows.

**Short-chain perfluoroalkyl acids**

According to the industry, the short-chain perfluoroalkyl acids and short-chain fluorotelomers are gradually substituting for the long-chain homologues because the short-chain substances are considered to have a better environmental and health profile.

The PFOS and PFHxS have to some extent been replaced by PFBS (with 4 carbon chain) and the long-chain perfluoroalkyl carboxylic acids and telomers are replaced by short-chain fluorochemicals. No data on actual consumption volumes have been available demonstrating to what extent this
shift has taken place, but data on the concentration of different PFCs in human blood and breast milk indicate a change in the exposure from the long-chain to the short-chain homologues.

The main question is how much better the short-chain substances are as compared to the long-chain substances and to what extent they still may be of concern even if they are better than the long-chain homologues.

The short-chain alternatives are as persistent in the environment as the long-chain homologues, but do not bioaccumulate to the same extent as the long-chain substances, as they are excreted more rapidly from the organisms studied. No data on the ecotoxicity of the shorter chain fluoroalkyl carboxylic and sulfonic acids have been obtained.

Concerning human health the short chain PFASs as compared to the long-chain homologues have significantly shorter half-life in human blood, do not appear to cause developmental toxicity, and have less genotoxicological potential.

**Fluorotelomers and side-chain-fluorinated polymers**

Fluorotelomers and side-chain-fluorinated polymers account for the major part of the present use of PFCs. The fluorotelomers do not have fully fluorinated carbon chains but a part of the chain is perfluorinated and may be degraded to a perfluorinated compound. As an example the fluorotelomer alcohol 8:2 FTOH have a perfluorinated part with 8 carbons (and 2 carbons without fluorine) and may degrade to PFOA and PFNA. The formation of more hazardous transformation products has traditionally been a major concern related to these substances. The substances themselves may, however, also have some environmental and health effects, and a proposal for a harmonised classification of 8:2 FTOH as toxic to reproduction has been submitted.

The world-wide production of fluorotelomers is estimated at 11,000-14,000 t/y. The targets amount is used as intermediates in the production of side-chain-fluorinated polymers but exactly how much is not reported. No exact data on the use in the EU is available, but the side-chain-fluorinated polymers accounted for 77% of the 3.2 t/y PFCs registered in the Danish Product Register. The polymers are used as surfactants for a wide range of applications and the major uses are all-weather clothing and other impregnated textiles, carpets and various coatings on other materials.

As side-chain-fluorinated polymers are polymers, they are exempt from registration under REACH and do in general not appear to have been pre-registered. The status of these polymers under REACH, and particularly side-chain-fluorinated polymers imported from countries outside the EU is not clear. More information on how the use of these substances can be assessed and regulated under REACH is needed.

It has been demonstrated in many studies that a wide range of perfluorinated substances at low concentrations can be extracted from e.g. textiles and packaging treated with side-chain-fluorinated polymers. The releases of substances from the different parts of the life cycle of the substances and the significance of the exposure of humans and the environment is still not fully understood and more information is needed.

**Alternatives**

Alternatives to PFOS for the remaining uses in Denmark were investigated in 2010/2011 and technically feasible alternatives were identified. The environmental properties of these are currently being evaluated by the Danish EPA.

Alternatives to PFOS for the remaining uses world-wide have been assessed in two studies for UNEP Chemicals in the context of the Stockholm Convention.
Alternatives to long-chain PFCs exist for most applications. The technologically best alternatives to long-chain fluorinated chemicals are short-chain chemicals with a carbon chain length of \( \leq C_8 \) for perfluoralkyl carboxylates and \( \leq C_6 \) for perfluoroalkyl sulfonates. The short-chain fluorinated alternatives are as mentioned still rather persistent but much less bioaccumulative and toxic than the long-chain homologues.

In addition some non-fluorinated alternatives, such as siloxanes, propylated aromatics and sulfosuccinates, can be used for specific applications. The non-fluorinated alternatives are in general less persistent and bioaccumulative, but some are toxic.

In general, there is a lack of public data on the properties of the alternatives, partly because the data are protected by commercial secrecy, partly because most scientific research has focused on the polyfluorinated substances.
Sammenfatning og konklusioner

I perioden 2012-2015 vil alle 40 stoffer og stofgrupper på Miljøstyrelsens liste over uønskede stoffer (LOUS) blive kortlagt, og Miljøstyrelsen vil på grundlag af resultaterne vurdere behovet for yderligere regulering, substitution/udfasning, klassificering og mærkning, forbedret affaldshåndtering eller øget udbredelse af information.

Denne undersøgelse vedrører perfluorocctansulfonsyre (PFOS), perfluorocctansyre (PFOA) og beslægtede forbindelser, som blev opført på LOUS i 2004. Betegnelsen i LOUS for disse stoffer er "PFOA og PFOS forbindelser" og gruppen af stoffer er angivet at omfatte mindst 175 stoffer, der er indeholdt i gruppen "perfluorocctansulfonat (PFOS) og beslægtede forbindelser" i den første liste over perfluorerede og polyfluorerede forbindelse, som blev udgivet af OECD. Denne undersøgelse omfatter alle perfluoralkyloster og stoffer, der kan nedbrydes til perfluoralkyloster dvs. også stoffer, som ikke vil være omfattet af betegnelsen "PFOA og PFOS forbindelser".

Undersøgelsen vedrører tre grupper af stoffer:

- perfluoralkyloster med en kæde af kulstofatomer, hvor alle brintatomer er erstattet af fluor (= perfluorerede stoffer);
- fluortelomerer og andre polyfluoralkyloster, hvor der ikke sidder fluoratomer på alle kulstofatomer, men hvor stofferne stadig indeholder en del hvor kulstofkæden er perfluoreret, og
- sidekæde-fluorerede polymerer, som er polymerer der er forsynet med sidekæder, der indeholder en perfluoreret del.


Stofgruppen er meget varieret; der er mere end 600 stoffer fra denne gruppe, som er præregistrerede under REACH. Der er mange sidekæde-fluorerede polymerer, der ikke er ikke præregistrerede, fordi de er fritaget for registrering under REACH. Stofferne er forskellige med hensyn til længden af den perfluorerede del, og de funktionelle grupper afhænger af kulstofkæden og dette har indflydelse på skæbnen af stofferne i miljøet og de potentielle sundheds- og miljømæssige effekter af stofferne og deres nedbrydningsprodukter. Stofferne bliver i miljøet delvist nedbrudt til de basale perfluoralkylsyrer, og stofferne er af OECD inddelt i kategorier baseret på deres potentielle nedbrydningsprodukter; eksempelvis er der en kategori, der består af stoffer, der kan nedbrydes til perfluorocctansulfonsyre (PFOS).

Der skelnes mellem langkædede perfluorerede forbindelser og kortkædede perfluorerede forbindelser, baseret på forskelle i toksicitet og bioakkumulering mellem de to grupper. Ifølge OECD henviser betegnelsen "langkædede perfluorerede forbindelser" til:
• perfluorcarboxylsyrer med C8 kulstofkædelængder (med otte kulstofatomer i kæden) og højere, herunder PFOA;
• perfluoralkylsulfonater med kulstofkædelængder C6 og højere, herunder PFOS og perfluorohexansulfonsyre (PFHxS), og
• forstadier (precursere) af disse stoffer, der enten fremstilles tilsigtet, eller er til stede som urenheder i produkterne.

PFOS og andre langkædede perfluoralkylsulfonater


Fisk udgør det vigtigste bidrag til PFOS i kosten, mens indtaget af andre PFC’er er mere jævnt fordelt på fødevaregrupper. Den Europæiske Fødevaresikkerhedsautoritet (EFSA) konkluderede i 2012, at indtaget med fødevarer er et godt stykke under det tolerable daglige indtag (TDI). EFSA bemærker dog, at usikkerheden på denne vurdering er særlig høj for børn under 1 år, på grund af manglende kostundersøgelser for denne aldersgruppe. Andre kilder end fødevarer kan bidrage væsentligt til den samlede ekspONering af mennesker, men opgørelser af det samlede indtag viser, at for voksne i den almenebefolkning er det samlede indtag stadig et godt stykke under TDI. Det samme viser beregninger i relation til børn, men i dette tilfælde er der nogle forbehold, fordi eksponerings situationen for børn ikke er velbeskrevet.

PFOS og fire derivater har en harmoniseret klassificering som kræftfremkaldende, reproduktions toksiske og akut giftige.

TDI’en er baseret på dyreforsøg og er under debate. Befolkningsundersøgelser har vist positive sammenhænge mellem niveauer af perfluoralkylsyrer (herunder PFOS og PFOA) i blodserum og urinsyre i blodet, sygdomme i skjoldbruskkirtlen, overvægt, insulin- og leptin-niveauer samt kronisk nyrersygdom (CKD), som er et stort problem for folkesundheden og med en øget udbredelse. En undersøgelse af børn fra Færøerne viste, at almindeligt forekommende ekspONeringer for perfluoralkylsyrer var forbundet med lavere antistofrespons over for vaccinationer mod børnesygdomme. Immun systemet synes at være meget følsomt over for perfluoralkylsyrer, og forskellige immunparametre blev påvirket ved niveauer, som findes i udsatte befolkningssyper.

PFOS og deriverer er medtaget på listen over stoffer underlagt begrænsninger i henhold til Stockholm konventionen om persistente organiske miljøgifte med nogle specifikke undtagelser og acceptable formål. Stofferne er desuden i EU begrænset bilag XVII til REACH med nogle få specifikke undtagelser. Som en del af deres reviderede implementeringsplaner for Stockholmkonventionen fra 2012, har både Danmark og EU-Kommissionen udarbejdet en handlingsplan for reduktion af de resterende anvendelser og emisjoner af PFOS.

De nuværende anvendelser af PFOS og deriverer til anvendelser undtaget i EU og Danmark er velbeskrevne. Data fra det danske Produktregister viser, at seks af de registrerede stoffer indgår i OECD kategorien af stoffer, der kan nedbrydes til PFOS. Den samlede registrerede produktion og import var 0,52 t/år. Det kendte forbrug fra anvendelser undtaget fra begrænsning, - som proces kemikalier i hårdforskromning - er kun omkring 0,02 t/år. Data fra Produktregistret viser et betydeligt forbrug af PFOS til anvendelser, der mest sandsynligt er omfattet af anvendelsesbegrænsningen,
men det er uklart, i hvilket omfang det skyldes utilstrækkelig opdatering af indberetningerne til registret.

Et af de vigtigste spørgsmål vedrørende PFOS i Danmark er tilstedeværelsen af PFOS i artikler, som stadig er i brug i samfundet. Affaldssituationen for PFOS er velbeskrevet både på EU-plan og i Danmark. Hovedparten af det faste affald, der indeholder PFOS og andre PFC'er, bliver i Danmark bortskaffet til kommunale affaldsforbrændingsanlæg, men det vides ikke, i hvilken grad stofferne destrueres ved de temperaturer, der anvendes i de disse affaldsforbrændingsanlæg. Begrænsede data er tilgængelige vedrørende destruktionsvejeflyktigheden under de faktiske forhold i forbrændingsanlæggen. Flere undersøgelser er nødvendige for at afklare, om det ville være nødvendigt, at bortskaffe PFOS-holdigt affald til forbrændingsanlæg for farligt affald for at kunne opfylde kravene i Stockholmkonventionen.

PFOS-derivater blev anvendt i brandslukningsskum før restriktionen blev indført, og der er fundet tilfælde, hvor overfladevand og grundvand er blevet forurenet med PFOS, PFOA og andre PFC'er på brandøvelsespladser. Omfanget af jordforureningen med PFOS og PFOA i Danmark er ikke kendt, og det er planlagt, at igangsætte et udredningsprojekt under teknologipuljen for jord- og grundvandsforurening. En undersøgelse af udledninger af PFOS og PFOA til Østersøen har anslået, at hovedparten af udledningerne af PFOS var en konsekvens af den tidligere anvendelse af brandslukningsskum.

En nyere dansk risikovurdering af perfluererede forbindelser i spildevandsslam konkluderer, at de aktuelle niveauer af PFOS i dansk slam kan udgøre en langsigtet risiko for økosystemerne i den jord hvor slammet anvendes, og at yderligere oplysninger om skæbene og effekter af PFC'er i jord er nødvendig.

Perfluorhexansulfonat (PFHxS) er en PFOS homolog med en kulstofkæde på 6 kulstofatomer. På grund af sin toksikologiske profil anses stoffet at være blandt de langkædede perfluoralkansulfonater. Stoffet er fundet i spildevand, miljøprøver, mad, humant blod og moderfoder, men i lavere koncentrationer end PFOS. Der er ikke fundet oplysninger om anvendelsen af stoffet i EU og stoffet ikke er registreret i det danske Produktregister. Kilderne til PFHxS i miljøet og spredningsvejene er ikke kendt. Stoffet er ikke reguleret og der er ikke registreret intentioner om yderligere tiltag under REACH.

PFOA og andre langkædede perfluoralkylcarboxylsyre

Anvendelser af PFOA og andre langkædede perfluoralkylcarboxylater og deres forstadier, fluortelomerer, er ikke begrænsede i EU. Disse stoffer har ikke en harmoniseret klassificering i EU. Et forslag om at betragte PFOA og dets salt APFO som særligt problematisk stof (SVHC) under REACH på grundlag af deres CMR-egenskaber er på vej, og en harmoniseret klassificering af de to stoffer er blevet foreslået. Desuden er der udarbejdet bilag XV dossier, som foreslår fire andre langkædede perfluoralkylcarboxylsyre som særligt problematiske stoffer på grund af PBT-egenskaber, og for to andre langkædede perfluoralkylcarboxylsyre, er et forslag om harmoniseret klassificering som reproduktionstoksisk i støbeskeen. PFOA og andre langkædede perfluoralkylcarboxylsyre og deres salte er alle meget persistente i miljøet og de bioakkumulerer især hos pattedyr og fugle.

PFOA, kan ligesom PFOS, findes i målbare koncentrationer i kommunalt spildevand, i prøver af sedimenter og organismer i miljøet, i fødevarer og i humant blod og mælk. Koncentrationerne er generelt lavere end koncentrationerne af PFOS (typisk 2-5 gange lavere). Ifølge en HELCOM vurdering er risici af PFOA for havmiljøet i Østersøen i øjeblikket vanskelige at vurdere på grund af mangel på data om stofferens økotoksikologi, og nul-effekt koncentrationen (PNEC) er ikke blevet grundigt vurderet.

2 CMR: kræftfemkaldende, mutagnet eller reproduktionstoksisk
3 PBT: Persistent, bioakkumulerbart og toksisk i vandmiljø
EFSA konkluderer i en vurdering fra 2012, at det samlede indtag af PFOA med fødevarer hos alle aldersklasser og for mennesker med både gennemsnitligt og højt indtag er langt under det tolerable daglige indtag (TDI). Opgørelser af den samlede eksponering fra alle kilder indikerer, at indtagelse med husstov kan være af samme størrelsesorden som indtagelse med fødevarer, men det samlede indtag er stadig et godt stykke under TDI. Undersøgelser fra flere lande har vist et fald i koncentrationen af både PFOS af PFOA i blod og modermælk for perioden 2000-2010, mens nogle undersøgelser har vist en samtidig stigning i koncentrationen af andre perfluoralkylstoffer som eksempelvis PFBS, PFHxS, PFNA og PFDA.

PFOA og PFNA (med et kulstof mere end PFOA) anvendes hovedsagelig som hjælpemiddel ved fremstilling af fluoropolymerer, såsom polytetrafluorethylen (PTFE). Emissioner fra produktionsprocesser og restindhold af PFOA i de færdige artikler har vakt bekymring. I USA har den amerikanske miljøstyrelse indledt et samarbejde (PFOA Stewardship Program) med de otte største virksomheder i industrien (herunder nogle europæiske virksomheder) vedrørende PFOA, stoffer der nedbrydes til PFOA og perfluoralkylcarboxylsyrer med længere kædelængder. Virksomhederne har forpligtet sig til på frivillig basis at reducere de globale emissioner fra produktionsenheder og reducere indholdet af stofferne i produkter med 95 % senest i 2010, og at arbejde hen imod helt at fjerne emissioner og indhold af disse kemikalier i 2015. De vigtigste alternativer er C6-fluortelomerer.

Brugen af PFOA i EU og emissionerne fra dets anvendelse er velbeskrevet. Stoffet anvendes i EU hovedsageligt til fremstilling af fluoropolymerer. I Produktregistret er det samlede registrerede forbrug af PFOA og stoffer, der kan nedbrydes til PFOA på 1 kg/år. Der er stort set ingen oplysninger om brugen af andre langkædede perfluoralkylcarboxylsyrer på EU-plan. De bilag XV dossier for langkædede PFCA-er, der for nylig er blevet udarbejdet, konkluderer på grundlag af data, der viser, at stofferne kan findes i miljøet, at stofferne må blive anvendt i en vis udstrækning. De nuværende registeringer under REACH indeholder meget få oplysninger om de faktiske forbrugte mængder af PFOC'er, da de fleste stoffer fremstilles eller importeres i mængder under 1.000 tons og derfor ikke er registrerede endnu.

En række stoffer kan være forstadiet til PFOA i miljøet og give anledning til eksponering af mennesker via transformation, nedbrydning eller metabolisme. Eksempler på disse forstadi er langkædede fluoralkoholer, perfluorerede phosphonsyrer og fluoralkylbaserede polymere (yderligere beskrevet i det følgende). Disse forstadi kan findes i en lang række forbrugerprodukter, såsom imprægneret tøj og tæpper. På grundlag af en gennemgang af litteraturen er det konkluderet, at FTOH'er kun kan udføre et mindre stort bidrag (1%) til den samlede PFOA eksponering af voksne. En vurdering af kilder til PFOA i Østersøen anslår, at 30% af udslippene skyldtes transformation af fluoralkylcarboxylsyrer. Hvis dette skøn er korrekt, kan forstadiene bidrage signifikant til indtagelse af PFOA med fødevarer. Der er ingen fluoralkylbaserede polymere, der er foreslået som om særligt problematiske stoffer (SVHC) under REACH. Der er imidlertid udarbejdet et forslag til en harmoniseret klassificering af 8:2 FTOH som reproductionstoxic.

Det franske agentur for fødevarerisikkerhed og det norske Institut for Folkesundhed har vurderet den potentielle helbredesrisiko i forbindelse med tilbageværende mængder af PFOA i slip-belægninger på kogeredskaber og har konkluderet, at den sundhedsmæssige risiko for forbrugeren er ubetydelig. Ifølge det tyske Institut for Risikovurdering (BfR), er det ikke blevet påvist, at forbrugere i betydelig grad udsættes for PFOA og FTOH fra tekstiler. Nogle forskere konkluderer dog, at det på grundlag af den aktuelle viden, ikke er muligt at sige, hvorvidt brugen af kogegrej med slip-belægninger eller emballagematerialer med PFC-baseret belægning kan føre til en væsentlig stigning i indtag af PFC'er med kosten.
Spredningsveje og stofstrømme, der giver anledning til PFOA i miljøet og eksponering af menneskers stadig ikke fuldt forstået. Den manglende viden om det faktiske forbrug forbundet med forbrugerprodukter og om skæbnen af de stoffer, der kan nedbrydes til PFOA ved anvendelse og bortskaffelse af artikler, begrænser en mere sikker modellering af stofstrømmene.

**Kortkædede perfluoroalkylsyrer**

Ifølge industrien er de kortkædede perfluoroalkylsyrer og kortkædede fluorotelomerer gradvist ved at erstatte de langkædede homologer, fordi de kortkædede stoffer anses for at have en bedre miljø- og sundhedsprofil.

PFOS og PFHxS er til en vis grad blevet erstattet af PFBS (med en kæde på 4 kulstofatomer) og de langkædede perfluoralkylcarboxylsyrer og fluorotelomerer er erstattet af kort-kædede fluorkemikalier. Data om de faktiske forbrugsmængder, som kunne vise i hvilken grad dette skift har fundet sted, har ikke været tilgængelige, men data om koncentrationen af forskellige PFC i humant blod og modernært indikerer en ændring i eksponering fra langkædede til kortkædede homologer.

Det vigtigste spørgsmål er, hvor meget bedre de kortkædede stoffer er sammenlignet med de langkædede stoffer, og i hvilket omfang de stadig kan give anledning til bekymring, selv om de er bedre end de langkædede homologer.

De kortkædede alternativer er ligeså persistente i miljøet som de langkædede homologer, men de bioakkumuleres ikke i samme omfang som de langkædede stoffer, idet de udskilles hurtigere fra de undersøgte organismer. Der er ikke fundet data om økotoksicitet af de kortkædede perfluoroalkylcarboxylsyrer og -sulfonsyrer.

Med hensyn til menneskers sundhed har de kortkædede PFASs sammenlignet med de langkædede homologer betydeligt kortere halveringstid i humant blod, de synes ikke at forårsage skader på afkommet og har mindre genotoksikologisk potentiale.

**Fluortelomerer og sidekæde-fluorerede polymerer**

Fluortelomerer og sidekæde-fluorerede polymerer udgør størstedelen af den nuværende anvendelse af PFC'er. Fluortelomerer har ikke en fuldt fluoreret kulstofkæde, men en del af kæden er perfluore-rat og kan nedbrydes til en perfluoreret forbindelse. Som eksempel har fluorotelomeralkoholen 8:2 FTOH en perfluoreret del med 8 kulstofatomer (og 2 kulstofatomer uden fluor) og kan nedbrydes til PFOA og PFNA. Dannelsen af nedbrydningsprodukter, som er farligere end stoffet selv, har traditionelt været en stor bekymring i forbindelse med disse stoffer. Selve stofferne kan dog også have nogle miljø- og sundhedsmæssige effekter, og der er udarbejdet et forslag til en harmoniseret klassificering af 8:2 FTOH som reproduktionsstofskisk.

Den globale produktion af fluorotelomerer er anslået til 11,000-14,000 t/år. Den største del anvendes som mellemprodukter ved fremstilling af sidekæde-fluorerede polymerer, men præcis hvor meget er ikke rapporteret. Der er ingen præcise oplysninger om brugen i EU, men sidekæde-fluorerede polymerer tegnede sig for 77% af de 3,2 t/år PFC'er, der er registreret i Produktregistret. Polymererne bruges som overfladeaktive stoffer til en bred vifte af anvendelser og de store anvendelsesområder er all-weather tøj og andre imprægnerede tekstiler, tæpper og forskellige belægninger på andre materialer.

Da sidekæde-fluorerede polymerer er polymerer, er de fritaget for registrering i henhold til REACH, og de synes i almindelighed ikke at have været præ-registrerede. Status for disse polymerer under REACH, og især for sidekæde-fluorerede polymerer importeret fra lande uden for EU er ikke klar. Der er behov for yderligere viden om, hvordan anvendelsen af disse stoffer kan vurderes og reguleres i henhold til REACH.
Det er i mange undersøgelser blevet påvist, at en lang række perfluorerede stoffer ved lave koncentrationer kan ekstraheres fra f.eks. tekstiler og emballage, som er behandlet med sidekæde-fluorerede polymerer. Afgivelse og udledninger af stoffer fra de forskellige dele af stoffernes livscyklus og betydningen heraf for eksponering af mennesker og miljø er stadig ikke fuldt forstået, og der er behov for mere viden.

**Alternativer**


Alternativer til PFOS for de resterende anvendelser på verdensplan er blevet vurderet i to studier for UNEP Chemicals som en del af arbejdet under Stockholmkonventionen.

Der findes alternativer til de langkædede PFC’er for de fleste anvendelser. De teknisk set bedste alternativer til langkædede fluorerede kemikalier er kortkædede kemikalier med en kulstofkædelængde på ≤ C8 for perfluoralkylcarboxylater og ≤ C6 for perfluoralkylsulfonater. De kortkædede fluorerede alternativer er som nævnt stadig temmelig persistente, men meget mindre bioakkumulerbare og giftige end de langkædede homologer.

Desuden kan nogle ikke-fluorerede alternativer, såsom siloxaner, propylerede aromater og sulfo-succinater, anvendes til specifikke formål. De ikke-fluorerede alternativer er generelt mindre persistente og bioakkumulerende, men nogle af dem er mere giftige.

Der er i almindelighed mangel på offentliggjorte data om alternativernes egenskaber, dels fordi data som oftest er beskyttet af forretningshemmeligheder, og dels fordi det meste af den videnskabelige forskning har fokuseret på de polyfluorerede stoffer.
1. **Introduction to the substance group**

The Danish EPA’s list of undesirable substances includes PFOA and PFOS and their derivatives, but the scope of the present report has been extended to cover more perfluorinated and polyfluorinated chemicals.

Perfluoroalkyl substances, polyfluoroalkyl substances and some types of fluorinated polymers are often collectively designated PFCs, e.g. by the OECD and other international organisations (e.g. in the context of SAICM and ICCM). Unfortunately the same acronym is used for the perfluorocarbon gases in Danish and EU regulatory contexts (e.g. in Commission Regulation (EC) No 1493/2007); consequently, some confusion may occur in using this acronym. In the absence of other acronyms covering all the relevant substances, however, PFCs will be used here in accordance with the use by OECD (2006). The group covers the following substances:

- Perfluoroalkyl and polyfluoroalkyl substances (PFASs) as defined below, and
- Chemicals (including polymers) which contain a perfluoroalkyl moiety attached to other atoms that may not be perfluorinated, and which have potential to transform to produce PFASs.

This survey does not include the following perfluorinated and polyfluorinated substances:

- Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs – another use of the acronym), hydrofluoroethers (HFEs) and other similar substances;
- Other polyfluorinated organic substances without at least two fully fluorinated carbons;
- Inorganic fluoride compounds.

### 1.1 Perfluoroalkyl and polyfluoroalkyl substances

The perfluoroalkyl and polyfluoroalkyl substances have recently been reviewed by Buck *et al.* (2011) who suggest a common terminology, classification and acronyms for the substances and substance groups. The suggested classification and terminology for these substances will be used, and extended as necessary, in this survey.

The entire group of perfluoroalkyl and polyfluoroalkyl substances will collectively be designated PFASs; some authorities and authors of scientific papers use this acronym only for some subgroups e.g. for the perfluoroalkyl substances or for the perfluoroalkyl sulfonates.

A systematic overview of manufactured perfluoroalkyl and polyfluoroalkyl substances is provided in Table 1. The table originates in a systematic overview provided in Buck *et al.* (2011). The table does not include substances which are indicated by Buck *et al.* (2011) as environmental transformation products only. Annex 1 includes a reference list of specific substance abbreviations used in this report with an indication of the chemical name, CAS No, chain length, substance group name and group abbreviation.
Perfluoroalkylated substances
The perfluoroalkylated substances consist of a large group of compounds consisting of a hydrophobic alkyl chain of varying length (typically 4 to 16 carbon atoms) and a fully fluorinated hydrophilic end group, \( F(CF_2)_n \cdot R \). 4

Within the group of perfluoroalkylated substances, the perfluoroalkyl acids (PFAAs) and their salts have been the main focal point for regulatory actions until now. The main subgroups are the perfluorooctane sulfonic acids (PFSAs) and their salts and the perfluoroalkyl carboxylic acids and their salts (PFCAs).

Perfluorooctane sulfonic acid (PFOS) is the most prominent of the perfluorooctane sulfonic acids (PFSAs). PFOS has a linear perfluoroalkyl carbon chain of 8 atoms and a sulfonic acid functional group.

\[
\text{Perfluorooctane sulfonic acid (PFOS)}
\]

PFSAs with shorter chain lengths discussed in this report are perfluorohexane sulfonic acids (PFHxS with a 6-carbon chain) and perfluorobutane sulfonic acid (PFBS with a 4-carbon chain).

Among the perfluoroalkyl carboxylic acids (PFCAs), the most prominent member is perfluorooctanoic acid (PFOA) with an 8-carbon chain. Note that the substance has 7 perfluorinated carbon atoms only. Annex 1 list a number of PFCAs which are named according to the number of carbon atoms in the perfluorinated carbon chain. Some of the substances are commercial products, but many may be transformation products which can be found e.g. in environmental samples or food.

\[
\text{Perfluorooctanoic acid (PFOA)}
\]

A distinction is made between long-chain perfluorinated compounds and short-chain perfluorinated compounds, based on the toxicity and bioaccumulation differences between the two groups (further described in Chapters 0 and 0). According to the OECD (2012), “Long-chain perfluorinated compounds” refer to:

- Perfluorocarboxylic acids with carbon chain lengths of \( C_8 \) and higher, including perfluorooctanoic acid (PFOA);
- Perfluorooalkyl sulfonates with carbon chain lengths of \( C_6 \) and higher, including perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonate (PFOS), and
- Precursors of these substances that may be produced or present in products.

The designation \( C_8, C_6 \), etc. will be used to designate the length of the carbon chain of the perfluoroalkyl moiety (part of the molecule) of the substances and not the total number of carbon atoms of the substance in this context. For the perfluorocarboxylic acids (PFCAs) and their salts, however, by tradition the C number has indicated the number of the carbon chain with the perfluorinated moiety although one of the carbon atoms in fact is not perfluorinated. PFOA, usually described as a \( C_8 \) PFCA, consequently only includes 7 perfluorinated carbons, as shown in the chemical formula above.

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1 Hydrophilic = attracted to and dissolved in water, oil repelling; Hydrophobic = water repelling, prefer non-polar solvents.
<table>
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</tr>
<tr>
<td></td>
<td>Perfluoroalkyl carboxylates</td>
<td>PFCAs</td>
<td>-COO⁻</td>
<td>Sodium perfluorooctanoate (Na-PFOA) Ammonium perfluorooctanoate (APFO) Ammonium perfluorononanoate (APFN)</td>
</tr>
<tr>
<td></td>
<td>Perfluoroalkane sulfonic acids</td>
<td>PFSAs</td>
<td>-SO₃H</td>
<td>Perfluoroctane sulfonic acid (PFOS) Perfluorohexane sulfonic acid (PFHxS) Perfluorobutane sulfonic acid (PFBs)</td>
</tr>
<tr>
<td></td>
<td>Perfluoroalkane sulfonates</td>
<td>PFSAs</td>
<td>-SO₃⁻</td>
<td>Tetrathylammonium perfluorooctane sulfonate (NEt₄-PFOS)</td>
</tr>
<tr>
<td></td>
<td>Perfluoroalkyl phosphonic acids</td>
<td>PFPAs</td>
<td>-(=O)(OH)₂</td>
<td>Perfluoroctyl phosphonic acid (C₈-PFPA)</td>
</tr>
<tr>
<td></td>
<td>Perfluoroalkyl phosphinic acids</td>
<td>PFPIAs</td>
<td>P(=O)(OH)(C₅F₁₁)</td>
<td>Bis(perfluorohexylyl) phosphinic acid (C₆/C₆-PFPIA)</td>
</tr>
<tr>
<td></td>
<td>Perfluoroalkane sulfonyl fluorides</td>
<td>PASFs</td>
<td>-SO₂F</td>
<td>Perfluoroctane sulfonyl fluoride (POSF)</td>
</tr>
<tr>
<td></td>
<td>Perfluoroalkane sulfonamides</td>
<td>FASAs</td>
<td>-SO₂NH₂</td>
<td>Perfluoroctane sulfonamide (FOSA)</td>
</tr>
<tr>
<td></td>
<td>Perfluoroalkanoyl fluorides</td>
<td>PAFs</td>
<td>-COF</td>
<td>Perfluoroctanoyl fluoride (POF)</td>
</tr>
<tr>
<td></td>
<td>Perfluoroalkyl iodides (Telomer A)</td>
<td>PFAIs</td>
<td>-I</td>
<td>Perfluorohexyl iodide (PFHxI)</td>
</tr>
<tr>
<td></td>
<td>N-Alkyl perfluoroalkane sulfonamides</td>
<td>MeFASA, EtFASAs, BuFASAs</td>
<td>-SO₂NH(R') where (R' = C_mH_{2m+1}) ((m = 1,2,4))</td>
<td>N-Methyl perfluoroctane sulfonamidoethanol (MeFOSE) N-Ethyl perfluoroctane sulfonamidoethanol (EtFOSE)</td>
</tr>
<tr>
<td></td>
<td>Perfluoroalkane sulfonamidoethanols and</td>
<td>FASEs, MeASEs,</td>
<td>-SO₂N(R')CH₂CH₂OH where (R' = C_mH_{2m+1}) ((m = 1,2,4))</td>
<td>N-Ethyl perfluorobutane sulfonamidoethanol (EtFBSE) Perfluoroctane sulfonamidoethanol (FOSE)</td>
</tr>
<tr>
<td>Group</td>
<td>Subgroup</td>
<td>Abbreviation</td>
<td>Functional group &amp; Examples</td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------------------</td>
<td>---------------------------------</td>
<td>--------------</td>
<td>-----------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>N-alkylperfluoroalkane sulfonamidoethanols</td>
<td></td>
<td>EtFASEs BuFASEs</td>
<td>$C_nF_{2n+1}R$, where $R = \text{N-alkylperfluoroalkane sulfonamidoethanols}$</td>
<td></td>
</tr>
<tr>
<td>N-Alkyl perfluoroalkane sulfonamidoethyl acrylates and methacrylates</td>
<td></td>
<td>MeFAS(M)ACs EtFAS(M)ACs BuFAS(M)ACs</td>
<td>$\text{-SO}_2\text{N}('R'\text{')CH}_2\text{CH}_2\text{OC}(-\text{O})\text{CH}=\text{CH}_2$ and $\text{SO}_2\text{N}('R'\text{')CH}_2\text{CH}_2\text{OC}(-\text{O})\text{C(CH}_3)=\text{CH}_2$ where $'R' = \text{C}<em>m\text{H}</em>{2m+1}$ (m = 1,2,4)</td>
<td></td>
</tr>
<tr>
<td>Fluorotelomer substances</td>
<td>Semifuorinated n-alkanes and alkenes</td>
<td>SFAs SFAenes</td>
<td>$\text{SFAs}$ SFAsenes $\text{-CH}_2\text{CH}_2\text{H}$ and $\text{-CH}_2\text{CH}('\text{CH}<em>2\text{)}</em>{m-\text{alt}}$, with m = 2–16 and n = 6–16 (Perfluoroctyl)ethane (F₈H₄)</td>
<td></td>
</tr>
<tr>
<td>n:2 Fluorotelomer iodides</td>
<td>n:2 FTIs</td>
<td>-CH₂CHJ</td>
<td>8:2 Fluorotelomer iodide (8:2 FTI)</td>
<td></td>
</tr>
<tr>
<td>n:2 Fluorotelomer olefins</td>
<td>n:2 FTOs</td>
<td>-CH=CH₂</td>
<td>6:2 Fluorotelomer olefin (6:2 FTO)</td>
<td></td>
</tr>
<tr>
<td>n:2 Fluorotelomer alcohols</td>
<td>n:2 FTOHs</td>
<td>-CH₂CH₂OH</td>
<td>4:2 Fluorotelomer alcohol (4:2 FTOH)</td>
<td></td>
</tr>
<tr>
<td>n:2 Fluorotelomer acrylates and methacrylates</td>
<td>n:2 FTACs</td>
<td>-H₂CH₂OC(-O)CH=CH₂ and -CH₂CH₂OC(-O)C(CH₃)=CH₂</td>
<td>6:2 Fluorotelomer acrylate (6:2 FTAC) 6:2 Fluorotelomer methacrylate (6:2 FTMAC)</td>
<td></td>
</tr>
<tr>
<td>n:2 Polyfluoroalkyl phosphoric acid esters, polyfluoroalkyl phosphates, fluorotelomer phosphates</td>
<td>PAPs</td>
<td>(-CH₂CH₂O)ₙP(=O)(OH)ₙ₊, where n = 1 or 2</td>
<td>10:2 Fluorotelomer phosphate monoester (10:2 monoPAP)</td>
<td></td>
</tr>
<tr>
<td>n:2 Fluorotelomer sulfonic acids</td>
<td>n:2 FTSAs</td>
<td>-CH₂CH₂SO₂H</td>
<td>6:2 Fluorotelomer sulfonic acid (6:2 FTSAs)</td>
<td></td>
</tr>
<tr>
<td>n:2 Fluorotelomer sulfonic salts</td>
<td>n:2 FTSAs</td>
<td>-CH₂CH₂SO₂H</td>
<td>6:2 Fluorotelomer sulfonic acid (6:2 FTSAs)</td>
<td></td>
</tr>
<tr>
<td>Miscellaneous</td>
<td></td>
<td></td>
<td>For example: -O(CₙFₘ)OCF₄(p)COOH</td>
<td></td>
</tr>
<tr>
<td>Polyfluoroalkyl ether carboxylic acids and others</td>
<td></td>
<td></td>
<td>4,8-Dioxa-3H-perfluoro-nonanoate</td>
<td></td>
</tr>
</tbody>
</table>
“Precursor” is defined by OECD as a substance that has been recognized as having the potential to degrade to perfluorocarboxylic acids with carbon chain lengths of C8 and higher (including PFOA) or perfluoroalkyl sulfonates with a carbon chain length of C6 of higher. Please note the difference in chain length between the long-chain perfluorocarboxylic acids and the long-chain perfluoroalkyl sulfonates.

The fact that e.g. PFOS and PFOA can be formed by degradation/transformation of other PFASs with similar perfluorinated chain lengths influences the way the substances are currently restricted. The restriction consequently may go across the different substance groups, but specifically address substances with a similar chain length.

As an example PFOS and related substances have been restricted in the EU since 2006 and the substances have recently been included in the list of restricted substances under the Stockholm Convention as further described in the next chapter. The restriction in the EU is currently covered by the POPs Regulation, but until 2011 was included as entry 53 of Annex XVII to the REACH Regulation with a similar definition of covered substances. The substance group is defined as all substances with the chemical formula C₈F₁₇SO₂X where X = OH (PFOS itself), metal salt (O-M⁺), halide, amide, and other derivatives including polymers. These substances are C8 substances within the following substance groups: perfluoroalkane sulfonic acids, perfluoroalkane sulfonates, perfluoroalkane sulfonyl halides, perfluoroalkane sulphonamides and perfluoroalkane sulfonamido substances, as shown in Table 1. Furthermore, the group includes side-chain-fluorinated polymers with C₈F₁₇SO₂⁻ groups attached to the carbon backbone (further discussed in section 1.2).

Other perfluoroalkyl and polyfluoroalkyl substances

Table 1 includes a number of other groups of perfluoroalkyl substances which are mainly used as raw materials for surfactant and surface protection products: perfluoroalkane sulfonyl fluorides, perfluoroalkane sulphonamides, perfluoroalkanoyl fluorides, perfluoro alkyl iodides and perfluoroalkane sulphonamido substances (PFAAs).

The PFAAs can be degraded to perfluoroalkyl sulfonates. Most attention has been given to the aerobic biotransformation of the perfluoroalkane sulphonamido derivatives having 8 perfluorinated carbon atoms, in particular N-ethyl perfluorooctane sulphonamidoethanol (EtFOSE) and n-methyl perfluorooctane sulphonamidoethanol (MeFOSE), which are ultimately degraded to PFOS.

The main product group of polyfluoroalkyl substances are the fluorotelomers. Fluorotelomers have non-fluorine substituted hydrogen atoms (a CH₂-CH₂ group) in between the perfluorinated carbon chain and the functional group. Fluorotelomers are produced with a variety of functional groups including alcohols, sulphonamides, sulphonamidoethyl acrylates and methacrylates, and sulphonamido acetic acids.

For the naming of the fluorotelomers, a notation is used indicating the length of the perfluorinated carbon chain and the length of the chain with non-substituted hydrogen atoms. Below is a 10:2 fluorotelomer phosphate monoester (10:2 monoPAP) with 10 fully fluorinated carbon atoms and 2 non-fluorine substituted atoms and an 8:2 fluorotelomer alcohol (8:2 FTOH).

![10:2 monoPAP and 8:2 FTOH](image)

Fluorotelomers may be precursors of perfluoroalkyl carboxylates by degradation. The 10:2 fluorotelomer phosphate monoester shown above may thus be degraded to C₁₀ or shorter perfluoroalkyl carboxylates.
As fluorotelomers are not degraded to perfluoroalkyl sulfonates, long-chain fluorotelomers are those with fully fluorinated carbon chains of eight or more C atoms (e.g. 8:2 fluorotelomer alcohol, 8:2 FTOH), whereas the short-chain fluorotelomers are those with less than 8 C atoms.

The majority of the fluorotelomers are used for manufacturing various fluorotelomer-based products including raw material building blocks, surfactant and side-chain-fluorinated polymers that all originate from the starting raw material, perfluoroalkyl iodide, PFAIs (Buck et al., 2011). The synthesis pathway is shown in Figure 1. The final products may to some extent contain the intermediates as impurities, i.e. the side-chain-fluorinated polymers may contain FTOH as an impurity.

1.2 Fluorinated polymers

Many of the polyfluorinated substances on the OECD list are polymers and not covered by the definition of PFASs as used above. According to the OECD, the majority of PFOS-related chemicals are e.g. high molecular weight polymers, in which the PFOS moiety represents a fraction of the total molecular weight (OECD, 2002). The same is true for other PFASs, where the PFAS moiety also represents a fraction of the total molecular weight.

Buck et al. (2011) organises the fluorinated polymers into three groups as shown in Table 2.
### TABLE 2
OVERVIEW OF FLUOROPOLYMERS, PERFLUOROPOLYETHERS, AND SIDE-CHAIN–FLUORINATED POLYMERS (BASED ON BUCK ET AL., 2011)

<table>
<thead>
<tr>
<th>Main group</th>
<th>Examples</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoropolymers: Carbon-only polymer backbone with F directly attached to backbone C atoms</td>
<td>Polytetrafluoroethylene (PTFE) Polyvinylidene fluoride (PVDF) Polyvinyl fluoride (PVF) Fluorinated ethylene propylene (FEP)</td>
<td>Plastics for a variety of uses The presence of the fluorine atoms provides the plastics with a high thermal and chemical resistance among other properties. The issues with these polymers are the possible emissions of PFASs and other substances during the production of the polymers and possible impurities in the final material originating from non-reacted raw materials and residues of PFOA and other PFASs used as processing aids (further described in section 3.2.6).</td>
</tr>
<tr>
<td>Perfluoropolyethers (PFPEs): Ether polymer backbone with F atoms directly attached to backbone C atoms</td>
<td>Polymers, in whose backbone -CF₂-, -CF₂CF₂-, and possibly -CF(CF₃)CF₂ units are separated by O atoms</td>
<td>Functional fluids, surfactants, and surface protection products</td>
</tr>
<tr>
<td>Side-chain–fluorinated polymers: Nonfluorinated polymer backbone with fluorinated side chains, ending in -CₙF₂ₙ₊₁</td>
<td>Fluorinated acrylate and methacrylate polymers Fluorinated oxetane polymers Fluorinated urethane polymers</td>
<td>Surfactants and surface protection products e.g. water proofing, stain proofing and grease proofing finishes for textile, leather, an paper surfaces Surfactants and surface protection, mainly for textile products Offered in many forms and functionalities primarily as fluorosurfactants and coatings additives</td>
</tr>
</tbody>
</table>

The degradation of the fluoropolymers and perfluoropolyethers cannot lead to the formation of long-chain PFCAs; these polymers are not included in the OECD list of possible precursors and are not a subject of the present survey.

In contrast to the two types of polymers described above, side-chain-fluorinated polymers are composed of variable composition backbones with polyfluoroalkyl (and possibly perfluoroalkyl) side chains. Through degradation of these polymers, the side chains may be released from the polymer chain to become PFASs. The PFASs formed will depend on the type and length of the side chains. The mechanism is further described in chapter 0. Side-chain-fluorinated polymers with side chains that may be precursors of PFOS, PFOA and other PFASs are included in the OECD surveys.

Side-chain-fluorinated polymers are mainly produced from fluorotelomers as illustrated in Figure 2. These polymers are often referred to as fluorotelomer-based polymers.

An example of polymers of this type is PolyFox™ (OMNOVA Solutions Inc.): fluorochemicals of short-chain fluorosurfactants based on fluorinated polyethers with a molecular weight greater than 1,000 and with C₂F₅ or CF₃ perfluoroalkyl side chain structures (Poulsen et al., 2005). The product line includes anionic and non-ionic surfactants, UV-radiation curable acrylic monomer derivatives and polyols. The basic structure of one of the products, PolyFox™ 656 polymer with C₂F₅ side chains, is illustrated in the following figure (x + y equals about 6):
The actual polymers produced are often complex structures with different side chains in order to obtain the desired properties. The polymer shown in the figure below have a fluorotelomer-derived perfluoroalkyl acrylate side chain to obtain water and oil repellancy and soil release, and a non-fluorinated alkyl acrylate to obtain film forming softness. Furthermore, the polymer has crosslinking monomers to provide durability.

![Polymer structure](image)

**FIGURE 2**

**POLYMER STRUCTURE OF OIL AND WATER REPELLANTS FOR TEXTILES (BASED ON DAIKIN, 2009)**

1.2.1 Polymers and REACH

Polymers may be subject to authorisation and restriction under REACH, but polymers are exempt from registration and evaluation. Nonetheless, manufacturers and importers of polymers may still be required to register the monomers or other substances used as building blocks of the polymer, as these molecules are generally recognised as of higher concern than the polymer molecule itself (ECHA, 2012c).

Of the 623 substances on the 2007 OECD list which have been pre-registered under REACH, only two include “polymer” in the chemical name used for the pre-registering. Among the five substances registered in the Danish Product Register with the highest consumption in Denmark, two are polymers which are not included in the list of pre-registered substances (further discussed in section 3.3).

In the REACH terminology the fluorinated side chains may be considered "Other reactant", which refers to a molecule that can be linked to one or more sequences of monomer units but which cannot be regarded as a monomer under the relevant reaction conditions used for the polymer formation process. Monomers and any other substances ending up chemically bound to the polymer and for which the corresponding tonnage as reagents makes up 1 tonne or more per year are to be considered for registration (ECHA, 2012).
Whereas fluorotelomers used for production of fluorotelomer-based polymers in the EU will be registered with this specific use, it is not clear how the side-chains of imported polymers are dealt with.

One of the substances with the indication of the 2013 registration intention is indicated as a “reaction mass” (generic name for multiconstituent substances) of telomers: heptadecafluorodecyl acrylate, henicosafluorododecyl acrylate and pentacosafluorotetradec. The final substance is likely a telomer-based polymer and the notation is an example of a transparent registration of these polymers.

Another issue is to what extent the PFASs in themselves may be considered polymers. Buck et al. (2011) briefly mention that some substances, based on certain members of a family of compounds which may potentially be alternatives to PFOS, have a sufficient number of repeating units (together with other characteristics) to enable them to be considered polymers under REACH.

FluoroCouncil has been contacted in order to clarify how the industry considers the status of the side-chain fluorinated substances under REACH, but has not answered.

The EU restriction of PFOS and related substances includes polymers with C₈F₁₇SO₂⁻ side chains. The restriction is currently covered by the POPs regulation, but was included as entry 53 of Annex XVII to the REACH Regulation with a similar definition of covered substances until 2011.

1.3 OECD surveys
The OECD has conducted three surveys on production and releases of PFASs and has published several lists of PFASs, the most recent full list dating back to 2007. The surveys have been used as gross lists for the previous Danish surveys of PFOS, PFOA and related compounds (Havelund, 2001, 2002; Jensen et al., 2008) and are generally used as reference lists for surveys in other countries.

The 2007 list (update of the 2006 survey list) includes about 960 substances divided into four main groups:

1. PFOS and related compounds;
2. Perfluoroalkyl sulfonate and related compounds (apart from those included in the previous group);
3. PFOA and related compounds, and
4. Other PFCAs “fluorinated chemicals that potentially degrade to PFCA” (polyfluorinated carboxylic acids).

The grouping of substances is indicated in Annex 2.

The three first groups in the lists are mainly based on the chain length of the substances and include substances from different chemical groups. PFOS-related chemicals include e.g. salts of PFOS or chemicals that can degrade to PFOS.

The list of PFOS and related compounds include:
- Fully fluorinated (eight-carbon chain length) organic compounds. Both fluorinated linear and isooctane sulfonate compounds;
- PFOS-related/PFOS based substances, which may be salts of PFOS, e.g. potassium, lithium, ammonium, diethanolamine, and potassium. The related chemicals include, but are not limited to: carboxylates, amines, ethers, iodides, phosphonic/phosphinic compounds, alcohols, esters, phosphates, sulfonates, siloxanes, thioethers, urethanes, and acrylates, or polymers that contain PFOS as only a portion of the entire polymer, and
- Substances containing a mixture of C₄-8 fluorinated carbon chains.
The most recent 2009 survey (OECD, 2011) has focused on collection of data on specific PFASs with chain lengths of C6 and higher (including PFOS), PFCAs with chain lengths of C8 and higher (including PFOA) and potential precursors of carboxylic acids in fluorotelomer based products. The survey results indicated that a total of 42 of the 73 perfluorinated chemicals surveyed were manufactured and/or formulated into products in 2008. The survey included requests to companies in non-OECD countries; however, no responses were received from companies in these countries.

Of the 960 substances on the 2007 OECD list, 623 substances are included in the list of pre-registered substances under REACH (ECHA, 2012b); these may potentially be relevant in an EU context. Besides these substances the list, which contains more than 100,000 pre-registered substances, may include PFASs which are not included in the 2007 OECD list. As previously mentioned, many side-chain-fluorinated polymers on the OECD list are not pre-registered.

1.4 Function of the substances for main application areas

The main functions of the substances are described in the assessments of alternatives to the substances (e.g. UNEP, 2010; UNEP, 2012; Poulsen et al., 2005).

The main application area of the PFASs and the side-chain fluorinated polymers is as surfactants and surface protection agents.

Surfactants are compounds that lower the surface tension of a liquid, the interfacial tension between two liquids, or the tension between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.

Applications of perfluoroalkyl compounds have made use of their unique surfactant properties. The alkyl tails of perfluoroalkyls make these substances both hydrophobic (water-repelling) and oleophobic (oil-repelling). Thus they repel water, oil and dirt and insulate electricity.

The hydrophilic end group of the substances can be neutral (e.g., -OH and -SO$_3$NH$_2$), or negatively charged (carboxylates (COO$^-$), sulfonates (-SO$_3$-) and phosphonates (-PO$_3^-$)) or positively charged (e.g., quaternary ammonium group). Thus, the resulting compounds are non-ionic, anionic or cationic surface active agents due to their amphiphilic character (EFSA, 2012).

Besides the surfactant properties, the substances are characterised by high thermal and chemical stability. The strong carbon-fluorine bond makes the perfluoroalkyl chain present in the PFASs extremely stable and nonreactive. PFASs resist even strong acids and high temperatures.
2. Regulatory framework

This chapter gives an overview of key legislation covering fluorinated substances within the scope of this report and summarises how specific substances are addressed in existing and upcoming EU and Danish legislation, international agreements, and in eco-label criteria, as well as a number of activities in non-EU countries and organisations. The overview reflects the findings from the data search.

For readers not used to dealing with legislative issues, Annex 4 gives a brief overview of the legal instruments used in the EU and DK and how they are related. The appendix also gives a brief introduction to the chemicals legislation, explains the lists referred to in section 2.1.2, and provides a brief introduction to international agreements and selected eco-label schemes.

2.1 EU and Danish legislation

This section will first list existing legislation and then give an overview of on-going activities, focusing on which substances are in the pipeline in relation to various REACH provisions.

2.1.1 Existing legislation

Table 3 gives an overview of existing legislation addressing fluorinated substances within the scope of this report. For each area of legislation, the table will first list the EU legislation (if applicable) and then possible transposition of this into Danish law and/or other national rules. The latter will only be elaborated in case of Danish rules differing from EU rules.

The table illustrates that current EU legislation mainly focuses on PFOS and derivatives including strict restrictions on the use of such substances (see next paragraph), a requirement for export notification procedure and potential listing as a possible priority substance in the Water Framework Directive. In contrast, EU legislation relating to food contamination and monitoring focuses broadly on perfluoroalkylated substances. Four fluorinated substances are on the positive list in relation to production and polymerisation of plastic food contact materials: the ammonium salt of PFOA (high temperature sintering and polymerisation) and three substances to be used for high temperature polymerisation of fluoropolymers, including a substance indicated to be a ‘mixture of telomers’ and a C6-perfluorinated ether. Finally, the import/export legislation stipulates that perfluoroctane sulfonates qualify for PIC notification.

Perfluorooctane sulfonic acid (PFOS) and its derivatives are strictly restricted by the POPs regulation (Regulation (EC) No 850/2004) which is the main implementing instrument of the Stockholm Convention in the EU. The Regulation includes a few exemptions which are more or less identical to the “acceptable purposes” listed in Annex B to the Stockholm Convention. The exemptions generally allow very low concentration in substances, preparations and the addressed articles. The applications listed under “specific exemptions” in Annex B to the Convention are not exempt in the POPs Regulation. PFOS and its derivatives are included in the list of substances subject to waste management provisions, but without specific concentration limits. The European Commission is currently working on setting specific concentration limits for the PFOS and other new substances under the Stockholm Convention.

### TABLE 3
**DANISH AND EU LEGISLATION ADDRESSING PFASs**

<table>
<thead>
<tr>
<th>Legal instrument</th>
<th>Substances</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants as regards Annexes I and III (POPs Regulation)</td>
<td>Perfluorooctane sulfonic acid and its derivatives (PFOS) C₈F₁₇SO₂X (X = OH, Metal salt (O-M +), halide, amide, and other derivatives including polymers)</td>
<td>The production, placing on the market and use of PFOS, whether on their own, in preparations or as constituents of articles, shall be prohibited.</td>
</tr>
<tr>
<td>PFOS added by Commission regulation No 757/2010 of 24 August 2010 amending Regulation (EC) No 850/2004 as regards Annexes I and III</td>
<td></td>
<td>1. Exemptions from control measures (Article 4(1)(b) of the regulation) shall apply to concentrations of PFOS equal to or below 10 mg/kg (0.001 % by weight) when it occurs in substances or in preparations.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Exemptions from control measures (Article 4(1)(b)) shall apply to concentrations of PFOS in semi-finished products or articles, or parts thereof, if the concentration of PFOS is lower than 0.1 % by weight calculated with reference to the mass of structurally or micro-structurally distinct parts that contain PFOS or for textiles or other coated materials, if the amount of PFOS is lower than 1 μg/m² of the coated material.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Use of articles already in use in the Union before 25 August 2010 containing PFOS as a constituent of such articles shall be allowed. Article 4(2), third and fourth subparagraphs shall apply in relation to such articles.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4. Fire-fighting foams that were placed on the market before 27 December 2006 may be used until 27 June 2011.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5. If the quantity released into the environment is minimised, production and placing on the market is allowed for the following specific uses provided that Member States report to the Commission every four years on progress made to eliminate PFOS: (a) until 26 August 2015, wetting agents for use in controlled electroplating systems; (b) photoresists or anti reflective coatings for photolithography processes; (c) photographic coatings applied to films, papers, or printing plates; (d) mist suppressants for non-decorative hard chromium (VI) plating in closed loop systems; (e) hydraulic fluids for aviation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6. Once standards are adopted by the European Committee for Standardisation (CEN) they shall be used as the analytical test methods for demonstrating the conformity of substances, preparations and articles to paragraphs 1 and 2. Any other analytical method for which the user can prove equivalent performance could be used as an alternative to the CEN standards.</td>
</tr>
<tr>
<td>Legal instrument</td>
<td>Substances</td>
<td>Requirements</td>
</tr>
<tr>
<td>---------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Regulation 649/2012 concerning the export and import of hazardous chemicals</td>
<td>Perfluoroalkylated substances</td>
<td>Subject to export notification procedure</td>
</tr>
<tr>
<td>Commission Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food</td>
<td>Perfluorooctanoic acid, ammonium salt (CAS No 3825-26-1) Perfluoro acetic acid, α-substituted with the copolymer of perfluoro-1,2-propylene glycol and perfluoro-1,1-ethylene glycol, terminated with chlorohexafluoropropoxy groups (CAS No 329238-24-6) Perfluoro[2-(poly(n-propoxy))propanoic acid] (CAS No 51798-33-5) perfluoro[2-(n-propoxy)propanoic acid] (CAS No 13252-13-6)</td>
<td>Requirements concerning the intentionally use in the manufacture of plastic layers in plastic materials and articles intended for contact with food: Only to be used in repeated use articles, sintered at high temperatures Only to be used in concentrations up to 0,5 % w/w in the polymerisation of fluoropolymers that are processed at temperatures at or above 340 °C and are intended for use in repeated use articles Only to be used in the polymerisation of fluoropolymers that are processed at temperatures at or above 265 °C and are intended for use in repeated use articles</td>
</tr>
</tbody>
</table>
### Classification and labelling

Table 4 shows that PFOS and a number of its derivatives are subject to CLP harmonised classification and labelling, most notably for carcinogenicity, reproductive toxicity, and chronic aquatic toxicity. No other fluorinated compounds within the scope of this report are subject to harmonised classification.

Self-classifications for substances without a harmonised classification and labelling are summarised in section 2.2.
TABLE 4
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

<table>
<thead>
<tr>
<th>Index No</th>
<th>International Chemical Identification *1</th>
<th>CAS No</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
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</tr>
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<td></td>
<td></td>
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<td>Carc. 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Repr. 1B</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>STOT RE 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Acute Tox. 4 *</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>Acute Tox. 4 *</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lact.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Chronic 2</td>
</tr>
</tbody>
</table>

*1 The abbreviations are added here for clarification. All substances are C8 PFSAs. Consult Regulation (EC) No 1272/2008 for the explanation of *, ** and *** which concerns the translation from Directive 67/548/EEC to the CLP Regulation for the hazard classes indicated.

Authorisation List/ REACH Annex XIV
None of the perfluorinated and polyfluorinated substances within the scope of this report are included in the Authorisation List as of August 2012.

2.1.2 Ongoing activities - pipeline

Community Rolling Action Plan (CoRAP)
Table 5 shows that REACH substance evaluations that may lead to restrictions are planned for two broadly defined fluorinated 'substances' suspected to possess PBT/vPvB properties probably due to the potential release of PFASs.

TABLE 5
SUBSTANCES IN THE COMMUNITY ROLLING ACTION PLAN (ECHA, 2012a)

<table>
<thead>
<tr>
<th>CAS No</th>
<th>EC No</th>
<th>Substance Name</th>
<th>Substance group, number of perfluorinated atoms</th>
<th>Year</th>
<th>Member State</th>
<th>Initial grounds for concern</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700-161-3 *1</td>
<td>reaction mass of mixed (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl) phosphates, ammonium salts</td>
<td>Mixed C6, fluoroalkyl phosphates</td>
<td>2013</td>
<td>the Netherlands</td>
<td>Environment/ Suspected PBT/vPvB</td>
</tr>
<tr>
<td></td>
<td>700-403-8 *1</td>
<td>ammonium salts of mono- and bis[3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl and/or poly (substituted alkene)] phosphate</td>
<td>fluoroalkyl phosphates, C6</td>
<td>2013</td>
<td>Belgium</td>
<td>Environment/ Suspected PBT/vPvB</td>
</tr>
</tbody>
</table>

*1 The EC Number is not available. Therefore, the number assigned to substances by the ECHA after inquiries is used.
**Registry of intentions**

Table 6 shows Registry of Intentions for restriction proposals, proposals for harmonised classifications and labelling and proposals for identifying fluorinated substances as Substances of Very High Concern (SVHC).

It shows that there are currently no intentions for initiation of further restriction procedures for substances within the scope of the current report, whereas SVHC intentions have been submitted for six PFCAs substances (C8 to C14, including PFOA) indicated to be CMRs or PBTs. A number of harmonised classification and labelling proposals are intended or have been submitted for four PFCAs (C8-C10, including PFOA) substances, as well as for an 8:2 fluorotelomer. All substances are suggested to be classified as reproductive toxicants, whereas for PFOA and APFO (a C8 PFCA) classification for carcinogenicity, target organ toxicity, acute toxicity and eye irritation have also been suggested. Classification for toxicity to the environment has not been suggested.

All substances are included in the OECD list of polyfluorinated substances (OECD, 2007).

**TABLE 6**

PFOS AND OTHER POLYFLUORINATED SUBSTANCES ON THE CANDIDATE LIST, IN REGISTRY OF INTENTIONS AND IN ANNEX XV DOSSIERS SUBMITTED

<table>
<thead>
<tr>
<th>Registry</th>
<th>CAS No</th>
<th>Substances</th>
<th>Substance group, perfluorinated C-chain length</th>
<th>Scope (as indicated in the registry)</th>
<th>Dossier intended by</th>
<th>Expected data of submission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Registry of current SVHC intentions</td>
<td>335-67-1</td>
<td>Perfluorooctanoic acid (PFOA)</td>
<td>PFCAs, C8</td>
<td>CMR</td>
<td>Germany</td>
<td>28/01/2013</td>
</tr>
<tr>
<td>Registry of submitted SVHC intentions</td>
<td>3825-26-1</td>
<td>Ammoniumpentadecafluorooctanoate (APFO)</td>
<td>PFCAs, C8</td>
<td>CMR</td>
<td>Germany</td>
<td>Submitted 03/04/2012</td>
</tr>
<tr>
<td>Registry of current Harmonised Classification and Labelling intentions</td>
<td>2058-94-8</td>
<td>Henicosafluoroundecanoic acid</td>
<td>PFCAs, C11</td>
<td>PBT</td>
<td>Germany</td>
<td>Submitted 06/08/2012</td>
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<tr>
<td></td>
<td>307-55-1</td>
<td>Tricosafluorododecanoic acid</td>
<td>PFCAs, C12</td>
<td>PBT</td>
<td>Germany</td>
<td>Submitted 03/04/2012</td>
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<tr>
<td></td>
<td>72629-94-8</td>
<td>Pentacosafluorotridecanoic acid</td>
<td>PFCAs, C13</td>
<td>PBT</td>
<td>Germany</td>
<td>Submitted 03/04/2012</td>
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<tr>
<td></td>
<td>376-06-7</td>
<td>Heptacosafluorotetradecanoic acid</td>
<td>PFCAs, C14</td>
<td>PBT</td>
<td>Germany</td>
<td>Submitted 03/04/2012</td>
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<tr>
<td>Registry of submitted Harmonised Classification</td>
<td>335-76-2</td>
<td>Nonadecafluorodecanoic acid</td>
<td>PFCAs,C10</td>
<td>Proposed classification according to CLP: Reproductive toxicity</td>
<td>Sweden</td>
<td>01/09/2012</td>
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<tr>
<td></td>
<td>375-95-1</td>
<td>Heptadecafluorononanoic acid</td>
<td>PFCAs, C9</td>
<td>Proposed classification according to CLP: Reproductive toxicity</td>
<td>Sweden</td>
<td>01/09/2012</td>
</tr>
<tr>
<td>Registry of submitted Harmonised Classification</td>
<td>678-39-7</td>
<td>8:2 Fluorotelomer alcohol (8:2 FTOH)</td>
<td>n:2 Fluorotelomer alcohols, C8</td>
<td>Proposed classification according CLP: Repr. 1B, H360 D</td>
<td>Norway</td>
<td>Submitted: 20/03/2012</td>
</tr>
</tbody>
</table>
### Registry and Labelling intentions

<table>
<thead>
<tr>
<th>Registry</th>
<th>CAS No</th>
<th>Substances</th>
<th>Substance group, per-fluorinated C-chain length</th>
<th>Scope (as indicated in the registry)</th>
<th>Dossier intended by</th>
<th>Expected data of submission</th>
</tr>
</thead>
<tbody>
<tr>
<td>3825-26-1</td>
<td>3825-26-1</td>
<td>Ammoniumpentadecafluorooctanoate (APFO)</td>
<td>PFCAs, C8</td>
<td>Carc. 2, H351, Repr. 1B, H360D, STOT RE 1, H372, STOT RE 2, H373, Acute Tox. 3, H331, Acute Tox. 3, H301, Eye Irrit. 2, H319</td>
<td>Norway</td>
<td>Submitted: 09/04/2010</td>
</tr>
<tr>
<td>335-67-1</td>
<td>335-67-1</td>
<td>Perfluorooctanoic acid (PFOA)</td>
<td>PFCAs, C8</td>
<td>Proposed classification according CLP: Carc. 2, H351, Repr. 1B, H360D, STOT RE 1, H372, STOT RE 2, H373, Acute Tox. 3, H331, Acute Tox. 3, H301, Eye Irrit. 2, H319</td>
<td>Norway</td>
<td>Submitted: 21/02/2011</td>
</tr>
</tbody>
</table>

### Candidate list

The Candidate list (2 August 2012) does not include any fluorinated substances within the scope of this report. ECHA launched a public consultation on 54 potential SVHC 3 September 2012; among these the four substances listed in Table 6 under Registry of submitted SVHC intentions.

### Annex XIV recommendations

The lists of Annex XIV recommendations (2 August 2012) do not include any fluorinated substances within the scope of this report.

### 2.2 Self-classification

The Classification & Labelling (C&L) Inventory database at the website of the European Chemicals Agency (ECHA) contains classification and labelling information on notified and registered substances received from manufacturers and importers. The database includes the harmonised classification as well. Companies have provided this information in their C&L notifications or registration dossiers. ECHA maintains the Inventory, but does not verify the accuracy of the information (EC-CHA, 2012a).

Classification of PFOS and other polyfluorinated substances listed in the database is shown in Table 7.
### TABLE 7
CLASSIFICATION INFORMATION FROM MANUFACTURERS AND IMPORTERS (C&L LIST) ON REGISTERED SUBSTANCES AND SUBSTANCES WITH 2013 INTENTIONS

<table>
<thead>
<tr>
<th>CAS No</th>
<th>Substance name</th>
<th>Substance group, per-fluorinated C-chain lenght</th>
<th>Hazard Class and Category Code(s)</th>
<th>Hazard Statement Codes</th>
<th>Number of notifiers</th>
</tr>
</thead>
<tbody>
<tr>
<td>56773-42-3</td>
<td>Tetraethylammonium heptadecafluoroctanesulfonate</td>
<td>PFSAs, C8</td>
<td>Total</td>
<td>Acute Tox. 3</td>
<td>H301</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td>Acute Tox. 4</td>
<td>H332</td>
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<td></td>
<td></td>
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<td>Carc. 2</td>
<td>H351</td>
</tr>
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<td></td>
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<td></td>
<td>Repr. 1B</td>
<td>H360</td>
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<td></td>
<td>Lact.</td>
<td>H362</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>STOT RE 1</td>
<td>H372</td>
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<td></td>
<td>Aquatic Chronic 3</td>
<td>H412</td>
</tr>
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<td></td>
<td></td>
<td>Acute Tox. 4</td>
<td>H302</td>
</tr>
<tr>
<td>307-35-7</td>
<td>Heptadecafluoroctanesulfonyl fluoride</td>
<td>PASFs, C8</td>
<td>Total</td>
<td>Acute Tox. 3</td>
<td>H301</td>
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<td>Eye Dam. 1</td>
<td>H318</td>
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<td>Acute Tox. 3</td>
<td>H331</td>
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<td>Repr. 1B</td>
<td>H360</td>
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<td>H372</td>
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<td>Aquatic Chronic 2</td>
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<td>Skin Corr. 1B</td>
<td>H314</td>
</tr>
<tr>
<td>85995-91-1</td>
<td>Alkyl iodides, C8-14, γ-ω-perfluoro</td>
<td>PFAIs, C8-14</td>
<td>Total</td>
<td>Acute Tox. 3</td>
<td>H301</td>
</tr>
<tr>
<td>90622-71-2</td>
<td>Alkyl iodides, C6-18, perfluoro</td>
<td>PFAIs, C6-18</td>
<td>Total</td>
<td>Acute Tox. 3</td>
<td>H301</td>
</tr>
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<td>Eye Dam. 1</td>
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<td>Acute Tox. 3</td>
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<td>Repr. 1B</td>
<td>H360</td>
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<td>Aquatic Chronic 2</td>
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</tr>
<tr>
<td>52299-25-9</td>
<td>Bis(nonfluorobutyl)phosphinic acid</td>
<td>Other, 2*C4</td>
<td>Total</td>
<td>Acute Tox. 3</td>
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<td>Eye Dam. 1</td>
<td>H318</td>
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<tr>
<td>62037-80-3</td>
<td>Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate</td>
<td>Other, C4</td>
<td>Total</td>
<td>Acute Tox. 4</td>
<td>H302</td>
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<td>Eye Dam. 1</td>
<td>H318</td>
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<td></td>
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<td>STOT RE 2</td>
<td>H373</td>
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<td>17527-29-6</td>
<td>3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl acrylate</td>
<td>(6:2) Fluorotelomer acrylates, C6</td>
<td>Total</td>
<td>Skin Irrit. 2</td>
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</tr>
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<td>Eye Irrit. 2</td>
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<td>2043-57-4</td>
<td>1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodooctane</td>
<td>(n:2) Fluorotelomer iodides, C6</td>
<td>Total</td>
<td>Skin Irrit. 2</td>
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<td>2144-53-8</td>
<td>3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl methacrylate</td>
<td>(n:2) Fluorotelomer methacrylates, C6</td>
<td>Total</td>
<td>Skin Irrit. 2</td>
<td>H315</td>
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<td>Eye Irrit. 2</td>
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<td>STOT SE 3</td>
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<td>CAS No</td>
<td>Substance name</td>
<td>Substance group, perfluorinated C-chain length</td>
<td>Hazard Class and Category Code(s)</td>
<td>Hazard Statement Codes</td>
<td>Number of notifiers</td>
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<td>27619-89-2</td>
<td>3,3',4,4',5,5,6,6,7,7,8,8,8'-Tridecafluoroctanesulfonyl chloride</td>
<td>6:2 Fluorotelomer sulfonyl chloride, C6</td>
<td>Total</td>
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<td>3,3',4,4',5,5,6,6,7,7,8,8,8'-Tridecafluoroctan-1-ol</td>
<td>(n:2) Fluorotelomer alcohols, C6</td>
<td>Total</td>
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<td>Eye Irrit. 2</td>
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<td>H372</td>
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<td>STOT RE 1</td>
<td>H411</td>
<td>18</td>
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<td>Aquatic Chronic 2</td>
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<tr>
<td>67584-55-8</td>
<td>2-[Methyl[(nonafluorobutyl) sulfanyl]amino]ethyl acrylate</td>
<td>N-Methyl perfluoroalkane sulfonamidooethyl acrylates, C4</td>
<td>Total</td>
<td>H317</td>
<td>208</td>
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<td>Skin Sens. 1</td>
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<td>119</td>
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<tr>
<td>68391-08-2</td>
<td>Alcohols, C8-14, γ-ω-perfluoro</td>
<td>Perfluoroalkyl alcohols/ketones, C8-14</td>
<td>Total</td>
<td>H26</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Flam. Liq. 3</td>
<td>H312</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Acute Tox. 4</td>
<td>H315</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Skin Irrit. 2</td>
<td>H332</td>
<td>86</td>
</tr>
<tr>
<td>85631-54-5</td>
<td>2-Propenoic acid, γ-ω-perfluoro-C8-14-alkyl esters</td>
<td>Mixture of perfluoroalkyl esters, C8-14</td>
<td>Total</td>
<td></td>
<td>26</td>
</tr>
</tbody>
</table>


### 2.3 Eco-labels

Table 8 shows that PFOS and to some extent PFOA, other PFAS, PFCA and related compounds are subject to Nordic Swan and/or the EU flower ecolabelling criteria for printing chemicals paint/varnishes, footwear, playground equipment, as well as furniture and fitments. The chemicals must not be intentionally added or present in the addressed products.
### TABLE 8
ECO-LABELS TARGETING PFOS AND OTHER POLYFLUORINATED SUBSTANCES

<table>
<thead>
<tr>
<th>Eco-label</th>
<th>Substances *1</th>
<th>Mixtures, articles, processes</th>
<th>Document title</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nordic Swan</strong></td>
<td>PFOS-related substances</td>
<td>Printing companies: must not be added to chemicals</td>
<td>Nordic Ecolabelling of Printing companies</td>
</tr>
<tr>
<td>PFOA PFOS</td>
<td>Furniture and fitments: must not be present in/added to the chemical product or material</td>
<td>Nordic Eco-labelling of Furniture and fitments</td>
<td></td>
</tr>
<tr>
<td>PFOA PFOS</td>
<td>Playground equipment: must not be present in/added to the chemical product or material</td>
<td>Nordic Ecolabelling of Outdoor furniture and playground equipment</td>
<td></td>
</tr>
<tr>
<td>PFAS, PFOA, PFOS, PFCA, Related compounds which may degrade to PFCA</td>
<td>Indoor paint and varnishes: are not permitted in the product.</td>
<td>Nordic Ecolabelling of Indoor paints and varnishes</td>
<td></td>
</tr>
<tr>
<td><strong>EU Flower</strong></td>
<td>PFAS, PFOA, PFOS, PFCA, Related compounds which may degrade to PFCA</td>
<td>Indoor paints and varnishes: are not permitted in the product</td>
<td>Commission Decision Of 13 August 2008 establishing ecological criteria for the award of the Community eco-label to indoor paints and varnishes</td>
</tr>
<tr>
<td>PFAS, PFOA, PFOS PFCA. Related compounds which may degrade to PFCA</td>
<td>Outdoor paints and varnishes: are not permitted in the product</td>
<td>Commission Decision Of 13 August 2008 establishing ecological criteria for the award of the Community eco-label to outdoor paints and varnishes</td>
<td></td>
</tr>
<tr>
<td>PFOS</td>
<td>Footwear production: shall not be used/added up until purchase.</td>
<td>Commission Decision of 9 July 2009 on establishing the ecological criteria for the award of the Community eco-label for footwear</td>
<td></td>
</tr>
<tr>
<td><strong>German Blue Angel</strong></td>
<td>No specific requirements have been identified</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1 In this context PFAS refers to perfluorinated alkylated substances only.

### 2.4 International agreements

Table 9 gives an overview of how fluorinated compounds within the scope of this report are addressed by various international agreements. It shows that PFOS is addressed by the OSPAR (priority substance), Helsinki (strict restriction on use) and the Stockholm convention (also addressing PFOS related compounds). As noted earlier and shown in Table 3, the latter is transposed into the EU POPs regulation. Further, PFOA is on the Helsinki convention radar screen for action.
A guidance on the best available techniques (BAT) and best environmental practices (BEP) for the production and use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention has been developed to assist Parties in developing strategies for applying those techniques and practices and for implementing the recommendations of the Conference of the Parties (COP) on risk reduction for PFOS.

### Table 9
INTERNATIONAL AGREEMENTS ADDRESSING PFOS AND OTHER POLYFLUORINATED SUBSTANCES

<table>
<thead>
<tr>
<th>Agreement</th>
<th>Substances</th>
<th>Scope</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSPAR Convention</td>
<td>Perfluorooctanyl sulfonic acid and its salts (PFOS)</td>
<td>OSPAR list of priority substances, Part A substances</td>
</tr>
<tr>
<td>Helsinki Convention</td>
<td>Perfluorooctane sulfonate PFOS</td>
<td>HELCOM Baltic Sea Action Plan adopted on 15 November 2007 by the HELCOM Extraordinary Ministerial Meeting: By 2008 to work for strict restrictions on the use in the whole Baltic Sea catchment area of the Contracting States By 2009, if relevant assessments show the need, to initiate adequate measures such as the introduction of use restrictions and substitutions in the most important sectors identified by the Contracting Parties</td>
</tr>
<tr>
<td>Stockholm Convention</td>
<td>Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride</td>
<td>The requirements are transposed in the EU POPs REGULATION (Regulation (EC) No 850/2004) and reference is made to Table 3</td>
</tr>
<tr>
<td>Rotterdam Convention</td>
<td>None of the substances within the scope of this report are included in Annex III of the Convention and subject to the PIC procedure</td>
<td></td>
</tr>
<tr>
<td>Basel Convention</td>
<td>Waste of polyfluorinated substances may be part of different hazardous waste types in Annex VIII, but are not specifically mentioned in the description of the wastes.</td>
<td></td>
</tr>
</tbody>
</table>

#### 2.4.1 Action plan for reduction of PFOS in Denmark

As part of the updated Danish national implementation plan for Stockholm Convention submitted to the secretariat for the Convention in August 2012, an action plan for the reduction of PFOS in Denmark was developed.

The following table indicates the new initiatives that will be taken in relation to the release of PFOS throughout the substances’ life cycle.
<table>
<thead>
<tr>
<th>No.</th>
<th>Initiative</th>
<th>Description</th>
<th>Responsible institution</th>
<th>Time frame</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Report on use of PFOS in Denmark</td>
<td>PFOS is included in the Danish EPA list of undesirable substances (LOUS). In the period 2012-2015 all substances in LOUS will be surveyed with a view to assessing the possible need for further regulation, labelling, information or phasing-out. In step with these endeavours, a detailed investigation will be carried out of the different uses of PFOS and other per- and polyfluorinated substances in Denmark, as well as their possible substitutes.</td>
<td>Danish EPA</td>
<td>2012</td>
</tr>
<tr>
<td>2</td>
<td>Notification of allowed uses</td>
<td>Notify the uses that are being allowed and report to the Secretariat of the Stockholm Convention on the development of work to phase out PFOS.</td>
<td>Danish EPA</td>
<td>2012/2016</td>
</tr>
<tr>
<td>3</td>
<td>Information to users of PFOS on acceptable uses in Denmark</td>
<td>Inform users of PFOS for hard chromium plating about the provisions of the POP Regulation. Inform other possible users of PFOS via sector organisations. Prepare a register of users of PFOS.</td>
<td>Danish EPA</td>
<td>2012-2013</td>
</tr>
<tr>
<td>4</td>
<td>Study of PFOS/PFOA as soil and groundwater contamination</td>
<td>PFOS/PFOA has been used in fire extinguishing foam, and cases have been observed in both Denmark and abroad of soil and groundwater having been contaminated with PFOS at fire drill sites due to the repeated use of fire extinguishing foam. An investigation will be launched under the technology programme for soil and groundwater contamination. The project is to investigate e.g. whether there are other sources of contamination of soil and groundwater with PFOA/PFOS, and to clarify whether PFOS/PFOA contamination of soil and groundwater in connection with fire drill sites is a generally occurring phenomenon.</td>
<td>Danish EPA</td>
<td>2012-2014</td>
</tr>
<tr>
<td>5</td>
<td>Assessment of the presence of PFOS in household waste</td>
<td>On the basis of a survey under Initiative 1, an assessment will be carried out of the presence of PFOS in waste from households.</td>
<td>Danish EPA</td>
<td>2012-2013</td>
</tr>
<tr>
<td>6</td>
<td>Validation of destruction of PFOS</td>
<td>Encourage the European Commission to carry out a survey to validate whether PFOS can be adequately destroyed in ordinary waste incineration processes. The results will form the basis for assessing to what extent a change in current treatment methods for waste containing PFOS in Denmark is required.</td>
<td>Danish EPA</td>
<td>Not set</td>
</tr>
<tr>
<td>7</td>
<td>Possible separation of household waste containing PFOS</td>
<td>Depending on the results of Initiative 6, requirements will possibly be prepared for separation of certain significant fractions of household waste containing PFOS.</td>
<td>Danish EPA</td>
<td>Not set</td>
</tr>
<tr>
<td>8</td>
<td>Guidelines concerning articles which must not be reused and recycled</td>
<td>Prepare guidelines concerning articles which must not be reused or recycled because they contain PFOS in concentrations that exceed the set limit values.</td>
<td>Danish EPA</td>
<td>Not set</td>
</tr>
</tbody>
</table>
Activities by other non-EU organisations

The PFASs are addressed by national authorities and international organisations all over the world. The following briefly describes some of the activities of highest relevance for the current survey.

2.5.1 OECD

The OECD Web Portal on perfluorinated chemicals (abbreviated PFCs) is designed to facilitate information exchange on perfluorinated chemicals (http://www.oecd.org/ehs/pfc/). Stakeholders can share information on government activities related to their regulatory and stewardship efforts, updates on scientific developments, new technologies, available alternatives, and events related to perfluorinated chemicals.

The OECD activities related to perfluorinated chemicals include efforts to collect more reliable data of the production and use of perfluorinated chemicals, including information from producers on environmental releases of targeted substances from manufacturing and the content of targeted substances in products. The OECD has conducted three surveys on production and releases of the substances. The most recent survey is from 2009 (OECD, 2011).

The 2006 OECD workshop on PFCAs and precursors concluded with a series of recommendations, including an information clearing house, areas where governments and industry could work towards risk reduction programmes, sharing information on effective technologies to reduce environmental releases and providing information on the chemical content of articles, among others.

2.5.2 ICCM and SAICM

In May 2009, the International Conference on Chemicals Management (ICCM) adopted Resolution II/5 for the management of polyfluorinated substances (abbreviated PFCs) and transition to safer alternatives. The resolution invites governments, international organisations and other stakeholders to consider the development, facilitation and promotion in an open, transparent and inclusive manner of national and international stewardship programmes and regulatory approaches to reduce emissions and the content of relevant perfluorinated chemicals of concern in products and to work toward global elimination, where appropriate and technically feasible.

Progress of the work was summarised for the 4th ICCM meeting in September 2012 (SAICM, 2012). The conference also proposed the Terms of Reference for a global PFC group. The group’s objective is to facilitate information exchange and information gathering on PFOS and PFOA, their related substances and products and mixtures containing these substances (collectively designated as PFCs).

2.5.3 USA

In January 2006 the US EPA initiated the PFOA Stewardship Program, in which the eight major companies in the industry committed voluntarily to reduce facility emissions and product content of PFOA, precursor chemicals and higher homologue chemicals on a global basis by 95 percent no later than 2010, and to work toward eliminating emissions and product content of these chemicals by 2015.

The progress of the program can be followed at US EPA’s website for perfluoroalkyl acid (PFOA) and fluorinated telomers at http://www.epa.gov/oppt/pfoa/index.html, which includes a description of the activities undertaken by the agency.

US EPA is reviewing substitutes for PFOA, PFOS, and other long-chain perfluorinated substances as part of its review process for new chemicals under the Toxic Substances Control Act (TSCA) New Chemicals Program (NCP). Through the end of 2008, over 150 alternatives of various types have been received and reviewed by EPA. US EPA reviews the new substances against the range of toxicity, fate and bioaccumulation issues that have caused past concerns with perfluorinated substances, as well as any issues that may be raised by new chemicals.
2.5.4 Canada

By an amendment to the Prohibition of Certain Toxic Substances Regulations of 30 Sep. 2010 (SOR/2010-211 September 30, 2010) Canada has prohibited four fluorotelomers, with an exemption for their presence in articles (Environment Canada, 2010). The four substances are (CAS No from UNEP, 2011 and Environment Canada, 2012b):

- Hexane, 1,6-diisocyanato-, homopolymer, reaction products with alpha-fluoro-omega-2-hydroxyethyl-poly(difluoromethylene), C16-20-branched alcohols and 1-octadecanol (CAS No. 126927-97-7);
- 2-propenoic acid, 2-methyl-, hexadecyl ester, polymers with 2-hydroxyethyl methacrylate, gamma-omega-perfluoro-C10-16-alkyl acrylate and stearyl methacrylate (CAS No 203743-03-7);
- 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 benzenecarboperoxoate-initiated (CAS No 459415-06-6), and
- 2-propen-1-ol, reaction products with pentafluoroiodoethane tetrafluoroethylene telomer, dehydroiodinated, reaction products with epichlorohydrin and triethylenetetramine (CAS No 464178-90-3).

The four fluorotelomer-based substances are primarily used in applications involving water-, oil-, soil- and grease-repellents for paper, fabric, leather, packaging, rugs and carpets, as well as tiles and grouts. They are also used as a levelling agent in coatings. The restriction is based on an assessments indicating that the four fluorotelomer-based substances are ultimately sources of long chain perfluorinated carboxylic acids (PFCAs) through the release of precursors (Environment Canada, 2010).

None of the four substances are included in the list of substances pre-registered under REACH. Cas No 203743-03-7 was identified as constituent of a textile impregnation spray for car interiors in a Danish survey from 2008, while CAS No 203743-03-7 was a constituent of SONAX textile impregnation (Jensen et al., 2008). CAS No 203743-03-7 is registered in the Danish Product Register (quantity and application confidential).

2.6 Summary on regulatory framework

PFOS and similar substances/derivatives

This chapter shows that the main legal focus so far has been on PFOS and its derivatives (sometimes including polymers with the potential to release PFOS). This includes harmonised EU classification and labelling, strict restrictions on use (following the Stockholm Convention), requirements for export notifications and via the Water Framework Directive. PFOS is also addressed in all ecolabelling criteria (EU flower and Nordic Swan) and in all international agreements (OSPAR, Helsinki and Stockholm Conventions) identified in this survey. Denmark has a specific focus on PFOS and has prepared an action plan for reduction of PFOS in Denmark. PFOS and derivatives have also high priority in non-EU countries and organisations.

PFCAs, including PFOA

PFOA and other PFCAs are currently less regulated than PFOS, but a range of these substances are in the pipeline with intentions for identifying six substances as Substances of Very High Concern (SVHC) due to CMR or PBT properties (possibly leading to Authorisation or Restriction requirements) and five with submitted or intended harmonised classification and labelling proposals indicating similar human health problems as with PFOS and similar substances. PFOA is also on the
Helsinki convention radar screen for possible action and addressed in ecolabelling criteria for several product groups.

**PFSAs**
Perfluorooctane sulfonates are subject to PIC notification under the import/export legislation.

**Perfluoroalkylated substances in general**
This broad group of substances is addressed in EU legislation related to content and monitoring in foodstuffs, as well as in a number of ecolabelling criteria.

**Fluorinated polymers**
As set out in Chapter 1 of this report, release of PFOS, PFOA and similar substances during production and use of fluorinated polymers may be an issue of concern. The only regulation of the polymers is the restriction on polymers with side chains with a similar structure as PFOS under the POP Regulation. Otherwise this substance group is not specifically addressed.

**Perfluoroalkyl and polyfluoroalkyl substances in general**
Activities in various international fora, including OECD, ICCM/SAICM, USA and Canada point to an increased focus on substances within the scope of this report, with Canada addressing e.g. specifically a number of fluorotelomers.
3. Manufacture and uses

3.1 Data available on global and EU manufacture of PFCs
This section provides an overview of the data available on the manufacture of PFCs world-wide across the different substance groups followed by a description of manufacture and use by each of the main groups.

3.1.1 Global manufacture of PFCs
The majority of the global production of PFASs and fluoropolymers are produced by eight major companies who all participate in the US EPA 2010/2015 PFOA Stewardship Program. These major manufacturers represent more than 90% of the global annual production of perfluorinated chemicals and fluoropolymers (Posner et al., 2009). Six of these companies, Arkema France, Asahi Glass Co. Ltd., Clariant International Ltd., Daikin Industries Ltd., DuPont Company and Solvay Specialty Polymers are organised in the Global Industry Council for Fluoro Technology, FluoroCouncil (FluoroCouncil, 2012). Two of the companies participating in the stewardship program, 3M/Dyneon and BASF Corporation, are not members of the FluoroCouncil.

The FluoroCouncil has been contacted in order to obtain updated information on the overall global production and consumption of PFASs and fluorotelomer-based polymers by substances groups and application areas. The council has not been able to provide detailed information on production volumes and uses of the chemicals.

The OECD has prepared surveys of the production of PFCs in its member countries in 2004, 2006 and 2009. The most recent, the 2009 survey, focuses on the long-chain PFCs and their precursors and the emissions from the production (OECD, 2011). Of the 73 substances surveyed, 42 were manufactured and/or formulated into products in 2009. The response rate of the 27 companies surveyed was 33% and no responses were obtained from non-OECD countries. The survey thus gives a quite incomplete picture of the world-wide situation and, due to the low response rate, it has been difficult to demonstrate a trend in production. The main results of the surveys are indicated for each substance group below.

3.1.2 Registration of manufacture and import under REACH
Among the major manufacturers of fluorinated chemicals, three companies, Arkema (France), Clar- iant International Ltd. (Switzerland) and BASF Corporation (Germany), have headquarters in the EU27+2 (EU+ Norway and Switzerland), but other companies may have production sites with PFASs or side-chain-fluorinated polymers within the EU.

An overview of the production of PFCs in the EU does not exist; it has been beyond the limits of the current survey to obtain detailed information on manufactured volume directly from the individual manufacturers.

Some information on the use of PFOS and PFOA and related substances exist; this is described in the following sections, but quantitative information on the volumes of production, use and release of PFASs and the side-chain-fluorinated polymers is limited.
All manufacturers and importers of chemical substances > 1 tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). The 1st of December 2008 was the deadline for pre-registration of substances that will be produced or imported in volumes of more than 1 tonne per year and company in the EU. Pre-registered chemicals benefit from tonnage and property dependent staggered deadlines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more per year,
- carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and
- substances dangerous to aquatic organisms or the environment above 100 tonnes per year;
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year, and
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

PFOS and related substances are classified carcinogenic and toxic to reproduction and should consequently be registered according to the REACH Regulation by November 2010 if manufactured or imported in quantities above one tonne. For the remaining PFASs, only substances manufactured or imported at 1000 tonnes or more per year had to be registered before 30 November 2010 while the substances manufactured or imported at 100 - 1000 tonnes per year have to be registered by 31 May 2013.

ECHA has prepared a list of substances for which companies have expressed their intentions for registration of the substances by 31 May 2013. The expression of interest could indicate that the substances are manufactured or imported in the 100-1000 tonnes range, but the tonnage may actually be lower, as is the situation for many of the substances currently registered.

Polymers are exempt from registration. This means that the majority of the relevant fluorinated substances would not be registered. However, monomers and any other substance(s) ending up chemically bound to the polymer, and for which the corresponding tonnage is above the tonnage limits, are to be considered for registration (ECHA, 2012).

Of the 960 substances on the 2007 OECD list of PFOS, PFOA, PFCA and related compounds and chemicals that may degrade to PFCA, 623 substances are included in the list of pre-registered substances under REACH (ECHA, 2012b) and may potentially be relevant in an EU context.

Of these substances, only 2 include the text string “polymer” in the substance name.

Registered substances and substances intended to be registered by 2013 are shown in Table 11. The total tonnage of manufacture and import of the registrants is indicated in ECHA’s registration database with tonnage bands (ECHA, 2012h). For substances used as intermediates, tonnage bands are generally not provided.

Currently 9 substances are registered; of these, four are registered as used as intermediate only without tonnage bands, and for one substance tonnage and use is confidential. Twelve substances are indicated to be registered by 2013. Of these 21 substances, 7 substances were not included in the 2007 OECD list, but have been identified from the chemical names going though the list of registered substances and the list of 2013 intentions.

The total reported tonnage of registered substances is in the range of 14-140 t/y. One substance, ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate, is in the 10-100 t/y category.

In order to obtain EU-wide information on the use of the substances an information request has been forwarded to the following European trade organisations: Euratex (apparel and textile), ECRA (carpets), CEPE (paint, printing ink and artists’ colours) and FEICA (adhesives). No information
was obtained. Besides, as mentioned elsewhere, the international FluoroCouncil has been contact-
ed, but no data have been obtained.

Substances registered in ECHA’s REACH registration database
The table overleaf shows substances included in ECHA’s database on registered substances and
substances for which industry has indicated the intention to register the substances by 2013.

3.1.3 Statistics on EU production and import/export
Production of PFASs is not covered by any specific activity code of the EU production statistics
(Prodcom). PFASs are not covered by any specific commodity codes (CN8 code) of the EU external
trade statistics (Comext).
<table>
<thead>
<tr>
<th>CAS No</th>
<th>EC No</th>
<th>Substance name *1</th>
<th>Abbreviation</th>
<th>Substance group, perfluorinated chain length *2</th>
<th>OECD 2007 group</th>
<th>Registered, tonnage band, t/y *3</th>
<th>Intention 2013 *4</th>
<th>Registered end uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>56773-42-3</td>
<td>260-375-3</td>
<td>Tetraethylammonium heptadecafluorooctadecasulfonate</td>
<td>PFSAs, C8</td>
<td>PFOS</td>
<td>1-10</td>
<td></td>
<td></td>
<td>Industrial use for metal (chromium) plating</td>
</tr>
<tr>
<td>307-35-7</td>
<td>206-200-6</td>
<td>Heptadecafluorooctanesulfonyl fluoride</td>
<td>PASFs, C8</td>
<td>PFOS</td>
<td></td>
<td>Intermediate Use Only</td>
<td></td>
<td></td>
</tr>
<tr>
<td>85995-91-1</td>
<td>289-100-3</td>
<td>Alkyl iodides, C8-14, γ-ω-perfluoro</td>
<td>PFAIs, C8-14</td>
<td>Perfluoroalkyl iodide compounds</td>
<td></td>
<td>Intermediate Use Only</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90622-71-2</td>
<td>292-474-2</td>
<td>Alkyl iodides, C6-18, perfluoro</td>
<td>PFAIs, C6-18</td>
<td>Perfluoroalkyl iodide compounds</td>
<td></td>
<td>Intermediate Use Only</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>700-161-3</td>
<td>Reaction mass of mixed (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl) phosphates, ammonium salts</td>
<td>Undefined mixture, C6</td>
<td>Not included</td>
<td>Tonnage Data Confidential</td>
<td>Not indicated</td>
<td>Industrial use of reactive processing aids ; Use as laboratory reagent</td>
<td></td>
</tr>
<tr>
<td>52299-25-9 *5</td>
<td>700-183-3</td>
<td>Bis(nonfluorobutyl)phosphinic acid</td>
<td>Other, C4</td>
<td>Not included</td>
<td>1-10</td>
<td>Industrial use of reactive processing aids ; Use as laboratory reagent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>62037-80-3 *5</td>
<td>700-242-3</td>
<td>Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate</td>
<td>Other, C4</td>
<td>Not included</td>
<td>10 - 100</td>
<td>Use as a surface active agent, industrial and professional settings, by consumers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>700-403-8</td>
<td>Ammonium salts of mono- and bis[3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl and/or poly (substituted alkene)] phosphate</td>
<td>one or two C6</td>
<td>Not included</td>
<td>1-10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAS No</td>
<td>EC No</td>
<td>Substance name *1</td>
<td>Abbreviation</td>
<td>Substance group, perfluorinated chain length *2</td>
<td>OECD 2007 group</td>
<td>Registered, tonnage band, t/y *3</td>
<td>Intention 2013 *4</td>
<td>Registered end uses</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
<td>----------------------------------------------------------------------------------</td>
<td>--------------</td>
<td>-------------------------------------------------</td>
<td>-----------------</td>
<td>---------------------------------</td>
<td>-----------------</td>
<td>----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>-</td>
<td>700-536-1</td>
<td>N,N,N,,-triethylethanaminium 1,1,2,2,3,3,4,4,4-nonfluorobutane-1-sulfonate</td>
<td>PFSAs (C4)</td>
<td>Not included</td>
<td>1 - 10</td>
<td>Manufacture of tetraethlammonium perfluorobutanesulfonate</td>
<td></td>
<td>Industrial use of tetraethlammonium perfluorooctanesulfonate for metal (chromium) plating</td>
</tr>
<tr>
<td>17527-29-6</td>
<td>241-527-8</td>
<td>3,3,4,4,5,5,6,7,7,8,8,8-Tridecafluoroctyl acrylate</td>
<td>6:2 FTAC</td>
<td>(6:2) Fluorotelomer acrylates, C6</td>
<td>Fluoro ester compounds (F5)</td>
<td>Not registered</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>2043-57-4</td>
<td>218-056-1</td>
<td>1,1,1,2,2,3,4,4,5,5,6,6-Tridecafluoro-8-iodooctane</td>
<td>6:2 FTI</td>
<td>(n:2) Fluorotelomer iodides, C6</td>
<td>Fluoro iodide compounds (F7)</td>
<td>Not registered</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>2144-53-8</td>
<td>218-407-9</td>
<td>3,3,4,4,5,5,6,7,7,8,8,8-Tridecafluoroctyl methacrylate</td>
<td>6:2 FTMAC</td>
<td>(n:2) Fluorotelomer methacrylates, C6</td>
<td>Fluoro ester compounds (F5)</td>
<td>Not registered</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>26650-09-9</td>
<td>607-977-8</td>
<td>Thiocyanic acid, 3,3,4,4,5,5,6,7,7,8,8,8-Tridecafluoroctyl ester</td>
<td>Fluorotelomer halogenides, C6</td>
<td>Partial fluoro &amp; miscellaneous fluoro compounds (F17)</td>
<td>Not registered</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27619-89-2</td>
<td>248-576-4</td>
<td>3,3,4,4,5,5,6,7,7,8,8,8-Tridecafluoroctanesulfonyl chloride</td>
<td>6:2 Fluorotelomer sulfonyl chloride, C6</td>
<td>Fluoro sulfonylate/sulfonylamide/sulfonyl compounds (F11)</td>
<td>Not registered</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>375-72-4</td>
<td>206-792-6</td>
<td>1,1,2,2,3,3,4,4,4-Nonfluorobutane-1-sulfonyl fluoride</td>
<td>PBSF</td>
<td>PASFs, C4</td>
<td>PFAS</td>
<td>Not registered</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>CAS No</td>
<td>EC No</td>
<td>Substance name *1</td>
<td>Abbreviation</td>
<td>Substance group, perfluorinated chain length *2</td>
<td>OECD 2007 group</td>
<td>Registered, tonnage band, t/y *3</td>
<td>Intention 2013 *4</td>
<td>Registered end uses</td>
</tr>
<tr>
<td>----------</td>
<td>---------</td>
<td>----------------------------------------------------------------------------------</td>
<td>--------------</td>
<td>-----------------------------------------------</td>
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<tr>
<td>647-42-7</td>
<td>211-477-1</td>
<td>3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctan-1-ol</td>
<td>6:2 FTOH</td>
<td>(n:2) Fluorotelomer alcohols, C6</td>
<td>Fluoro alcohol compounds (F1)</td>
<td>Not registered x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>67584-55-8</td>
<td>266-733-5</td>
<td>2-[Methyl[(nonafluorobutyl)sulfonyl]amino]ethyl acrylate</td>
<td>MeFBSAC</td>
<td>N-Methyl perfluoroalkane sulfonamidoethyl acrylates, C4</td>
<td>PFAS</td>
<td>Not registered x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68391-08-2</td>
<td>269-927-8</td>
<td>Alcohols, C8-14, γ-ω-perfluoro</td>
<td></td>
<td>Perfluoroalkyl alcohols/ketones, C8-14</td>
<td>Fluoro alcohol compounds (F1)</td>
<td>Not registered x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>85631-54-5</td>
<td>288-003-5</td>
<td>2-Propenoic acid, γ-ω-perfluoro-C8-14-alkyl esters</td>
<td></td>
<td>Mixture of perfluoroalkyl esters, C8-14</td>
<td>Fluoro ester compounds (F5)</td>
<td>Not registered x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34455-22-6</td>
<td>608-993-8</td>
<td>1-Octanesulfonamide, N-[3-(dimethylamino)propyl]-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-</td>
<td></td>
<td>C6 telomer</td>
<td>Not included</td>
<td>Not registered x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>915-328-8</td>
<td>Reaction mass of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluoroacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoroacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoroacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoroacrylate and 3,13,14,14,14-pentacosaffluorotetradecafluoroacrylate</td>
<td>Undefined mixture of C8, C10, C12 telomers.</td>
<td>Not included</td>
<td>Not registered x</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1 For registered substances the registered name is indicated; for other substances included in the ESIS database (with EC number), the substance name in ESIS is indicated (http://esis.jrc.ec.europa.eu/)

*2 Describes the number of perfluorinated atoms in one chain.

*3 As indicated in the lists of registered substances at ECHA's website (ECHA, 2012h). For each separate registration (which may cover more than one manufacturer) the registered tonnage is indicated. For substances indicated as "Intermediate use only" no tonnage band is reported.

*4 Included in the list of substances that companies have told ECHA they intend to register by the 2013 REACH registration deadline. It is based on responses to a survey ECHA conducted. 31 May 2013 is the deadline for industry to register all phase-in substances manufactured or imported in the EU at or above 100 tonnes a year.

*5 CAS No not indicated in registration, but added here.
3.2 Global and EU manufacture and use of PFCs

3.2.1 PFOS and other polyfluoroalkyl sulfonates and derivatives

Global manufacture and consumption

3M was, prior to the phase-out announced in 2000, the major global producer of perfluorooctanesulfonyl fluoride (POSF) although smaller producers existed in Europe and Asia. POSF is used as an intermediate in the production of PFOS and PFOS derivatives, and the production of POSF can be used as an indicator of the total production of PFOS-related substances.

The total historical worldwide production of POSF between 1970 and 2002 was estimated by Paul et al. (2009) to be 96,000 tonnes (or 122,500 tonnes, including unusable wastes). The majority of this was produced by 3M. The company manufactured approximately 3,665 t/y POSF, or 78% of the estimated global POSF production of 4,650 t/y, when the production peaked in 2000.

The major uses for the POSF-derived substances were in providing grease, oil and water resistance to materials such as textiles, carpets, paper and coatings in general.

From 1970 to 2002, the main end uses of the POSF-derived substances were carpets (48,000 tonnes for the entire period), paper and packaging (24,000 tonnes), apparel (12,500 tonnes), performance chemicals (6,000 tonnes), and aqueous fire fighting foams (10,000 tonnes) (Paul et al., 2009).

Between 2000 and 2003 the global production dropped sharply as a consequence of 3M’s phase out of the chemical’s production. However, production of POSF-derived chemicals is still ongoing in other countries, although at a much smaller scale than before 2003.

The global production and consumption of PFOS and related substances in recent years have been reviewed in a study undertaken for UNIDO in 2009 (Carloni, 2009). According to this study, China started larger-scale production of PFOS in 2003 (Carloni, 2009). Since 2005 China’s annual output has grown rapidly due to the increase of the applications of PFOS in the country and overseas demand. The cumulative PFOS production for the period 2003-2008 is estimated at 250 tonnes; of this, 200 tonnes was used in China. In 2006, POSF was produced by 15 Chinese enterprises. The accumulated global production of PFOS and related compounds for the period 2003-2008 was 410 tonnes. China accounted for more than half of this. Japan and Germany ranked second and third with cumulative productions of 100 and 25 tonnes, respectively.

The 2009 OECD survey reported on production of 2.5 t/y of PFOS and related substances. The results showed that products containing PFOS are used mainly in the photolithography process as antireflective coatings, as intermediates in industrial applications (e.g. as raw material of photoacid generators,) and as precursors for ammonium PFOS production. The potassium salt of PFOS (CAS No 2795-39-3) had a variety of uses including those as a mist suppressant for chromium (VI) plating, a processing aid in the manufacture of fluoropolymers and in medical devices.

An important difference between developing countries and developed countries seems to be in the number of sectors in which PFOS is currently used. China, for example, used PFOS in a large range of applications in 2008: textiles, fire fighting foams, pesticides, metal plating, semiconductors and cleaning products. For 2008 it is reported that 100 tonnes PFOS were used for textile treatment in China (Lim et al., 2011). As China is party to the Stockholm Convention, it must be expected that many of these uses will cease (or have ceased) as China implements its obligations under the Convention.

Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances 53
In the developed world, small volumes are still used for applications exempt under the Stockholm Convention: mainly chromium plating, photolithography, photography and in hydraulic fluids for aviation.

**Consumption in the EU**

The use of PFOS and its derivatives has been restricted in the EU since 2006. The substances are listed in Annex 1 (banned substances) to the POPs regulation with an exemption for five application areas.

The total consumption for these areas was estimated at about 8 t/y in 2010 (Table 12) in a study for the European Commission (ESWI, 2011). For some of the application areas, the estimate is based on data from a UK report from 2004 (RPA, 2004), which are considered the best estimate, but may not be up-to-date.

The major application area was the metal plating industry. PFOS lowers the surface tension of the chromium bath and therefore reduces the size of bubbles in the bath. The surface of the bath is therefore calmer and emissions to air are reduced. Most of the industries have switched to alternatives when it became evident that PFOS was problematic; however, in some branches a shift to other chemicals has been difficult. Today only the use in nondecorative hard chromium (VI) plating in closed loop systems is allowed. In hard chromium (VI) plating, the industry continues to use PFOS to limit chromium (VI) emissions to air from the chromium bath.

The most common PFOS-related surfactant used in the chromium plating industry in Denmark today is tetraethylammonium perfluorooctane sulfonate (CAS no. 56773-42-3) (Poulsen *et al.*, 2011).

The substance is registered for use in chromium plating with a tonnage of 1-10 t/y (Table 11).

PFOS derivatives are used in the photographic industry as ingredients in photographic material (film, paper, plate). The concentration of PFOS in films is indicated at 0.1–0.8 µg/cm².

<table>
<thead>
<tr>
<th>Industry</th>
<th>PFOS consumption, kg/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal plating industry</td>
<td>6,500</td>
</tr>
<tr>
<td>Photographic industry</td>
<td>562</td>
</tr>
<tr>
<td>Semiconductor industry</td>
<td>9.3</td>
</tr>
<tr>
<td>Hydraulic fluids in aviation industry</td>
<td>730</td>
</tr>
</tbody>
</table>

Detailed flow charts showing the flow of PFOS to the different waste streams and to the environment for each application area is provided in the report from ESWI (2011) and discussed in section 4.1.1.

Perfluorooctanesulfonyl (heptadecafluorooctanesulfonyl) fluoride (POSF) which is used as an intermediate in the production of PFOS and its derivatives is registered for intermediate use only under REACH, without any tonnage band.
3.2.2 PFOA, longer chained PFCAs and related substances

Global production and consumption

Historically, commercial polyfluorinated carboxylic acids (PFCA) products were mixtures containing linear C8 or C9 PFCAs as their major component (Prevedouros et al., 2006).

The estimated global production of perfluorooctanoate (PFOA) and ammonium perfluorooctanoate (APFO) from 1951-2004 is 3,600-5,700 tonnes, while the manufacturing of perfluorononanoate (PFNA) and ammonium perfluorononanoate (APFN) during the same period is estimated at 800-2,300 tonnes (Prevedouros et al., 2006). In 1999, global annual APFO production was approximately 260 tonnes.

PFOA and PFNA have mainly been used as polymerisation aids in the manufacture of fluoropolymers such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) (Prevedouros et al., 2006). Furthermore, PFOA was used as a component in aqueous fire-fighting foam from approximately 1965 to 1975. Historically the PFCAs and derivatives also had widespread use as additives in various industrial and consumer products. Manufacture of fluoropolymer was the single largest direct use of the ammonium salts APFO and APFN. They act among other to solubilise fluoromonomers to facilitate their aqueous polymerization.

As a result of the US EPA Stewardship Program (see section 2.5.3) and further activities to substitute the PFOA, precursor chemicals and higher homologue chemicals in many uses, the production of PFOA and other C8-fluorochemicals have decreased significantly at least in Europe and North America.

For the most recent OECD survey, the seven companies that responded to the survey reported the manufacture of a total of <5.5 tonnes PFOA and related compounds (OECD, 2011). Furthermore, the mass of five different 8:2 fluorotelomers which potentially may degrade to PFOA and PFNA was reported. These substances were present as residuals or impurity of products at a total of <20 tonnes.

No data have been identified on the global production and use of PFCAs of chain lengths longer than C9. Four recently published Annex XV dossiers for C11-14 PFCAs (ECHA 2012e, f, g, h) and an ecological screening assessment for C9-C20 PFCAs (Environment Canada, 2012a) do not indicate any current uses of the substances.

Consumption in the EU

The following section is largely extracted from a report prepared for the European Commission on the risks arising from the industrial use of PFOA and APFO (RPS Advies, 2010). According to the report, the market volume of production and import of PFOA and APFO showed a decreasing trend from 2002 onwards in the EU-27 Member States. For the period 2004-2008 the average market volume is estimated to be a maximum of 100 t/y. The trend in the use of PFOA and related compounds shows a further decrease, and the report estimated that the market for 2010 would likely be less than 50 t/y.

According to the information available to RPS Advies (2010), only one manufacturer of APFO was active in the EU in 2009 and this company planned to cease production as per April 2010. The annual average sales volume of APFO of the company during the years 2004-2008 was reported to be about 40 t/y of which 10 tonnes was exported or storaged. The import of the substances into the EU was estimated at 20-25 t/year.

Three applications of PFOA /APFO were identified: fluoropolymer production, and use as surfactants in the semiconductor industry and photographic industry.
The fluoropolymer production was the major direct user of PFOA as a processing aid. PFOA may be present at residual levels in the fluoropolymer products that are placed on the market as resins or as dispersions. The study does not provide specific data on the quantities of PFOA ending up in the polymers.

APFO was used in the photographic industry in a total average annual volume of 2.6 t/y. In the photographic industry PFOA and PFOA-derivatives play an essential role in manufacturing and performance of certain imaging products because these chemicals provide critical antistatic, surfactant, friction control, and dirt repellent properties. The substances also provided important safety features by controlling the build-up and discharge of static electricity and preventing employee injury, operating equipment and product damage, and fire and explosion hazards.

According to the study, the semiconductor industry had a minor usage of PFOA and related substances, and the total consumption for the entire EU semiconductor industry was estimated at less than 50 kg/year.

The total tonnage of imports of PFOA and APFO as residuals in mixtures and articles imported from countries outside the EU was estimated with high uncertainty at <5 t/y.

No data are available on the use of other long-chained PFCAs and related substances in the EU.

3.2.3 Short-chain PFCAs

Global manufacture and consumption
Limited information has been identified regarding the current production and consumption of short-chain polyfluorinated carboxylates and sulfonates and their derivatives. Information on these substances is not included in the 2009 OECD survey. Information from industry (FluoroCouncil, 2012) indicates a general transition trend in the use of PFCAs and PFSAs:

- **Surfactants:**
  - Moving from ≥6 carbon to 4-carbon-based fluoroalkane sulfonate chemicals
  - Moving from 8 and 9 carbon perfluoro carboxylate polymerization aids (PFOA/PFNA) to certain mono- or poly-fluoroether carboxylates or other shorter-chain fluorinated substances;
- **Surface modification polymers:**
  - Moving from ≥6-carbon to 4-carbon-based fluoroalkane sulfonate chemicals
  - Moving from ≥8-carbon to 6-carbon fluorotelomer chemicals.

The 4-carbon-based sulfonate chemistry is based on perfluorobutane sulfonate (PFBS) and derivatives e.g. perfluorobutane sulfonamido-based fluorosurfactants. PFBS-based chemistry was introduced by 3M as replacement for the PFOS-based chemistry and PFBS-based substances are today used mainly for protective treatments (e.g. of textiles) and surfactants.

Information from Australia Department of Health and Ageing (NICHAS, 2005) indicates that potassium perfluorobutane sulfonate based chemicals have main applications in industrial and consumer carpet protection treatments, industrially applied corrosion resistant paints and coatings, and high performance industrial chemical applications in the metal processing industry. Further applications include electronic grade fluorochemical surfactants in etch solutions, photoresists (light-sensitive material used in several industrial processes, such as photolithography and photengraving), photoresist strippers and edge bead removers, anti-reflective coatings, spin-on glass films and as flame retardant additives.
Consumption in the EU
Limited information is available on the use of short-chain PFSAs in the EU.

One short-chain PFSA is included in the list of registered substances: N,N,N-,triethylethanaminium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (EC Number 700-536-1; no CAS No indicated = triethylethanaminium perfluorobutanesulfonate). The registered quantity of this C4 perfluorosulfonate salt is 1-10 t/y. The use indicated in the registration dossier is manufacture of tetraethylammonium perfluorobutanesulfonate, which is used for metal (chromium) plating (ECHA, 2012h). This substance is the C4 analogue to the C8 tetraethylammonium perfluoroctane sulfonate used for metal chromium plating and mentioned in the section above. It is not clear why it is the intermediate and not the final substance which is registered.

Three other short-chain PFASs, not included in the OECD list, were registered with a total tonnage of 12-120 t/y. For two of the substances (each with 1-10 t/y) the uses were indicated as reactive processing aids, laboratory reagents and surface active agents.

3.2.4 Fluorotelomers and fluorotelomer-based polymers

Fluorotelomer-based products have been manufactured since the early 1970s and used in many of the same industrial and consumer product applications as POSF-derived products (Prevedouros et al., 2006). From 1985 to 2000, the global production of fluorotelomers increased from 2,000 to 11,000 t/y (Korzeniowski, 2008).

According to US EPA (2009), world-wide production of fluorotelomers in 2006 was estimated at about 9,000 t/y and the USA accounted for more than 50 percent of this fluorotelomer production. This estimate was low compared with another estimate made by the German Umweltbundesamt (2009) that indicates that the annual worldwide production of the basic fluorinated telomer alcohols (FTOH) was estimated at 11,000 to 14,000 tonnes.

According to US EPA (2009) most of the fluorotelomers are used to produce side-chain-fluorinated polymers as described in section 1.2. No data have been identified indicating the percentages of the total used as fluorotelomer compounds and fluorotelomer-based polymers, respectively.

US EPA (2009) reports that the final application of the world-wide production of fluorotelomers in 2006 was as follows (apparently mainly used as fluorotelomer-based polymers):

- Textiles and apparel accounted for approximately 50% of the volume;
- Carpet and carpet care products accounting for the second largest share in consumer product uses, and
- Coatings, including those for paper products, are the third largest category of consumer product uses.

Limited data are available on the manufacture of fluorotelomers and side-chain-fluorinated polymers in China, but the production volume was in 2009 apparently still relatively low. In 2009, the China Dyeing and Printing Association reported that approximately 10,200–10,600 tons of fluorinated finishing agents were used each year in China (Lim et al., 2011). Of this 9,800–10,200 tons were imported and 300 tons were domestically made. According to a presentation at a UNEP workshop, the imported agents are from foreign companies, such as 3M, Dupont, Clariant, Huntsman, Daikin and Asahi (ChinaPops, 2009). The total content of fluorinated substances is not indicated.

The overall trend in global manufacturing and consumption of fluorotelomer and fluorotelomer-based polymers is a shift from ≥C8 to C6 fluorotelomer chemicals (FluoroCouncil 2012).
No data, however, have been available on the distribution between the pure telomers and PFT-based polymers based on ≥C8 and C6 fluorotelomer chemistry, respectively.

**Consumption in the EU**

Very limited information has been available on the production and consumption of fluorotelomers and fluorotelomer-based polymers in the EU. None of the registered substances are within the group of fluorotelomers and fluorotelomer-based polymers.

Considering a worldwide production in the range of 11,000 to 14,000 t/y (Umweltbundesamt, 2009), the consumption in the EU would likely be in the range of 3,000 – 5,000 t/y. It means that none of the substances are likely to be manufactured or imported in quantities above 1,000 t/y and consequently not registered as of today.

A number of telomers belonging to the groups: (n:2) fluorotelomer acrylates, (n:2) fluorotelomer iodides, (n:2) fluorotelomer methacrylates, fluorotelomer halogenides, (n:2) fluorotelomer sulfonic salts, and (n:2) fluorotelomer alcohols are among the substances with a 2013 registration indication are. All the substances are based on C6 chemistry which is in accordance with the current shift from C8 to C6 chemistry. However, one “reaction mass” (probably telomer-based polymer) is based on C8, C10, C12 telomers.

The available data do not indicate to what extent the side-chain-fluorinated polymers are produced in the EU or imported from countries outside the EU.

### 3.2.5 Emission from manufacture

PFASs have historically been manufactured using four distinct routes. Today PFASs are principally manufactured by two different processes: electrochemical fluorination (EFC) and telomerisation. The brief description below is extracted from Buck et al. (2011).

Electrochemical fluorination (ECF) is a technology in which an organic raw material (e.g. octane sulfonyl fluoride) undergoes electrolysis, leading to the replacement of all the H atoms by F atoms. The free-radical nature of the process leads to carbon chain rearrangement and breakage, resulting in a mixture of linear and branched perfluorinated isomers and homologues of the raw material as well as perfluorocarbons and other species. The ECF process has traditionally been used to produce PFOS (via POSF) and PFOA (via perfluorooctanoyl fluoride). Today the ECF process is, among other functions, used to produce products based on perfluorobutane.

Telomerisation is a technology in which a perfluoroalkyl iodide (PFAI) is reacted with tetrafluoroethylene (TFE), to yield a mixture of perfluoroalkyl iodides with longer perfluorinated chains. The starting iodide is referred to as the “telogen” and the TFE as the “taxogen.” The product perfluoroalkyl iodide mixture is often then reacted further, in a second process step, where ethylene is inserted. The perfluoroalkyl commonly known as Telomer A, resulting from telomerisation, the 1st step, and the “fluorotelomer iodides”, commonly known as Telomer B, formed in the 2nd step, are raw material intermediates used to produce additional building blocks that are further reacted to create a family of “fluorotelomer-based” surfactant and polymer products. When a linear telogen and taxogen are employed in the telomerisation process, the resulting perfluoroalkyl iodides have exclusively linear perfluoroalkyl chains. Mainly linear substances are produced by the process, but branched substances may be formed if a branched telogen is employed and reacted with the TFE.

The total emission of POSF from the manufacture of 122,500 tonnes POSF (including waste) from 1970 to 2002 is estimated at 650-2,600 tonnes, while the emission of PFOS is estimated at 6.5-130 tonnes.
According to the most recent OECD survey, total releases of PFOS (and related substances) to the environment (incl. off-site landfill, underground injection and water treatment) from the manufacture by seven companies in five countries replying to the survey was <1.5 t/y in 2009. The release to the environment of other PFCs was <5.5 t/y of PFOA, <6.0 t/y of PFOA ammonium salt and perfluoroctyl iodide (in total) while the releases of C8:2 telomers were confidential.

Under the US EPA Stewardship Program, eight major companies operating in the USA have committed to reduce global facility emissions and product content of PFOA, precursor chemicals and higher homologue chemicals by 95% by 2010. The kg PFOA released per kg produced was in the 0.001-0.1 kg/kg range and the total releases in 2009 were reported to be 2-20 tonnes (US EPA, 2011).

Fluorotelomer alcohols (FTOHS) are used as intermediates in the production of other fluorotelomers and side-chain-fluorinated polymers. Fluorotelomer alcohols are volatile and the main sources are the manufacture and use of fluorotelomer-based products. No specific data on emissions of FTOHs from manufacturing processes have been identified.

3.2.6 Impurities in products
PFOA and other PFASs may be present as impurities in a variety of products. The focus has so far mainly been on PFOA and FTOHs.

PFOA in fluorotelomers
PFOA and other PFCAs may be found at very low trace levels in some fluorotelomer products as a by-product of their synthesis and as a result of residuals/precursors breaking down to PFCAs.

The total amount of PFOA as impurity in fluorotelomer products from non-US based production locations was reported to the US EPA PFOA Stewardship Programme at <50 kg/y while the total content of PFOA, PFOA precursors and higher homologues was 1 t/y (US EPA, 2011).

Residual PFOA and related substances in fluoropolymer resin products range between 0-150 mg/kg and 5-3000 mg/kg in the fluoropolymer dispersion products of the non-US based production locations. Reductions of PFOA, PFOA salts and higher homologues of PFOA in fluoropolymer dispersion products are reported as between 54% and 100% in the EPA’s 2009 summary tables (US EPA, 2011).

Dupont reports that it has been possible to reduce the PFOA content in aqueous-based dispersions from 1,000-5,000 ppm to a level below 50 ppm (Shelton, 2009).

Environment Canada has made an agreement with the fluorinated products industry (some of the same companies participating in the US EPA Stewardship Program) to work towards the elimination of residual perfluorooctanoic acid (PFOA), residual long chain PFCAs and residual precursors in their fluorochemical products sold in Canada. Compared to a 2004 baseline, the reduction in 2009 was in the range of 23.6 to 99.9% depending on the company (Environment Canada, 2012c).

PFOA in PTFE and other fluoroplastics
PFOA has traditionally been used as a processing aid (surfactant) in the production of certain fluoropolymers and other grades of fluoropolymers and fluoroelastomers. The surfactant is removed when the fluoropolymer aqueous emulsion is dried. Residual surfactant may remain in the polymer and PFOA has been demonstrated to be present in articles with fluoropolymers, such as coated non-stick kitchen ware (Washburn et al., 2005). As part of the US EPA Stewardship Program (see section 2.5.3), the PFOA content of fluoropolymers has been reduced significantly in recent years. Guo et al. (2009) found the PFOA concentration of PTFE cookware in the USA in at a level of <1.5 to 4.4 ng/g which is lower than the 4-75 ng/g previously reported by Begley et al. (2005).
FTOHs and FTOs in fluorotelomers and fluorotelomer-based polymers

FTOHs or fluorotelomer iodide is used to make acrylate monomer, a fundamental building block for the polymeric products representing >80% of the fluorotelomer-based products manufactured and used worldwide (Prevedouros et al., 2006). The reaction of fluorotelomer alcohol to make fluorotelomer acrylate or methacrylate esters leaves 0.1-0.5 wt % unreacted residual FTOHs. Alternatively, reaction of fluorotelomer iodide with acrylic acid salt to form acrylate monomer results in 3-8 wt% FTOs (fluorotelomer) byproduct. The FTOHs and FTOs are present in the resulting sales products unless removed. Prevedouros et al. (2006) estimated that approximately 100 t each of FTOHs and FTOs were present annually in fluorotelomer-based products (Prevedouros et al., 2006). These substances may be released from the products and can be found in the indoor environment and in the atmosphere as described elsewhere in this report.

3.3 Manufacture and use of PFCs in Denmark

PFCs are not manufactured in Denmark.

The use of PFCs in Denmark has previously been surveyed in 2001 (Havelund, 2001), 2002 (Havelund, 2002) and 2008 (Jensen et al., 2008).

The 2008 survey was based on data from the Danish Product Register (retrieved in 2007) on the import, production and export of preparations used for professional applications combined with estimates on the use of substances not included in the register, and import of the substances with articles. As part of the survey an extensive consultation among trade organisations, manufacturers of the substances and downstream users within the main application areas was undertaken. However, hardly any quantitative information on the use of the substances for the different application areas was obtained from the market actors. Therefore the authors had to estimate the total content of marketed articles on the basis of knowledge of the quantities of traded articles and some assumptions on the PFASs content of the articles, based on information from the literature and specifications of PFASs containing agents from major manufacturers of these agents.

It has been beyond the scope of the current survey to prepare a full update of the 2008 survey; the focus is rather to discuss new findings that may influence the total picture regarding use of the substances in Denmark.

Trade organisations covering the main application areas and a few key market actors have been contacted as part of the survey as described for each application area in the following.

3.3.1 Manufacture, import and export of PFASs and side-chain-fluorinated polymers on their own and in mixtures

The combined nomenclature (CN) used for the import/export statistics in Denmark and the EU does not have any specific commodity codes (CN8 codes) for PFASs or mixtures containing PFASs. The substances and mixtures are included in more aggregated commodity groups.

Data was retrieved from the Danish Product Register in July 2012 in order to obtain an overview of current uses of the PFASs and side-chain-fluorinated polymers in mixtures and assess any trend in their use as compared with the 2008 survey. The data represents mainly 2011 figures.

The Product Register includes substances and mixtures used operationally and containing substances classified as hazardous in a concentration of at least 0.1% or 1% (depending on the classification of the substance). Only PFOS and derivatives have a harmonised classification (see section 2.1.1), and for the other non-classified substances the registration will only occur, if they are con-
stituents of products, which are classified and labelled as hazardous due to the presence of other constituents. The data consequently do not provide a complete picture of the presence of the substances in mixtures placed on the Danish market. Furthermore, for substances included in mixtures used for production of mixtures in Denmark (e.g. included in raw materials used for production of paint) the quantities may be doubly-accounted for as both the raw material and the final mixture are registered. The amounts registered are for occupational use only, but for substances used for the manufacture of mixtures in Denmark the data would still indicate the quantities of the substances in the final mixtures placed on the market both for professional and consumer applications.

The results of the data retrieval by substance are shown in Annex 3 together with the data from the 2008 survey. The annex also briefly describes how the list of substances was generated.

The data can further be summarised as follows:

- In total 54 PFCs were registered in the Product Register in 2012 against 92 substances in the 2008 survey.
- The total registered quantity was 3.3 tonnes, 13.2 tonnes less than the 16.5 tonnes registered in the 2008 survey.
- 48 of the substances registered in 2007 were not registered in 2012;
- 11 of the substances registered in 2012 were not registered in the 2007 survey, partly because they were not included in the 2006 OECD list used for this survey. The total import + production of these 11 substances was 0.2 tonnes while 0.0 tonnes was exported. For all except one substance the data are confidential.
- For 21 substances in the 2012 survey, the data were confidential. The total quantity for these substances was 0.2 tonnes.
- None of the substances in the database of registered substances or the list of 2013 intentions, which are not on the OECD 2007 list, were registered in the Product Register.

Five of the seven substances with highest registered quantity, which account for 83% of the total registered consumption, are shown in Table 13. Two substances for which the quantity is confidential are not indicated.

None of the substances are registered under REACH or on the list of the 2013 intentions. Three of the substances are not pre-registered, probably because they are polymers and not subject to registration under REACH. Four of the substances are side-chain-fluorinated polymers.

Besides these side-chain-fluorinated polymers, the mixtures in the Product Register may also contain fluoropolymers, which are beyond the scope of the OECD surveys and this study, because they are not considered precursors of PFASs. Three substances identified in the Jensen et al. (2008) (but not included in the data retrieval in the Product Register in the study) were included in the data retrieval for this study, but the data are not included in the list of substances in Annex 3. Tetrafluoroethylene polymer (CAS No 9002-84-0) in PTFE polymer-based waxes was registered in 168 products used for various applications with a total of 12 tonnes. Most likely more mixtures with fluorinated polymers are used, and the total quantity may be significantly higher than the quantities of the side-chain-fluorinated polymers. This situation illustrates the necessity to clearly distinguish between the different types of polymers.
### TABLE 13
FIVE OF TOP SEVEN SUBSTANCES REPRESENTING 88 % OF THE TOTAL TONNAGE REGISTERED IN THE PRODUCT REGISTER IN 2012

<table>
<thead>
<tr>
<th>CAS No</th>
<th>Chemical name (as indicated in OECD, 2007)</th>
<th>OECD class</th>
<th>Number of products</th>
<th>Production and import, t/y</th>
<th>Export, t/y</th>
<th>Application areas *1</th>
<th>REACH</th>
</tr>
</thead>
<tbody>
<tr>
<td>143372-54-7</td>
<td>Siloxanes and silicones, (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10, 10,10- heptadecafluorodecyl)oxy Me, hydroxy Me, Me, octyl, ethers with polyethylene glycol mono-Me ether</td>
<td>Fluorosiloxane/silicone/silanes (F12), C8</td>
<td>84</td>
<td>1.9</td>
<td>1.3</td>
<td>Paint, lacquer and varnishes</td>
<td>Not pre-registered</td>
</tr>
<tr>
<td>65545-80-4</td>
<td>Poly(oxy-1,2-ethanediyl), α-hydro-ω-hydroxy-, ether with α-fluoro-ω-(2-hydroxyethyl) poly(difluoromethylene) (1:1)</td>
<td>Fluoro ether (F6), n *1</td>
<td>10</td>
<td>0.9</td>
<td>0.0</td>
<td>Paint, lacquer and varnishes</td>
<td>Pre-registered</td>
</tr>
<tr>
<td>24448-09-7</td>
<td>1-Octanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-N-methyl(MeFOSE)</td>
<td>PFOS, C8</td>
<td>21</td>
<td>0.5</td>
<td>0.08</td>
<td>Paint, lacquer and varnishes</td>
<td>Pre-registered</td>
</tr>
<tr>
<td>65530-70-3</td>
<td>Poly(difluoromethylene), α, α’-[phosphinicobis(oxy-2,1-ethanediyl)]bis[ω-fluoro-, ammonium salt</td>
<td>Fluoro phosphate (F8), n *1</td>
<td>19</td>
<td>0.3</td>
<td>0.0</td>
<td>Paint, lacquer and varnish, polishing agents</td>
<td>Not pre-registered</td>
</tr>
<tr>
<td>65530-69-0</td>
<td>Poly(difluoromethylene), α-[2-[[(2-carboxyethyl)thio]ethyl]-ω-fluoro-, lithium salt</td>
<td>Fluoro thioether (F14)</td>
<td>17</td>
<td>0.2</td>
<td>0.2</td>
<td>Polishing agents, cleaning/washing agents</td>
<td>Not pre-registered</td>
</tr>
</tbody>
</table>

*n Notation from the OECD list (OECD, 2007), “n” presumably indicate a polymer of various lengths.

*1 As indicated for Denmark in the SPIN database of the Nordic Product Registers. Most of the substances are also used for confidential applications.

### PFOS and related substances
Six of the registered substances are included in the OECD classes of PFOS and PFOS/PFAS. The total registered production and import was 0.52 tonnes while the registered export was 0.08 tonnes. Of this MeFOSE (CAS No. 24448-09-7) shown in the table above accounted for 85%. The substance with the CAS No 68298-62-45, with a registered consumption of 0.04 t/y in 32 mixtures, is a multiconstituent substance and included in the OECD class PFOS/PFOA. It contains CsF;SO2-moieties and is consequently subject to restriction. The main registered application area is paint, varnishes and lacquers.

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5 2-Propenoic acid, 2-[butyl [(heptadecafluorooctyl)sulfonyl]amino]ethyl ester, telomer with 2-[butyl[[pentadecafluoroheptyl)] sulfonyl]amino]ethyl 2-propenoate, methyl oxirane polymer with oxirane di-2-propenoate, methyl oxirane polymer with oxirane mono-2-propenoate and 1-octanethiol
Tetraethylammonium perfluorooctanesulfonate (CAS no. 56773-42-3) is used for non-decorative chromium (Poulsen et al., 2011), one of the exempt applications further described below, but the total quantity is confidential.

The total registered consumption of the PFOS and PFOS/PFAS substances in the 2008 survey was 2 tonnes.

As mentioned below, the total identified consumption of PFOS for exempt applications in Denmark was estimated at 0.020-0.028 t/y in 2010. The discrepancy between this amount and the 0.5 tonne registered in the Product Register may be due to inadequate update of the notifications or uses not in compliance with the POP Regulation.

**PFOA and related substances**
The total registered production and import of substances in the OECD class PFOA was 1 kg. The consumption of substances from this class was also insignificant in the 2008 survey.

The main issue with regard to PFOA is consequently to what extent some of the registered fluorotelomers and side-chain fluorinated substances may contain perfluorinated moieties that may be precursors for PFOA when the substances degrade.

**Side-chain fluorinated polymers**
Fourteen of the registered substances include “poly” in the substance name. In total these substances accounted for 77% of the total consumption. The major application areas were paint, lacquers and varnishes, polishing agents and cleaning/washing agents.

**Other substances**
Fluorotelomers and short-chained PFAS in total accounted for 0.2 t/y corresponding to 7% of the total. The actual substances and applications are confidential.

**3.3.2 End-use of PFASs in articles and mixtures**
The total registered quantities of the substances by application area are shown in Table 14. The table includes the minimum and maximum estimates of the quantity of the substances in end-products from the 2008 survey. The minimum estimate was mainly based on data from the Product Register and is thus comparable with the 2012 data shown. For paint, however, the data from the Product Register were used as the maximum estimate. The maximum estimate was based partly on the data from the Product Register, partly on expert estimates based on knowledge on tonnage of articles and mixtures and some assumptions regarding the likely content of the fluorinated substances.

The total registered quantity in 2012 is 3.2 tonnes. Two of the major registered application areas in the 2008 survey were releasing agents and glues, which accounted for more than half of the registered quantity. In 2012 the registered consumption for these application areas was close to zero.

For some of the application areas the registered consumption was higher in 2012: cleaning agents, impregnating agents and soldering agent. For some of the registered use areas in 2012, the 2008 survey did not indicate any use, such as fuel additives and process-regulating agents.

For two major application areas, carpets and impregnated clothing, the 2008 survey did not base the estimates on the Product Register data, but on general knowledge of the use of these substances for the manufacturing of such articles.

For paint and lacquers, polish and car-care products it was assumed that the substances were present in mixtures which were not notified to the Product Register because they do not contain con-
stituents classified as hazardous. For many of the use areas it was assumed that the total quantity was higher than the minimum estimate but no data were available to make any qualified estimates.

The total in 2007 was estimated at 38 tonnes. Considering that the global production of fluorotelomers and telomer-based substances is estimated at 11,000 to 14,000 t/y, and that these account for the majority of global use of the substances concerned, it can be assumed that the total consumption in Denmark with end-products would be in the range of 10 to 100 tonnes.

TABLE 14
TOTAL ESTIMATED QUANTITY OF PFCs IN END-PRODUCTS IN 2007 AND QUANTITY REGISTERED IN THE PRODUCT REGISTER IN 2012

<table>
<thead>
<tr>
<th>Use area</th>
<th>Estimated quantity of PFCs in end-products in 2007, kg/y</th>
<th>Quantity registered in the Product Register in 2012 *1 kg/y</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min. estimate</td>
<td>Max. estimate</td>
</tr>
<tr>
<td>Releasing agents</td>
<td>7,200</td>
<td>&gt;7,200</td>
</tr>
<tr>
<td>Paint, lacquers and varnishes</td>
<td>100</td>
<td>3,500</td>
</tr>
<tr>
<td>Printing inks</td>
<td>15</td>
<td>&gt;15</td>
</tr>
<tr>
<td>Adhesives</td>
<td>2,500</td>
<td>&gt;2,500</td>
</tr>
<tr>
<td>Surface active agents</td>
<td>1,100</td>
<td>&gt;1,100</td>
</tr>
<tr>
<td>Cleaning agents</td>
<td>100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Polish and care products</td>
<td>170</td>
<td>590</td>
</tr>
<tr>
<td>Auto polish and wax</td>
<td>0.08</td>
<td>358</td>
</tr>
<tr>
<td>Floor polish</td>
<td>0.24</td>
<td>60</td>
</tr>
<tr>
<td>Carpets</td>
<td>745</td>
<td>18,000</td>
</tr>
<tr>
<td>Sunshades/awnings, tents, umbrellas, parasols etc.</td>
<td>not estimated</td>
<td>not estimated</td>
</tr>
<tr>
<td>Impregnated clothing</td>
<td>400</td>
<td>3,500</td>
</tr>
<tr>
<td>Footwear</td>
<td>not estimated</td>
<td>not estimated</td>
</tr>
<tr>
<td>Impregnating agents</td>
<td>170</td>
<td>340</td>
</tr>
<tr>
<td>Impregnation agents for footwear only</td>
<td>12</td>
<td>24</td>
</tr>
<tr>
<td>Impregnation agents for car/ textiles only</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Galvano-technical products</td>
<td>760</td>
<td>&gt;760</td>
</tr>
<tr>
<td>Fire inhibitors</td>
<td>400</td>
<td>&gt;400</td>
</tr>
<tr>
<td>Pesticides</td>
<td>180</td>
<td>&gt;180</td>
</tr>
<tr>
<td>Soldering agents</td>
<td>280</td>
<td>&gt;280</td>
</tr>
<tr>
<td>Other surface treatment agents for metal</td>
<td>not indicated</td>
<td>not indicated</td>
</tr>
<tr>
<td>Fuel additives</td>
<td>not indicated</td>
<td>not indicated</td>
</tr>
<tr>
<td>Process-regulating agents</td>
<td>not indicated</td>
<td>not indicated</td>
</tr>
<tr>
<td>Application not indicated and other</td>
<td>not indicated</td>
<td>not indicated</td>
</tr>
<tr>
<td>Total</td>
<td>14,120</td>
<td>&gt;38,465</td>
</tr>
</tbody>
</table>

*1 Registered consumption with the mixtures placed on the market in Denmark = production + import – export

*2 Agents used for manufacturing of these articles may be included in the group “impregnating agents”.

*3 It is known that PFCs are used in galvano-technical products, but they are not indicated as such in the Product Register. May be included in the product group “process-regulating agents”.

Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances
As mentioned it has been beyond the scope of this study to prepare a full update of the survey, but readily available newer information is briefly discussed in the following.

**Hard chromium plating**
PFOS is used in non-decorative hard chromium plating in Denmark which is one of the exempt applications of PFOS. Around the year 2010, 10-28 kg of PFOS was used annually in hard chromium plating in Denmark (Poulsen et al., 2011). In hard chromium plating, a thin layer of chromium is applied electrochemically to the surface of metals. The PFOS substances were used to limit the formation of Cr (VI) aerosols, which are considered of concern in terms of both occupational health and safety and the environment. The most commonly used PFOS substance for this purpose was tetraethylammonium perfluorooctanesulfonate (CAS no. 56773-42-3). This chemical substance is typically found in preparations with a concentration of 5-10%; e.g. Fumetrol® 140. Some users were contacted in May 2012 as part of the preparation of the updated national implementation plan for the Stockholm Convention. PFOS is still being used for this purpose by about 5 companies in Denmark, and there are currently no plans to phase out PFOS. PFOS is used in recirculating systems without wastewater drainage outlet. The substances are decomposed gradually in the baths, which are subsequently disposed of to the hazardous waste treatment plant, Kommunekemi.

In a project under the programme "Miljøeffektiv Teknologi – Substitution af problematiske kemikalier" (Environmentally efficient technology - substitution of chemicals of concern) (Poulsen et al. 2011), feasible chemical and physical alternatives to PFOS were developed with support from the Danish EPA in 2009-2011. Several chemical and physical alternatives were evaluated. The results showed that a 6:2 fluorotelomer substance 1H,1H,2H,2H perfluorooctane sulfonic acid (Fumetrol® 21, CAS No. 27619-97-2) in a large scale test:

- works as effective as PFOS as mist suppressing agent,
- seems to have the same durability as PFOS as mist suppressing agent,
- has the same price level as PFOS as mist suppressing agent,
- can be substituted right away, when PFOS is burnt out in the chrome bath, without the need of changing the entire chrome bath chemicals, and
- is an environmental improvement as it is less persistent, less bioaccumulative, and less toxic than PFOS (Poulsen et al., 2011).

**Paint and lacquers**
The data from the Product Register demonstrates that the fluorinated substances are widely used as surfactants in paint.

The trade organisation Danmarks Farve- og Limindustri (DFL, Danish Paint and Adhesives Industry) was contacted. An enquiry to the members revealed that the fluorinated substances were not used as substances on their own in the industry, but are likely to be present in some of the imported raw materials. The 2008 survey describes the discrepancy between the registered quantities in the Product Register (3.5 tonnes) and answers from the industry which did not recognise the fluorinated substances registered in the Product Register. For this reason the total quantity in paints was estimated at 100 kg, a minimum estimate.

A likely explanation is that the fluorinated substances are included in raw materials, but not specified in safety data sheets as the substances are used in concentrations below 0.005%. The registered quantities have remained at a level of several tonnes, making it likely that it reflects actual use in Denmark.

**Impregnated clothing**
As mentioned in section 3.2.4, the production of apparel is estimated to consume around 50% of the global production of fluorotelomer-based substances. It is further indicated that in 2009 approxi-
mately 10,000 tons of fluorinated finishing agent (the quantity in terms of fluorinated substances is not indicated) were imported to China for the production of apparel and other textile products.

The fluorinated agents are typically used for clothing for outdoor uses to make the clothing water and soil repellent. It was reported that about 400 kg fluorinated substances being used for impregnation of textiles in Denmark (excluding carpets) in the 2008 survey. The average content of fluorinated substances in the agents was about 17%. However, the majority of the impregnated textiles is imported and in 2007, the production was 15-20% of the imported amounts.

The main issue is to what extent PFASs are present in trace concentrations in the textiles or formed from side chains released from the fluorinated polymers. The 2008 survey (Jensen et al., 2008) quoted Norwegian and Swedish investigations of PFASs in all-weather jackets showing an unbound content of fluorotelomer alcohols (FTOH) of 25 to 1000 µg/m² of textile, an unbound content of PFCA between <5 and 400 µg/m² of textile and an unbound content of PFOS-related compounds between <5 and 100 µg/m² of textile (Schulze and Norin, 2006; Berger and Herzke, 2006 as cited by Jensen et al., 2008).

A study of PFASs in 11 textiles (mainly all-weather apparel) marketed in Norway by the Norwegian Pollution Control Authority (SFT, 2006) found the following levels of unbound PFASs in the textiles (number of samples with detectable content of the substances indicated in bracket): FTOH: 0-10,683 µg/m²(10), FTS/-FTCA: 0-6 µg/m²(7), PFSAs :0-31 µg/m²(9), PFCAs :3-170µg/m²(11), FASA/-FASE:0-23µg/m²(8), PFOS: <0.02-30 µg/m²(9), PFOA: 0.4-34 µg/m²(11).

A recent report by Greenpeace (2012) has found similar levels in 13 items of outdoor clothing from major brands purchased in Germany, Austria and Switzerland. The highest concentration of PFOA was 5 µg/m² while the total sum of the analysed PFCAs reached 11 µg/m². The highest concentrations for the FTOHs were 352 µg/m² 6:2 FTOH and 240 µg/m² 8:2 FTOH. PFOS was not detected in any of the samples.

Similar levels as cited above can be expected to be found in outdoor clothing marketed in Denmark by major brands.

**Carpets**

Carpets have historically been the major application area for PFOS in the EU. The 2008 survey estimated that carpets may likely be the major application area of the fluorinated substances in Denmark. It was confirmed by manufacturers of carpets that fluorinated agents were used for the carpets, and it was assumed that between 56 and 90% of the carpets in Denmark were impregnated with fluorinated substances, but information on which specific substances were used was not obtained.

A major supplier of fluorinated substances for carpets has been contacted but no specific information has been obtained.

**Packaging**

The 2008 survey did not specifically estimate the total use of the substances for packaging which was not within the scope of the survey. The use for packaging may have been included in the aggregated group “surface active substances”. On a global scale, coatings, including those for paper products, are the third largest category of consumer product uses of fluorotelomer-based substances. In particular the use of the substances for food contact materials, and the possible consumer exposure to the substances in the packaging, has been intensively studied in recent years.

A recent Danish study explored the identity of a range of polyfluorinated surfactants used for food contact materials, primarily to impart oil and water repellancy to paper and board. More than 115 molecular structures were found in industrial blends from the EU, USA and China, belonging to the groups of polyfluoroalkyl-mono and diester phosphates (monoPAPS, diPAPS and S-diPAPS),-ethoxylates, -acrylates, -amino acids, -sulfonamide phosphates and -thio acids, together with residuals and synthesis byproducts. In addition, a number of starting materials such as perfluorooctane
sulfonamide N-alkyl esters were analysed. Dialkylated and trialkylated PAPS and S-diPAPS were found in migrates from European food contact materials (Trier et al., 2011).

In fourteen screened food-contact materials collected in Denmark, both diPAPS and S-diPAPS were identified above the detection level in four of the materials while one of the materials contained diPAPS only (concentrations not indicated). In popcorn migrates, diPAPS and S-diPAPS was detected semi-quantitatively at 0.2–0.7 mg/kg food which correlate well with levels found in studies from the USA (Trier et al., 2011).

In 2012, the Danish Veterinary and Food Administration screened 84 food-contact materials for the presence of PFASs (DVFA, 2012c). In 41 of the materials, the screening indicated that the substances were not present. The remaining 43 materials were subsequently analysed for 36 PFASs.

The substances were divided into two groups of substances: those which can be degraded to PFOA and PFCA, and those which can be degraded to PFOS and PFSA. None of the materials contained substances that can be degraded to PFOS and PFSA. Most of the 43 materials contained PFOA/PFCA precursors in the µg/kg range while three materials contained more than 1 mg/kg of the substances, calculated as total PFOA equivalent to 1.5 mg/kg, 2.2 mg/kg and 10.2 mg/kg respectively. In these materials the main PFASs were 6:2/8:2 DiPAPs, 8:2 FTOH and 10:2 FTOH.

In a study of migration of PFASs from food contact materials, the Danish Veterinary and Food Administration analysed the content of PFCAs, PFSAAs, FTOHs, monoPAPs, diPAPs and S-diPAPS in 66 samples of paper and cardboard (DVDA, 2012d). In 10 of the samples, the concentration of one or more PFASs was above the detection limit. For these 10 samples, migration to the food and to a food simulator of 50% ethanol was measured. The migration of the substances to the simulator was generally higher than the migration to the food items. The highest migration was found originating from packaging and parchment paper to cakes. Migration of PFASs from the packaging or parchment paper to the cakes was detected for all five cake samples. In one of the samples, migration of six different PFAS was found. In popcorn popped in packaging with a content of PFHxA and PFBA, the latter substance was found in a concentration of 24 µg/kg popcorn. In another popcorn sample, the packaging contained FTOH and other FPASs, but these substances could not be detected in the popcorn after it was popped. No migration from the packaging to coffee and flour could be detected.

In response to the results demonstrating the presence of a wide range of PFASs in packaging, the Danish trade organisation for the packaging industry “Emballageindustrien” (Emballageindustrien, 2012) undertook a survey of PFASs used in food-contact packaging materials in late 2011. The survey covered 85% of the members of the trade organisation which produce food-contact packaging. The survey included paper, cardboard and printing inks used for manufacture. According to the survey, the food-contact packaging produced in Denmark does not contain PFAS. However, it is indicated that some of the suppliers of cardboard use PFASs of the type that are recommended by the German Federal Institute for Risk Assessment (BfR) on paper and board for food contact (BfR, 2012). The recommendation lists 14 fluorinated substances with a maximum content in the range of 0.4–1.2% based on dry fibres weight, depending on the actual substance. The substances are mainly polymers and co-polymers based on short-chain fluorochemicals.

The trade organisation has been contacted as part of the present survey in order to obtain more information on the actual substances and quantities used, but specific data have not been obtained.

Cleaning products
A survey of the chemical substances in cleaning products for ovens, cookers and ceramic hobs from 2010 did not find PFOS the four mixtures analysed for the content of PFOS (Andersen et al., 2010).
Fire extinguishers
PFOS-related substances have traditionally been used in fire fighting foams in Denmark as well as other countries (Havelund, 2002). The remaining PFOS-containing foams were allowed to be used until June 2011. Investigation of sites contaminated by the former use of fire extinguishers is addressed by the Danish action plan for PFOS (section 2.4.1).

In the 2008 survey, 400 kg/y of PFCs were registered for use in fire-fighting foams. In 2012 three different PFCs were registered as used for this application area in the Product Register, but names of the substances and the registered quantities are confidential. According to a study of alternatives to PFOS and PFOA from 2005, both PFC-based fire-fighting foams and fluorine-free foams were used in Denmark at that time (Poulsen et al., 2005). It was indicated that a significant amount of the foams came from the company Solberg Scandinavia which still market fire-fighting foams with PFCs and fluorine-free foams. The foams were based on C6 fluorinated compounds (e.g. dodecafluoro-2-methylpentan-3-one, a mixture of different C6 fluorinated telomers possibly containing some C8 fluorinated compounds as well) and protein-based foams or synthetic detergent foams (Poulsen et al., 2005). It has not been attempted to make an updated survey of the use of PFCs in fire-fighting foams.

Trace content of PFOS in products
A Norwegian study analysed PFOS and other PFAS in 30 consumer products in 2009 (Herzke, 2012). Notably, PFOS, which has been strictly regulated in Norway since 2007 and is regulated in the EU, was found in amounts close to or exceeding the EU regulatory level in 4 of the 30 analyzed products, all within the leather or carpet product groups. Two pooled (n=8) leather samples (38 and 21.2 µg/m²) exceeded the EU regulatory level of 1 µg/m², whereas two pooled (n=4) carpet samples (0.7 and 1.04 µg/m²) were close to the regulatory limit. One of the carpets was labelled as Teflon®, which is a PTFE fluoropolymer, but it apparently contained PFOA 6:2 FTS, PFHxS, PFHxA, PFHpA and PFOA at trace levels.

A recent report by Greenpeace (2012) did not find PFOS-related substances in any of the samples of outdoor garments.

The Norwegian results indicate that many textiles or other coated materials which are coated with a fluoropolymer or other fluorinated agents may contain PFOS above the limit value of 1 µg/m².

3.4 Summary on the use of PFCs in the EU and Denmark
Table 15 summarises information on the use of PFCs at EU level and consumption of the substances registered in the Danish Product Register in 2012.

The consumption of PFOS, PFOA and APFO at EU level has recently been surveyed in studies for the European Commission. Limited information is available at EU level on the use of PFCs other than PFOS and PFOA by application area. The registrations under REACH provide limited information on the current use of the substances in the EU. Apart from PFOS and some derivatives, the substances do not have a harmonised classification and all substances are apparently imported or produced in tonnages below 1,000 t. After 2013 more information will be available, as companies have notified of their intentions for registration of 12 substances more. It is, however, unclear how fluorinated side chains of imported side-chain-fluorinated polymers, which are not subject of registration, are pre-registered.

The total registered tonnage is in the range of 15-150 t/y, but the total consumption of PFCs with end-uses, considering global production, is likely in the 2,000-4,000 t/y range (excl. of fluortelomers used as intermediate in the production of fluortelomer-based polymers in order to prevent double counting).

The international industry organisation FluoroCouncil are not able to provide aggregated data on consumption by substance group at EU level. More information would be needed to assess the use of the substances at EU level and monitor any changes from long-chain fluorochemistry to short-chain (e.g. ECHA, 2012g).

In Denmark, the total consumption with mixtures registered in the Product Register has decreased from 16.5 tonnes in 2007 to 3.2 tonnes in 2012. A significant part of the decrease was due to a decrease in the use of “releasing agents” from 7.2 t/y to nearly zero. Of the 3.4 tonnes in 2012, side-chain-fluorinated polymers accounted for 77% of the total. Of the 92 substances registered in 2007, 48 substances were not registered in 2012, while 11 new substances were registered in 2012. Notably 0.5 tonnes of PFOS-related substances were registered for uses not in compliance with the restrictions of the POP Regulation.

The actual consumption in Denmark in mixtures is probably significantly higher than the quantity registered in the Product Register, as notification of the register is only required for mixtures defined as hazardous. Areas with a significant consumption not registered could be agents for treatment of carpets and textiles, water-based paints and adhesives, and fire-fighting foams.

The total quantity of PFC in end-products in Denmark has not been updated, but it is expected that the total quantity for the main application areas may be at the same level as in 2007. The total in 2007 was estimated to be in the range of 14 to in excess of 34 t/y (no upper limit indicated). The major application areas were estimated to be releasing agents (probably used in the plastics industry), surface active agents (probably used for production of articles), paint, lacquers and varnishes, adhesives, carpets, impregnated clothing, and galvano-technical products (probably surfactants used in the industry). A significant part of this total may be imported in clothing (taking up 50% of global consumption), carpets, packaging and other articles treated with PFCs.
**TABLE 15**
CONSUMPTION OF THE PFCs IN THE EU AND DENMARK

<table>
<thead>
<tr>
<th>Substance group</th>
<th>EU</th>
<th>Denmark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Estimated consumption in 2011, t/y</td>
<td>Use areas, remark</td>
</tr>
<tr>
<td>PFOS and related substances</td>
<td>8</td>
<td>Metal plating industry (81%)</td>
</tr>
<tr>
<td></td>
<td>Registrations : 1-10</td>
<td>Photographic industry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Semiconductor industry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydraulic fluids in aviation industry</td>
</tr>
<tr>
<td>PFOA and APFO</td>
<td>25-50</td>
<td>Fluoropolymer production (majority)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photographic industry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Semiconductor industry</td>
</tr>
<tr>
<td>Longer chained PFCAs and related substances</td>
<td>no data</td>
<td>no data</td>
</tr>
<tr>
<td>Short-chain PFASs</td>
<td>Registrations : 30-130</td>
<td>Limited data: Surfactants, reactive processing aids</td>
</tr>
<tr>
<td></td>
<td>Probably significantly higher</td>
<td></td>
</tr>
<tr>
<td>Fluorotelomers</td>
<td>No registrations</td>
<td>Probably same as world market: Textiles and apparel (50%)</td>
</tr>
<tr>
<td>Side-chain-fluorinated polymers</td>
<td>Probably some 2,000-4,000 based on world-wide consumption</td>
<td>Coatings, including those for paper products</td>
</tr>
</tbody>
</table>

*1 Not registered in the Product Register. Data from Poulsen et al., 2011.
4. Waste management

4.1 EU
Detailed information is available on PFOS in waste at EU level, whereas limited information has been identified on other PFASs in the waste streams at EU level.

4.1.1 PFOS in waste
This section is mainly based on selected information contained in the report prepared by the ESWI consortium on behalf of the European Commission, DG Environment, “Study on waste related issues of newly listed POPs and candidate POPs” (ESWI, 2011).

In the past, perfluorooctane sulfonic acid and its derivatives have been used for a wide range of products and processes. Among these uses are pesticides, plumbing fluxing agent, medical applications and devices, flame retardants, coatings and coating additives, adhesives as well as uses in rubber and plastics, upholstery, and the leather and carpet industries.

At present, PFOS is used in the metal plating industry, as content in hydraulic fluids in the aviation industry, in the photographic industry and the semiconductor industry as described in section 3.2.

Current PFOS uses in metal plating and photographic industries, as well as use in hydraulic fluids in the aviation industry, are considered relevant sources of PFOS to waste. In case of the photographic industry there has been a continuous reduction of the use of PFOS, but due to the existing storages of pictures in households or x-rays in hospitals, this application area generates a relevant PFOS-containing historical waste stream. The current use of PFOS in the semiconductor industry is not considered relevant for waste.

With respect to past uses, upholstery and carpets are considered relevant due to their long lifetime regarding PFOS entering the waste stream.

Industries with products having a shorter lifetime, such as textiles, paper and cardboards, do not significantly influence the current waste stream anymore, even if they still contribute to current and future PFOS emissions, in particular as releases from waste disposal or contaminated sites. Industries which used PFOS during their production processes with end-products not containing PFOS, such as the mining industry, do not pose a current input of PFOS to waste streams.

The results of ESWI (2011) are summarised in Table 10. According to the study, generally there was a considerable drop in the use of PFOS in the EU in the period from 2000 to 2004, where many uses of PFOS ceased before the use PFOS for the applications was restricted at EU level. Articles in use in society will therefore primarily be articles with relatively long lifetimes, such as leather furniture and carpets made of synthetic fibres. The EU study calculates specific amounts in the waste stream from leather furniture and carpets. The study indicates that use of PFOS for the two product groups ceased in 2002.

In the years up to 2002, an estimated 146 tonnes of PFOS per year were used for production of carpets in the EU27, and the average concentration of PFOS in PFOS-impregnated carpets was 88 mg/kg. It is also estimated that about 146 tonnes per year of PFOS will be disposed of in the period...
from 2012 to 2016 in a waste volume of 1.9 million carpets (both with and without PFOS) with an average content of 75 mg/kg.

In the years up to 2002, about 6 t/y of PFOS were used in the EU27 for leather furniture, and in 2010 a corresponding amount was disposed of with this furniture in a total waste volume of about 71,000 tonnes of upholstered furniture (both with and without PFOS) with an average content of PFOS of 2.4 mg/kg. Calculations in the study assume PFOS concentrations in leather furniture of typically around 80 mg/kg (in the furniture where PFOS was used in production). Calculations in the study also assume an average lifetime of 10 years for the articles and that everything will have been disposed of by 2012. Considering the uncertainty of the lifetime estimates and the fact that the leather articles are generally expensive, there may still be amounts to be disposed of in 2012 and the following years.

Certain types of fire-extinguishing foam produced before 2002 may contain PFOS. Based on information on the operational lifetime of fire extinguishing foam, the EU study estimates that the amounts of PFOS in fire extinguishing foam stored in the EU fell from 122 tonnes in 2004 to about 84 tonnes in 2011, and that at the cut-off date on 27 June 2011, between 54 and 87 tonnes of PFOS in fire extinguishing foam were still being stored. After this date the fire extinguishing foam containing PFOS was to be destroyed. However, some stocks of PFOS containing fire fighting foams remain in the EU, but are in the process of disposal (EC, 2012).

### Table 1
**PFOS in Articles in Use and in Waste in the EU (ESWI, 2011 as summarised by Danish EPA, 2012)**

<table>
<thead>
<tr>
<th>Articles</th>
<th>Amounts used in the EU</th>
<th>Lifetime</th>
<th>Amounts in articles in use in the EU in 2012</th>
<th>PFOS concentration in waste</th>
<th>PFOS amounts in waste in the EU in 2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carpets</td>
<td>Before 2002, 146 tonnes of PFOS were used annually in 1.7 million tonnes of carpets, i.e. the average content of PFOS in these carpets was 88 ppm.</td>
<td>14 years</td>
<td>About 584 tonnes of PFOS in 2012, corresponding to 4 years consumption in the period up to 2002.</td>
<td>It is assumed that the concentration of PFOS in the total amount of carpets disposed of is 75 ppm as not all carpets contain PFOS</td>
<td>About 146 tonnes of PFOS in a total waste fraction of 1.9 million tonnes of carpets (will continue at this level until 2016).</td>
</tr>
<tr>
<td>Leather upholstery in furniture and car interiors</td>
<td>Until 2002, about 5.7 tonnes of PFOS in 71,342 tonnes of leather upholstery were used annually (3% of the market for leather upholstery). Leather furniture is assumed to represent 50% whereas vehicles make up the remaining 50%.</td>
<td>10 years</td>
<td>0 tonnes (assuming that everything is disposed of by 2012).</td>
<td>PFOS represents about 0.04% of the used leather, and leather represents 20% of upholstery, i.e. PFOS represents 80 ppm in leather upholstered articles treated with PFOS</td>
<td>0 tonnes (assuming that everything is disposed of by 2012).</td>
</tr>
</tbody>
</table>
Overall substance flow

The management of the relevant waste streams related to PFOS’ specific occurrence is described in detail in the ESWI study (2011). The following figure shows the overall results of the PFO mass flow analysis showing the situation in 2010.

“In Product” represents the existing stock of the substance in product in use. Due to limited data for a number of sectors and countries, the mass flow is partly based on assumptions and extrapolation. However, the mass flow provides an impression of the dynamics of the PFOS flow to the environment and to waste and on the relative contribution of major relevant sectors related to PFOS.

It is important to consider that fire fighting foams had to be destroyed by 27 June 2011 and do not currently significantly contribute to the PFOS substance flow.

<table>
<thead>
<tr>
<th>Articles</th>
<th>Amounts used in the EU</th>
<th>Lifetime</th>
<th>Amounts in articles in use in the EU in 2012</th>
<th>PFOS concentration in waste</th>
<th>PFOS amounts in waste in the EU in 2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Other textiles, cardboard and paper</td>
<td>It is assumed that PFOS has been used for these but the volumes are not indicated.</td>
<td>Paper: 1 year</td>
<td>0 tonnes (assuming that everything is disposed of in 2012).</td>
<td>Not stated.</td>
<td>0 tonnes (assuming that everything is disposed of in 2012).</td>
</tr>
<tr>
<td>Fire extinguishing foam</td>
<td>About 18 tonnes/year until 2006. About 144 tonnes were accumulated in the EU in 2006.</td>
<td>15 years</td>
<td>0 tonnes (requirement that all stocks be destroyed as at 27 June 2011).</td>
<td>Typically 0.5-1.5% in the foam but there are also examples of concentrations up to 10%.</td>
<td>0 tonnes (requirement that all stocks be destroyed as at 27 June 2011).</td>
</tr>
</tbody>
</table>
**Contribution of the relevant sectors**

Table 16 shows the contribution of the different sectors to the European PFOS flow to emissions, products and waste.

Considering the current situation (i.e. without fire fighting foams), the table shows that the overall discharge of PFOS from the investigated sources in Europe to the environment and to waste accounts for about 158 t/y. Almost all of the PFOS is discharged to waste (157 t/y), whereas only a small fraction (0.41 t/y) reaches the environment.

Emission to the environment from current processes (0.4 t/y) is dominated by metal plating (90%). Other relevant source sectors are the photo industry (7 %) and hydraulic fluids from aviation (4%). The leather and carpet sector do not contribute to PFOS emissions to the environment. Losses during their lifetime have not been considered due to the lack of data.

PFOS discharge to waste is dominated by waste resulting from the carpet industry (93 %), followed by the leather industry (4%), metal plating (1%), sewage sludge (1%), photo industry (1%) and hydraulic fluids for aviation (0.5%).
TABLE 16
CONTRIBUTION OF THE RELEVANT SECTORS IN THE EU 27 TO PFOS IN EMISSIONS, PRODUCTS AND WASTE (BASED ON ESWI, 2011)

<table>
<thead>
<tr>
<th>Sector/Activity</th>
<th>Emission t/y</th>
<th>Product t/y</th>
<th>Waste t/y</th>
<th>Total t/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal plating</td>
<td>0.37</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Photo industry</td>
<td>0.03</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hydraulic fluid</td>
<td>0.02</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Fire fighting foams (FFF) *1</td>
<td>0.45</td>
<td>84</td>
<td>6</td>
<td>91</td>
</tr>
<tr>
<td>Leather industry</td>
<td>0</td>
<td>11</td>
<td>5</td>
<td>17</td>
</tr>
<tr>
<td>Carpet industry</td>
<td>0</td>
<td>1,635</td>
<td>146</td>
<td>1,781</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>*<em>Total (including FFF) <em>1</em></em></td>
<td><strong>0.87</strong></td>
<td><strong>1,730</strong></td>
<td><strong>163</strong></td>
<td><strong>1,895</strong></td>
</tr>
<tr>
<td><strong>Total (excluding FFF)</strong></td>
<td><strong>0.41</strong></td>
<td><strong>1,646</strong></td>
<td><strong>157</strong></td>
<td><strong>1,804</strong></td>
</tr>
</tbody>
</table>

*1  The fire fighting foams should be disposed of by June 2011.

**Sewage sludge**

PFOS is concentrated in sewage sludge from waste water treatment. Emissions to the environment occur to water (PFOS which is not concentrated in sewage sludge) and to soil when the sewage sludge is used for agricultural purposes. About 5.3 million tonnes of sewage sludge with a content of approximately 770 kg of PFOS result in additional possible emissions to the environment. The substance flow of PFOS in sewage sludge at EU level is shown in the figure below.
Waste incineration
As shown above, the majority of the PFOS-containing waste in the EU is disposed of to municipal waste incineration or landfilling. In Denmark, the majority is disposed of using incineration, as described in the following. Destruction of the PFOS by incineration is a key issue in relation to the disposal of PFOS-containing waste and is discussed separately in section 4.3.

4.1.2 Other PFCs in solid waste
Assessments of other PFCs in solid waste at EU level have not been identified. The analysis of the risks arising from the industrial use of PFOA and APFO and from their use in consumer articles (RPS Advies, 2010) contains hardly any information on PFOA in waste and waste water. It is noted that the release from the use of PFOA in the semiconductor industry may give rise to 4 kg/y in emissions though waste water.

4.1.3 PFCs in waste water and sewage sludge
As part of the EU project “Perfluorinated organic compounds in the European environment” (PERFORCE), the presence of perfluorinated substances in influent, effluent and sewage sludge in six MWWTP in four EU Member States were analysed (de Voogt et al., 2006). The report does not provide mean and median values for the results. The highest concentration in the dissolved phase of the influent was found for PFOS (10-200 ng/L), PFOA (20-65 ng/L), PFNA (8-45 ng/L) and FTS (15-300 ng/L). The particular phase of the influent contributed significantly to the overall concentration in the case of the carboxylic acids (53-95% of the total) but less for the sulfonates (15-48%) and for PFOSA (55%). The concentrations in the effluents were: PFOS (15-200 ng/L), C4-PFSAs (2-50 ng/L), C6-PFSAs (2-59 ng/L), PFHpA (4-18 ng/L), PFOA (20-111 ng/L), and PFNA (2-19 ng/L). The removal efficiencies in the MWWTPs for the PFSAs were found to be in the range of 0-47%, while for the PFCAs the efficiencies were higher, in the range of 20-80%. The PFCAs showed the following order (from higher to lower efficiency): C12>C9=C7>C8>C11>C10. For PFOSA, large differences between plants were observed with a mean value of 28% (de Voogt et al., 2006).

In the sewage sludge PFOS and 6:2 FTS were the most abundant of the analysed PFSAs, ranging from <d.l. to 110 µg/kg for PFOS and <d.l. to 110 µg/kg for FTS. The PFCAs concentrations were generally in the 0-25 µg/kg range with the following general order: C9>C8>C10>C11>C12>C14 (de Voogt et al., 2006).

In a screening study supported by the Nordic Council of Ministers, sewage sludge samples from 15 MWWTPs in six Nordic countries were analysed for seven perfluoralkyl substances (Kallenborn et
al., 2004). The total of the seven substances ranged from 0.6 to 1.5 µg/kg dry weight. The predominant substances in the Danish sludge samples were PFOS, PFOA and PFNA, as shown in the map below. The map shows the median concentrations of the substances in the sludge from the six countries. As shown in the map, a high variability in sewage sludge composition was found across the various Nordic countries. PFOS and PFOA were the predominant perfluorooalkyl substances in sludge samples from all the countries apart from Finland, where PFHxA ranked second among the analysed PFAS.

![FIGURE 5 MEDIAN CONCENTRATION OF 7 PERFLUORALKYL SUBSTANCES IN SEWAGE SLUDGE FROM NORDIC COUNTRIES. (KALLENBORN ET AL., 2004)](image)

Sweden has a national monitoring programme of hazardous substances in sewage sludge which includes PFASs (Haglund and Olufson, 2010 as cited by Jensen et al., 2012). In 2009, the average concentrations of PFOS and PFOA in sludge from eight different WWTP were 15.9 (1.6-37.4) and 4.9 (0.8723.9) µg/kg dry weight, respectively. Generally, the concentrations have been stable over the last five years, but with a small tendency to a decline.

Compared to the data from the Nordic countries, significantly higher concentrations of PFOS have been reported from the USA and Germany. In Germany, the mean concentration of PFOS in 61 waste water treatment plants in 2008 was reported to be 271 µg/kg (range 14 – 2,615 µg/kg) (UBW, 2009 as cited by Jensen et al., 2012).

4.2 Denmark

4.2.1 PFOS and other PFASs in solid waste

If the use of PFOS in Denmark corresponds to the use in a number of EU countries up to 2016, on the order of 1-2 tonnes of PFOS will be disposed of annually in carpets, with an average concentration of around 75 mg PFOS/kg. Similarly, it is assessed that there may be smaller quantities of PFOS that will be disposed of with leather furniture, containing an average concentration of around 80 mg PFOS/kg (Danish EPA, 2012).

Considering the use of PFCs in Denmark in 2007, it must be expected that the majority of PFCs in solid waste would be in discarded carpets and impregnated clothing with a total quantity in the 10-30 t/y range; of this, the majority would be present as various side-chain fluorinated polymers.
There is no selective waste collection of articles containing PFOS or other PFCs. In Denmark today, carpets, textiles, upholstered furniture, packaging and other articles that may be surface-treated with PFOS and other PFCs, are disposed of via waste incineration with energy recovery. The main question in this respect is the fate of the incinerated substances, as discussed in section 4.3.

In a letter of 16 May 2011, the Danish EPA informed the Danish Emergency Management Agency, the safety industry and the largest dealers of fire extinguishing foam that PFOS, after 27 June 2011, must no longer be found in fire extinguishing foam. This information was to be further communicated to customers and collaboration partners alongside the requirement that the municipality must classify waste and provide instructions as to where to dispose of the waste (Danish EPA, 2012). Many users, however, disposed of the foams years ago. For example, in 2005 all fire extinguishing foam containing PFOS from DONG’s offshore installations in Denmark were destroyed (Danish EPA, 2012).

In the context of the NOVANA programme, in 2004-2005 leachate from two landfills was analysed for PFOS and a number of perfluorinated substances (Strand et al., 2007). PFOS was found in a concentration of 3.8 ng/L in a single sample of leachate from Stige landfill. In all other samples, the concentration of all of the substances was below the detection level of 0.2 to 2.2 ng/L, depending on the substance.

For comparison, in a German study, samples of untreated and treated leachate from 22 landfill sites in Germany were analysed for 43 PFCs (Buch et al., 2010). \( \sum \text{PFC} \) concentrations ranged from 31 to 12,819 ng/L in untreated leachate and 4–8,060 ng/L in treated leachate. The dominating compounds in untreated leachate were perfluorobutanoic acid (PFBA) (mean contribution 27%) and perfluorobutane sulfonate (PFBS) (24%). The discharge of PFCs into the aqueous environment depended on the cleaning treatment systems. The mass flows of \( \sum \text{PFCs} \) into the aqueous environment from the landfills ranged between 0.08 and 956 mg/day.

4.2.2 Recycling
Recycling of waste containing PFOS is prohibited. Waste containing PFCs is generally not recycled in Denmark.

4.2.3 Waste water and sewage sludge
A study of seven PFASs in the influent, effluent and sludge from Danish waste water treatment plant was carried out as part of the NOVANA programme (Strand et al., 2007). The same data are published in English by Bossi et al. (2008).

Measurements were carried out at nine MWWTP and in three industrial waste water treatment plants. In the influent of the MWWTPs the highest median concentrations were found for PFOA (14.7 ng/L), PFHxA (7.4 ng/L), PFOS (3.4 ng/L) and PFNA (2.5 ng/L). The highest concentrations in effluents were found for PFOA (13.4 ng/L), and PFOS (4.5 ng/L). The concentrations of PFOS and PFOA in the effluents were of approximately the same concentration in the influent.

PFOS was found in the sewage sludge from all 9 MWWTPs, in concentrations ranging from 4.8-74.1 µg/kg dry matter and with a median concentration of 8.6 µg/kg dry matter. The concentration of PFOS in the sludge was considerably higher than the concentration of other fluorinated substances. It was also about 10 times higher than the concentrations reported from the Nordic study described in section 4.1.3 (Kallenborn et al., 2004).

Of the other substances, the highest concentrations were found for PFUnA (3.3 µg/kg d.m., mistakenly not indicated on the figures), PFHxS (1.8 µg/kg d.m.) and FPOA (1.0 µg/kg d.m.).
A risk evaluation of perfluorinated compounds and four other groups of persistent organic contaminants in sewage sludge has recently been published (Jensen et al., 2012). For the risk evaluation Jensen et al. (2012) used the highest concentration of PFOS and PFOA found in sewage sludge from Danish MWWTPs. According to the study, a comparison of the lowest test concentration, where no significant effects were observed, and the predicted concentrations in soils after sewage sludge amendment, reveals a margin of safety which is on the borderline of what would be accepted according to the risk assessment procedure outlined in REACH. On this basis it is concluded that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystem and that more information on the fate and effects of PFCs is needed (Jensen et al., 2012). The study notes that the restrictions in the use of PFOS in Denmark and the EU are likely to result in concentration in sewage sludge in the future.

4.3 Destruction of PFASs by waste incineration

The majority of PFOS and other PFASs used in consumer products will ultimately end up in municipal waste incinerators in Denmark. Because of the very strong C-F binding, the perfluoroalkyl chain is extremely resistant to heat and the fate of the PFOS and other PFASs by the incineration is one of the main issues concerning the management of the substances in the waste stream.

According to the Stockholm Convention on persistent organic pollutants (POPs), PFOS and other POPs should be disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of POPs, or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option (SC, 2009).

The updated draft European Community implementation plan for the Stockholm Convention (EC 2012) states that full scale tests with assessment of destruction efficiency and degradation products have not been published for municipal solid waste incinerators and sewage sludge incinerators. Comparable information from municipal waste incinerators and sewage sludge incinerators should be gathered for an assessment of the appropriateness of destroying PFOS in incinerators operating at conditions according to Directive 2000/76/EC but below 1,100°C.

The available literature about the subject is briefly reviewed below.

The 2008 survey of PFASs in Denmark (Jensen et al., 2008) discuss the results of Yamada et al. (2005) who investigated the thermal degradation of a small polyester/cellulose fabric substrate treated with a fluorotelomer-based acrylic polymer under laboratory conditions. The conditions conservatively represented typical combustion conditions of time, temperature, and excess air level in a municipal incinerator, with an average temperature of at least 1000°C and two second residence time. The fabric was destroyed by this treatment and no PFOA was detected, only SiF₄. Yamada et al. (2005) concluded that under typical municipal waste incineration conditions no significant quantity of PFOA would be formed from the incineration of a textile or paper substrate treated with a fluorotelomer based acrylic polymer, even without consideration of post-combustion pollution control equipment for acid gas scrubbing in place at municipal incinerators. This conclusion is questioned by Poulsen et al. (2008) who underline the fact that actual waste incineration is performed on a larger scale and is inhomogeneous and less controlled.

In a German study, the PFOS content of contaminated sludge which was incinerated in a sewage sludge incinerator at conditions in accordance with Directive 2000/76/EC was largely destroyed i.e. measured at below the detection limit of 15 ng/m³ in the exhaust air and below detection limits of all other output fractions (<10 µg/kg dry matter for solid residues and <25 ng/L for water discharges) (NRW, 2007). The incinerator was operating at a temperature up to 900°C and the following technical conditions: Above the fluidized bed, secondary air was fed to the process in order to en-
sure the burn-off of exhaust gas with an O₂ content of at least 6%. On the way to the exit of the afterburning chamber, the off-gas reaches a temperature of at least 850°C for at least 2 seconds.

A US laboratory-scale incineration study of PFOS and C8 perfluoro sulfonamides determined that a properly operating full-scale (high temperature) incineration system can adequately dispose of PFOS and C8 perfluorosulfonamides (UDRI, 2003). The study also indicated that incineration of these substances was not likely to be a significant source of PFOS into the environment. The C-S bond was completely destroyed, indicating that transformation of any combustion products to form PFOS was also highly unlikely.

A Norwegian study investigated emissions from incineration of fluoropolymers in municipal waste (Otterlei et al, 2011). The objective of the study was to investigate to what extent fluorine-containing gases, which are strong greenhouse gas contributors, may be formed and emitted from Norwegian waste incineration plants incinerating fluoropolymers. The study did not address incineration of PFCs.

A Swiss substance flow analysis for PFOS and PFOA from 2009 reviewed the existing literature with the aim of establishing the destruction efficiency of PFOS by waste incineration (Buser and Morf, 2009). Apart from the literature mentioned above, the study quotes research on the efficiency of destruction of perfluorinated substances in carpets (Lemieux et al., 2007). In this study the content of perfluorinated substances in the stack from a pilot-scale rotary kiln incinerator simulator to qualitatively and, where applicable, quantitatively assess the potential for emissions of fluorinated compounds from combustion devices was measured. The concentration was below 1 µg/m³ in the stack, and the concentrations were relatively independent of kiln feed. According to Lemieux et al. (2007) the results indicated that the perfluorinated substances were effectively destroyed even under mild combustion conditions and that the trace levels that were found were due either to trace contamination of the sampling duct with fluorinated compounds due to historical use of Teflon and other fluoropolymers, or sampling artefacts. The Swiss substance flow analysis concludes on the basis of the review that the available information in the literature was not sufficient for establishing a destruction efficiency coefficient.

In summary, a few studies show that PFOS is effectively destroyed at 1,100°C (comparable to high-temperature hazardous waste incineration), and the studies available suggest that this may also be the case at a temperature of 850°C. On the other hand, there are no studies which document clearly that destruction is complete at 850°C.

### 4.4 Summary on waste management

The waste situation for PFOS is well described on both the EU-level and in Denmark. The majority of the solid waste containing PFOS and other PFCs in Denmark is disposed of to municipal solid waste incinerators, and the main issue is to what extent the substances are destroyed at the temperatures used in municipal solid waste incinerators. Limited data are available on the destruction efficiency under the actual conditions in the incinerators, and more studies are necessary to clarify whether it would be necessary to dispose of PFOS-containing waste to hazardous waste incinerators in order to comply with the requirements of the Stockholm Convention.

PFOS and PFOA are the main substances among the analysed PFCs in effluents from municipal waste water treatment plants, but PFNA, PFDA and PFHxS are found in measureable concentrations as well. The removal efficiencies in the waste water treatment plants are relatively low and, in measurements in Danish plants, the effluent concentration of PFOS and PFOA were comparable to the influent concentration. PFOS is the predominant substance in the sewage sludge. For PFOA the data are more variable. Measurements from Danish plants showed relatively low concentrations of PFOA in the sludge, but in another study with data from all Nordic countries, PFOA was the main
substance in the sludge. Both PFHxA and PFDA are present in the sludge in measureable concentrations.

Data on sources of the substances’ emissions to waste water are scarce and more information on sources and levels of other PFASs than PFOA and PFOS would be of advantage.

A Danish risk evaluation of perfluorinated compounds in sewage sludge concludes that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystems and that more information on the fate and effects of PFCs is needed. It should, however, be noted that the concentration of PFOS may already have decreased significantly as a consequence of the current regulation and the fact that PFOS-containing articles in service are gradually being disposed of.
5. Environmental effects and fate

PFOA, PFOS and other long-chain perfluorinated chemicals are found world-wide in environmental compartments, in biota and in humans. These chemicals are all highly persistent in the environment due to the inherent high strength of the C-F covalent bond and they show bioaccumulative properties in higher animal life, including humans. Therefore, there is a growing concern that in the long term they may have significant adverse effects at population level in wildlife as well as in human populations (US EPA, 2009).

PFOS, PFOA and related substances being present globally in the environment today may originate from different sources:

- Emission from the manufacture of the substance or industrial processes where the substance is used as an intermediate, as a raw material or a process aid for the manufacturing of fluoropolymers;
- Emission from industrial processes where the substances are used for formulation of mixtures, or mixtures including the substances are used for processing articles;
- From the use and disposal mixtures and articles that intentionally include the substances;
- From use and disposal of mixtures and articles that may contain them as an impurity, and
- From the abiotic or biotic degradation of derivatives or larger functional derivatives and polymers that contain a perfluoroalkyl moiety and degrade in the environment to form the substances.

5.1.1 PFOS and other perfluoroalkyl sulfonates

Fate in the environment

Abiotic degradation

PFOS does not undergo hydrolysis; in a study conducted at 50 °C to enhance possible transformation processes, no indications of reaction were observed. The half-life of PFOS was set to be greater than 41 years (UNEP, 2006). Likewise, there was no evidence of direct or indirect photolysis in a US EPA guideline study, in which the indirect photolytic half-life in water at 25 °C was calculated to be more than 3.7 years (UNEP, 2006).

In 3M studies, the PFOS-related substances N-EtFOSE and N-MeFOSE were found to have hydrolytic half-lives of 35 and 99 days respectively at neutral pH. However, there are also reports of much longer half-lives; 6.3 years for N-MeFOSE and 7.3 years for N-EtFOSE. No photolysis occurred in the studies (Brooke et al., 2004).

Regarding atmospheric degradation there are no experimental data, but the AOP program estimates a rate constant leading to an estimated half-life of 114 days, indicating that degradation in the atmosphere is not likely to be significant. The volatility of PFOS is low (Environment Agency, 2004).

The substance N-EtFOSE is calculated to be more reactive in the atmosphere with an estimated half-life of 16 hours; however, it probably only results in formation of the PFOS backbone (Brooke et al., 2004).
Biodegradation
Brooke et al. (2004) refers to previous assessments by OECD (2002) and 3M (2003) both concluding that PFOS is not biodegradable either under aerobic or under anaerobic conditions. Only a MITI-test showed a small (3%) removal of the parent compound, while in no other tests was any degradation observed. There appears to be no degradation in soil either.

N-EtFOSE and N-MeFOSE are believed to undergo primary degradation in sewage sludge, likely leading to the formation of PFOS and PFOA. The rate of biodegradation is not indicated (Brooke et al., 2004).

Adsorption and distribution
According to Jensen et al. (2012), PFOS adsorbs to soil, sediment and sludge with distribution coefficients ($K_d$) ranging from 9.7 L/kg to 35 L/kg and not desorbing readily, once adsorbed to these matrices. The average $K_d$ for three soils was 26.9 L/kg.

EUSES 2-Modeling of the environmental distribution of PFOS gave the result shown in the following table.

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Release to Air</th>
<th>Release to Water</th>
<th>Agricultural soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater</td>
<td>0.38%</td>
<td>83.18%</td>
<td>0.26%</td>
</tr>
<tr>
<td>Seawater</td>
<td>0.04%</td>
<td>9.06%</td>
<td>0.03%</td>
</tr>
<tr>
<td>Air</td>
<td>&lt;0.01%</td>
<td>&lt;0.01%</td>
<td>&lt;0.01%</td>
</tr>
<tr>
<td>Soil (combined)</td>
<td>99.55%</td>
<td>3.42%</td>
<td>99.7%</td>
</tr>
<tr>
<td>Freshwater sediment</td>
<td>0.02%</td>
<td>4.20%</td>
<td>0.01%</td>
</tr>
<tr>
<td>Marine sediment</td>
<td>&lt;0.01%</td>
<td>0.14%</td>
<td>&lt;0.01%</td>
</tr>
</tbody>
</table>

Therefore, once released to the aquatic environment, PFOS will stay in the water compartment while soil is the sink for releases to air and soil.

Bioconcentration
Because PFOS is both hydrophobic and lipophobic it does not follow the typical pattern of partitioning into fatty tissues followed by accumulation, the typical pattern of many persistent organic pollutants. Instead, it binds to proteins in the plasma and, as a result, is present in highly perfused tissues such as the liver and kidneys rather than lipid tissue. Therefore, the mechanism of bioaccumulation likely differs from most other bioaccumulative chemicals (UNEP, 2006).

UNEP (2006) uses references from studies with fish BCFs in the range 2,800-3,100, i.e. below the "standard" Stockholm Convention criteria for bioaccumulation. However, monitoring data from top predators at various locations show highly elevated levels of PFOS and demonstrate the substantial bioaccumulation and biomagnification (BMF) properties of PFOS. Notable is that the PFOS concentrations in polar bears (1,700-2,000 ng/g) exceed all other individual organohalogens. A BMF >160 has been estimated based on concentrations in Arctic seals. BMFs of 10-20 relative to prey items have been calculated for the bald eagle. The levels of PFOS in biota have been shown to be increasing since the 1970s, e.g. in a retrospective Swedish study on guillemot eggs where the level was about 100 ng/g in 1975 and about 600 ng/g in 2005 (UNEP, 2006).
The bioaccumulation potential of PFOS and other PFASs in the soil environment has been shown to be significantly lower than in the marine environment. A BSAF (biota-to-soil accumulation factor) of up to 4.7 was found for earthworms (*Eisenia fetida*), while accumulation in plants was lower (Jensen et al., 2012).

### Environmental effects

Ecotoxicity data for PFOS are mainly found for aquatic organisms such as fish, invertebrates and algae, and for birds. The acute toxicity (LC₅₀) of PFOS to a number of freshwater and saltwater fish species were found to be in the range 4.7-133 mg/L with *Pimephales promelas* being the most sensitive species in the review by Brooke et al. (2004). The lowest long-term (42 days) NOEC was 0.30 mg/L, also for *P. promelas*.

According to Brooke et al. (2004), the acute toxicity (EC/LC₅₀) to aquatic invertebrates is in the range of 2.66-223 mg/L (*D. magna* most sensitive) and a lowest long-term (21 days) NOEC = 0.25 mg/L for the mysid shrimp *Mysidopsis bahia*.

A 10-day NOEC = 0.049 mg/L has been reported for the aquatic midge *Chironomus tentans* (UNEP, 2006). The authors consider chironomids to be 2-3 times more sensitive to PFOS than other aquatic organisms probably due to an interaction with haemoglobin, which is unique to this group of organisms. The lowest toxicity values for algae are for the green alga *P. subcapitat*, with a 96-hour IC₅₀ = 48.2 mg/L and NOEC = 5.3 mg/L (UNEP, 2006).

The most sensitive endpoints for different groups of aquatic organisms are summarized in the table below. The harmonised classification is Aquatic Chronic 2 with the hazard statement H411: “Toxic to aquatic life with long lasting effects”.

<table>
<thead>
<tr>
<th>Table 18</th>
<th>OVERVIEW OF AQUATIC TOXICITY OF PFOS (MOST SENSITIVE ENDPOINTS) (BROOKE ET AL., 2004)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fish</strong></td>
<td>Fathead minnow (<em>Pimephales promelas</em>) (96-h): LC₅₀ = 4.7 mg/L</td>
</tr>
<tr>
<td></td>
<td>Rainbow trout (<em>Oncorhynchus mykiss</em> - saltwater) (96-h): LC₅₀ = 13.7 mg/L</td>
</tr>
<tr>
<td><strong>Invertebrates</strong></td>
<td>Daphnia magna (48-h): EC₅₀ = 27 mg/L</td>
</tr>
<tr>
<td></td>
<td>Mysid shrimp (<em>Mysidopsis bahia</em> - saltwater) (96-h): LC₅₀ = 3.6 mg/L</td>
</tr>
<tr>
<td><strong>Algae</strong></td>
<td>Selenastrum capricornutum (96-h): EC₅₀ = 126 mg/L</td>
</tr>
<tr>
<td></td>
<td>Skeletonema costatum (saltwater) (96-h): EC₅₀ &gt; 3.2 mg/L</td>
</tr>
<tr>
<td><strong>Fish</strong></td>
<td>Fathead minnow (<em>Pimephales promelas</em>) (42-day): NOEC = 0.3 mg/L</td>
</tr>
<tr>
<td><strong>Invertebrates</strong></td>
<td>Daphnia magna (28-day): NOEC = 7 mg/L</td>
</tr>
<tr>
<td></td>
<td>Mysid shrimp (<em>Mysidopsis bahia</em> - saltwater) (35-day): NOEC = 0.25 mg/L</td>
</tr>
<tr>
<td><strong>Algae</strong></td>
<td>Selenastrum capricornutum (96-h): NOEC = 44 mg/L</td>
</tr>
<tr>
<td></td>
<td>Skeletonema costatum (saltwater) (96-h): NOEC &gt; 3.2 mg/L</td>
</tr>
<tr>
<td></td>
<td>Duckweed (<em>Lemna gibba</em>) (7-day): NOEC = 15.1 mg/L</td>
</tr>
</tbody>
</table>

Mallard duck and bobwhite quail were exposed to PFOS in a 21 week study (UNEP, 2006). At a dose of 10 mg/kg diet PFOS, effects in male mallards included reduced testes size and decreased spermatogenesis. For quails, at the same dose level, minor effects were observed in adults including increase in liver weight and in incidence of small testes size, and a reduction in survivability in quail chicks.

Doses of 4.5 mg/kg bw/day were lethal to Rhesus monkeys over a seven week exposure period. Sub-lethal and biochemical effects observed in rats exposed to PFOS were considered to show that PFOS can affect the neuro-endocrine system in rats (UNEP, 2006; Brooke et al., 2004).
A 14-day LC50 = 373 mg/kg soil dw and corresponding NOEC = 77 mg/kg soil dw have been reported for earthworms (Brooke et al., 2004).

The POP Review Committee under the Stockholm Convention considers PFOS to meet all the POP criteria (persistence, bioaccumulation, long-range transport potential and toxicity) (UNEP, 2006).

5.1.2 PFOA and other perfluoroalkyl carboxylic acids

Fate in the environment
The fate properties of PFOA are similar to those of PFOS. Once in the environment, PFOA is extremely persistent and not known to undergo significant further abiotic or biotic degradation under relevant environmental conditions.

PFOA is highly soluble in water (3.5 g/L) and predominantly present as an anion in solution under environmental conditions (pKa = 2.5). It has a relatively low vapour pressure (2.2 Pa), and therefore the aquatic environment is expected to be the primary sink with some additional partitioning to sediment. The presence in PFOA in the Arctic environment is most likely attributable to long range transport via ocean currents and/or of volatile precursors via the atmosphere (Environment Canada, 2012b).

There is experimental evidence indicating that PFOA is not highly biocumulative in fish. Reported BCFs for fish species range from 3.1-27. However, fish may not be the most relevant group of organisms to consider (Vierke et al., 2012) and the results cannot be extrapolated to non-aquatic species since gills provide a mode of elimination that air-breathing animals do not possess. Monitoring studies and field studies indicate that biomagnification in various terrestrial and marine mammals occur (prey: predator BMFs from 0.03 to 31 have been reported). The polar bear in particular appears to accumulate PFOA and related substances, ringed seal:polar bear BMFs of 45-125 have been reported (Environment Canada, 2012b) and PFOA concentrations in polar bear as high as 3.4 mg/g with an increasing trend from 1990 to 2006 (Vierke et al., 2012).

Precursors
Exposure to PFOA can be due to releases of PFOA itself, but there also exist a considerable number of precursors which can lead to PFOA exposure in the environment. Environment Canada (2012) defines precursors as substances where the perfluorinated alkyl moiety has the formula CnF2n+1 (where n=7 or 8) and is directly bonded to any chemical moiety other than a halogen atom. Potential precursors include e.g. fluorotelomer alcohols (FTOHs), fluorotelomer iodides and fluorotelomer olefins. A total of 27 PFOA precursors have been listed by Environment Canada.

The precursors listed by Environment Canada have been evaluated by Nielsen (2012), who, based on their physico-chemical properties, found that seven of the 27 precursors listed were actually not PFOA precursors, while another two could only partially be considered PFOA precursors.

Environmental effects
PFOA exhibits moderate to low toxicity in traditional acute studies with aquatic species such as fish (LC50 ranging from 70-2470 mg/L) and in general PFOA appears to be about 10 times more toxic to aquatic organisms than PFOA (Jensen et al., 2012). The most sensitive pelagic organism reported is the freshwater green alga Pseudokirchneriella subcapitata for which a 96-hour NOEC = 2.0 mg/L was calculated, while for Daphnia magna the lowest EC50 reported was 34 mg/L. The 10-day NOEC to the benthic organism Chironomus tentans was found to be 100 mg/L (Environment Canada, 2102).

There are studies in aquatic organisms showing potential of PFOA to affect endocrine function, e.g. in rare minnows at PFOA concentrations of 3-30 mg/L, thyroid hormone biosynthesis genes were
inhibited, vitellogenin expression was induced in males, oocytes developed in the testes of male fish and caused ovary degeneration in females. Other studies show hepatotoxicity, immunotoxicity and chemosensitivity in other different organisms such as mussels, seals, dolphins, turtles and rats (Environment Canada, 2012b).

The toxicity of PFOA to reproduction of earthworms was studied and a NOEC = 80 mg/kg soil was determined. PFOA is less toxic to earthworms than PFOS (Jensen et al., 2012).

One study is available where the toxicity of PFOA and its salts to avian wildlife was tested. PFOA was found not to have an effect on embryonic pipping success for white leghorn chickens at concentrations up to 10 µg/g of embryos but to bioaccumulate 2.9-4.5 times in the liver of the embryos (Environment Canada, 2012b).

**Precursors**

No relevant data on the ecotoxicity of the precursors of PFOA were identified.

### 5.1.3 Other PFASs and side-chain-fluorinated polymers

#### Fate in the environment

**Long-chain PFCAs**

Recently, Annex XV dossiers have been prepared for four long-chain perfluoroalkyl carboxylic acids; henicosafluoroundecanoic acid, tricosafluorododecanoic acid, pentacosafluorotridecanoic acid and heptacosafluorotetradecanoic acid (ECHA, 2012a, b, c, d). Only very few experimental studies on the fate of the four substances are available and the assessment therefore to a large extent builds on the read-across approach and use of data from other PFCAs such as PFOA. For all four substances it is concluded in the dossiers (ECHA 2012a, b, c, d) that they fulfil the vP as well as the vB criterion and thus are to be regarded as vPvB-substances according to Article 57 e) of REACH.

A number of C14-C15 PFCAs have been found to bioaccumulate as they are present ubiquitously in fish, invertebrates and top predators (e.g. seals and polar bears) even in Arctic regions far away from any sources (US EPA, 2009).

**Short-chain PFCAs and PFSAs**

Due to the increasing concern about the persistence and bioaccumulation of PFOS, PFOA and other long-chain perfluorinated alkyl carboxylic acid and alkyl sulfonic acids, a number of shorter chain alternatives, notably butane-based products (e.g. PFBS), have been introduced. These substances have been shown not to bioaccumulate due to rapid elimination in multiple organisms tested. However, as a result of this conversion, increasing levels of e.g. PFBS in surface waters have been observed (Buck et al., 2011). This indicates that the alternatives are also significantly persistent in the environment.

Modelling exercises indicate that the BCFs of C4-PFSas and C4-PFCAs are about 3 orders of magnitude lower than the corresponding C8-chain compounds (PFOS and PFOA) (Rayne et al., 2009).

**Fluorotelomers**

Buck et al. (2011) provides the following description of the transformation and degradation of fluorotelomer alcohols (FTOH) to e.g PFOA: “The aerobic biodegradation and metabolic degradation pathways for fluorotelomer alcohols have been well studied. The pathways and yields of transformation products depend on the matrix in which the environmental microbial degradation or metabolism takes place and the length of the perfluoroalkyl chain in the fluorotelomer alcohol. Ultimately the fluorotelomers will be degraded to stable transformation products, including PFCAs. A n:2 fluorotelomer alcohol (n:2 FTOH) may ultimately be degraded to perfluoroalkyl acids with n or less than n atoms. As an example the 8:2 FTOH may ultimately be degraded to
PFOA (perfluorooctanoate), PFHxA (perfluorohexanoate) or PFHpA (perfluorooheptanoate), but also other degradation products are formed.”

Parsons et al. (2008) refers to results of biodegradation studies conducted with 8:2 FTOH in diluted sewage sludge from a domestic WWTP and conclude that the results demonstrate that perfluorinated carbon atoms in 8:2 FTOH are indeed defluorinated and the products are degraded by microorganisms from WWTPs to form shorter chain products.

Frömel & Knepper (2010) studied the biodegradation of fluorotelomer ethoxylates (FTEO) and found that they were de-ethoxylated relatively rapidly down to seven intact ethoxy units at which level further degradation virtually ceased (no degradation observed in 48 days).

Aqueous phase photo-oxidation of CF₃(CF₂)₆CH₂OH will result in the formation of PFOA. Gas phase photo-oxidation will lead to the formation of CF₃(CF₂)₆CHO and subsequently in part to formation of PFOA (Wallington et al., 2006 as cited by Nielsen, 2012).

Most recently, Russell et al. (2010, as cited by Martin et al., 2010) investigated degradation of a fluorotelomer urethane polymer and observed an average half life of 102 years (range 28–241 years). PreFOS based urethanes (e.g.Xb.) are also known to have been incorporated into 3M’s ScotchGard line of products, and thus it is reasonable to speculate that these also may yield free PreFOS, and ultimately PFOS, via similar pathways. The important unknowns are the overall emission of such copolymers to the environment, and the rate of degradation, which needs to be assessed experimentally (Martin et al., 2010).

Results from analyses of PFASs in polar bears indicate that fluorotelomers also contribute to the total bioaccumulation of per- and polyfluorinated compounds in these animals because perfluorononic acid (PFNA) was almost only found in its linear form while both linear and branched isomers were observed for PFOA (Ellis et al., 2004).

Smog chamber experiments have shown that FTOHs can degrade in the atmosphere by OH-initiated oxidation pathways, with the intermediates FTCAs and FTUCAs, to PFCAs. A half-life of approx. 20 days for the FTOHs was estimated (Ahrens, 2010).

Side-chain fluorinated polymers

By degradation of side-chain fluorinated polymers, the side chains may be released from the polymer chain to become PFASs. The PFASs formed will depend on the type and length of the side chains.

The principle is shown below, exemplified with the degradation of the side-chain-fluorinated polymer 2-propenoic acid, 2-methyl- 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octyl ester (CAS No 53515-73-4) (Nielsen, 2012). This co-polymer contains ester side-chains >C-C(O)OCH₂(CF₂)₆CF₃ and may in principle undergo hydrolysis to give 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-
octanol (CAS No 307-30-2). Gas phase photo-oxidation will lead to CF$_3$(CF$_2$)$_6$CHO and subsequently in part to PFOA.

\[
\begin{align*}
\text{COOH} & \quad \text{COOH} \\
\text{COOH}_{\text{HCl}} & \quad \text{COOH}_{\text{HCl}} \\
\text{CF}_3\text{CF}_2 & \quad \text{CF}_3\text{CF}_2 \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
\end{align*}
\]

Source: Nielsen, 2012

Environmental effects

Very little information is available about the environmental effects of PFASs other than the perfluorinated alkyl carboxylic acids and the perfluorinated alkyl sulfonic acids. Overall, these substances are not regarded to be as toxic as PFOS and PFOA.

Long-chain PFCAs

Environment Canada has made an ecological screening assessment of long-chain PFCAs, i.e. C9-C20 PFCAs, and their salts and precursors (Environment Canada, 2012b). They find that in standard toxicity studies with long-chain PFCAs, the acute toxicity of this group of substances was low to moderate with acute EC/LC$_{50}$ values ranging from 8.8 to 285 mg/L. Two terrestrial studies on long-chain PFCAs exist: In one study with chickens, no adverse effects were observed up to 1.0 mg/kg bw dosed three times/week for three weeks with C10 PFCA. In another study with a soil-dwelling nematode, the acute LC$_{50}$ was 306 mg/L while multi-generation effects (decreased fecundity) was observed at 0.000464 mg/L, i.e. a much lower level than the acute effect level.

Various biochemical responses to long-chain PFCAs, including vitellogenin induction, oxidative stress and chemical sensitization, have also been observed in a number of species such as marine mussels, rainbow trout and Baikal seals (Environment Canada, 2012b).

Short-chain PFCAs and PFSAs

No data on the ecotoxicity of the shorter chain fluorinated carboxylic and sulfonic acids have been identified.

5.2 Summary of environmental effects and fate

PFOS, PFOA and other long-chain perfluorinated carboxylic and sulfonic acids and their salts, and the longer chain homologues, are all extremely persistent in the environment (abiotically and biotically) and they bioaccumulate in particular in mammals and birds, despite not fulfilling the traditional bioaccumulation criteria based on bioconcentration in fish. They are not very toxic to aquatic and other organisms based on standard toxicity endpoints, but there are indications that they have certain endocrine disrupting properties. Annex XV concluded that they fulfill the vPvB criteria.

Precursors like FTOHs may undergo some initial transformation and degradation but eventually result in formation of the corresponding carboxylic or sulfonic acid compounds.

Some shorter chain (e.g. butane-based) alternatives also appear to be persistent but not to bioaccumulate to the same extent, as they are excreted rapidly from the organisms studied.

No data on the ecotoxicity of the shorter chain fluorinated carboxylic and sulfonic acids have been identified.
6. Human health effects

There are more than 600 preregistered polyfluorinated chemicals (PFC) in REACH but most of these substances are chemical intermediates, and the general population seems only to be directly exposed to a few of them, and analytical chemistry methods only exist for the most important perfluoroalkylated substances (PFAS), such as perfluorooctane sulfonates (PFOS) and perfluorooctanoic acid (PFOA) and for polyfluorinated substances, such as fluorotelomer alcohols (FTOH) and some metabolites.

Most detailed studies of toxic and adverse health effects are done for PFOS and PFOA, although more and more data for fluorotelomers and shorter chain homologues are published. For the less investigated polyfluorinated chemicals, preliminary properties may be estimated from structure and homologues.

In population studies several perfluoroalkylated acids (PFAAs) are normally measured/monitored in blood and tissues, and the sum of all or of the most abundant (PFOS and PFOA) are used for studying associations.

Although the perfluoroalkane sulfonic acids and the perfluoroalkyl carboxylic acids (PFCAs) are closely related structurally, these chemicals elicit different biological responses in vitro and in vivo. The acute lethal toxicities of PFOS and PFOA correspond to a classification as Acute tox 3 or 4. PFOS is more toxic than PFOA, and the toxicity of PFAAs increases generally with the length of the alkyl chain.

6.1 Introduction to human health effects of PFOS and other polyfluorinated substances

Uptake, distribution and elimination
It is known from animal studies that perfluoroalkylated substances (PFASs), such as PFOS and PFOA, are well absorbed orally but poorly eliminated; they are not metabolised, and undergo extensive uptake from enterohepatic circulation (Lau et al., 2004; 2007). Inhaled PFOA is also easily absorbed in rodents and may also be absorbed through the skin (Hinderliter et al., 2006). The oral uptake of perfluorohexanoate (PFHxA) in rats and mice was also rapid and complete (Gannon et al., 2011).

An oral dose of 8:2 FTOH was readily absorbed in rats but the skin absorption was negligible (Fasano et al., 2006).

Perfluoroalkylated substances (PFASs) such as PFOS and PFOA have, contrary to most other persistent organic pollutants (POPs), a low affinity to lipids but bind to proteins. PFASs are associated with cell membrane surfaces and accumulate in various body tissues of exposed organisms with especially high concentrations in the blood, liver, kidneys and spleen, but also in the testes and brain. The accumulation in fats and muscles is minimal.

In the blood PFASs are bound to plasma/serum proteins (Bischel et al., 2010). Regarding PFOA, more than 90% is bound to serum albumin in both rodents and humans (Han et al., 2003). PFOS
binds to serum albumin at a ratio of 2:1 (Luo et al., 2012) and displaces hormones from sex-hormone binding and corticosteroid-binding globulins (Jones et al., 2003).

Both in animals and humans these chemicals cross the placenta and are excreted in the milk. In rats, levels of PFOA in the blood of the foetus were about half of the maternal levels. The levels of PFOA in the maternal blood were about 10 times higher than in their milk, and milk levels were comparable with plasma levels in the pups (Hinderliter et al., 2005).

Regarding PFCAs with fluoroalkyl chain length (C7 - C10), the longer the chain, the more of the compound was accumulated in the liver of male rats (Kudo et al., 2001).

In the tissues, PFAS have affinity for binding to β-lipoproteins and the liver fatty acid-binding protein (L-FABP) which can contribute to the toxicities of these chemicals (Luebker et al., 2002). The binding of PFOA to this protein has an affinity of an order of magnitude less than the natural ligand, oleic acid, and has at least 3:1 PFOA: L-FABP stoichiometry (Woodcroft et al. 2010).

The mean blood elimination half-lives for PFASs depend on the chemical and animal species and sex. The half-lives of PFASs:

- are longer for sulfonates than for carboxylates,
- are shorter for branched isomers,
- are often shorter in females mainly due to the difference in renal clearance (and hormones),
- increase with chain length for carboxylates,
- in rodents were hours or a few days,
- in monkeys were a little longer, and
- in humans blood half-lives were measured in years.

In retired fluorochemical workers, half-lives were 5.4 years for PFOS (av. 800 ng/mL), 8.5 years for PFHxS (perfluorohexane sulfonate) (av. 290 ng/mL), and 3.8 years for PFOA (av. 690 ng/mL) (Olsen et al., 2007). Later studies have reported half-lives of about 1 month for PFBS (perfluorobutane sulfonate) and 2-4 days for PFBA (perfluorobutanoic acid) (Olsen et al., 2009; 2011; Chang et al., 2009).

In a study of populations in USA being exposed to PFOA via drinking water polluted by an industrial facility, serum half-lives were determined at 2.9 and 8.5 years for water districts with higher and lower exposure levels, respectively (Seals et al., 2011). A highly exposed (180 ng PFOA/mL compared to an average of 4 ng/mL in USA) subset of these populations which was studied previously exhibiting a serum half-life of 2.3 years (Bartell et al., 2009). These studies indicate that the half-lives are dose-dependent (Seals et al., 2011).

The whole body half-life may be longer, since the elimination of these chemicals from the human body appears to be insignificant compared to the experimental animals (Harada et al., 2005).

**Elimination**

Once absorbed in the body and distributed via the blood, PFOA is eliminated as the free carboxylic acid mainly with the urine and to a lesser extent in faeces. Therefore, renal elimination has been considered critical for detoxification (Vanden Heuvel et al., 1991).

The elimination with the urine of PFAS is also greater in female rats than in males and increases with age and decreases with increasing chain length. These differences may be due to the actions of sex dependent organic anion transporters (OATs) in the kidney (Kudo et al., 2002; Hinderliter et al., 2006). For the shorter chain PFHxA, 100% of an oral dose in rats and mice was eliminated in the urine within 24 hrs (Gannon et al., 2011).
The sex-related clearance of PFOA differs between animal species (Hundley et al., 2006). In hamsters it is the opposite of what happens in rats. Male and female hamsters excreted respectively 99% and 58% of a dose in 5 days. In mice and rabbits there was no sex difference, and mice had a slower excretion rate than male rats, and rabbits had faster excretion rates than female rats.

The elimination half-lives in male and female Cynomolgus monkeys for PFOA were 33 days and 21 days, respectively, and the urine was the major excretion route (Butenhoff et al., 2004a).

For the non-polar fluorotelomers such as 8:2 FTOH, the majority was excreted unchanged with faeces. A small part (about 1%) was excreted in the urine as the metabolite PFOA (Fasano et al., 2006).

PFOS has a slower elimination rate than PFOA, and the half-life of PFOS in the female Cynomolgus monkey was about 200 days, about 40 times more than that for males (Kudo & Kawashima 2003; Seacat et al., 2002; Andersen et al., 2006).

Perfluorooctane sulfonamide (PFOSA) is also eliminated rapidly in rodents with a half-life of a few days. Branched isomers have a faster half-life than linear isomers (Benskin et al., 2009; Ross et al., 2012). The shorter-chain perfluorobutane sulfonate (PFBS) has a serum elimination half-life of about 5 hours in rats, 95 hrs in monkeys and 26 days in humans (Olsen et al., 2009).

In humans there is no active excretion by the kidneys. The renal clearance in humans is almost negligible and approximately 1/5 of the clearance is based on the blood serum half-life, assuming accumulation in other body compartments. The sex differences seen in rats are not always found in humans. Although active excretion also was absent for PFOA and PFOS in monkeys their renal clearances were still 300-1000 times greater than those in humans, making extrapolations from animal data questionable (Harada et al., 2005).

**Biotransformation**

PFOA, PFOS and other PFAAs are considered to be metabolically inert. The strong C-F bonds exclude any normal degradation pathway (Clark et al., 1973). Other perfluoroalkyl acids with shorter or longer alkyl chains do have similar persistence. Any functional derivative (precursor) will ultimately be transformed to the acids.

For example, in mice and rats, the fluorotelomer alcohol 8:2 FTOH and its phosphates were transformed to PFOA, PFNA (perfluorononanoic acid) and other metabolites (Hagen et al., 1981; Kudo et al., 2005; Fasano et al., 2006; Henderson and Smith 2007; D’Eon and Mabury 2007). The transformation in the liver is catalysed by cytochrome P<sub>450</sub> (Martin et al., 2005).

Perfluoroalkane sulfonamides (and N-substituted) are precursors of perfluoroalkane sulfonates but may sometimes also occur in environmental and human samples. That is the case for e.g. perfluorooctane sulfonamide (PFOSA).

Regarding EtFOSE (N-ethyl perfluorooctane sulfonamidoethanol), about 20% of an oral dose of 100 ppm is metabolised to PFOS in male rats (Thomford et al., 2002). Rat liver microsomal fractions also degrade EtFOSE by de-ethylation to FOSE (perfluorooctane sulfonamidoethanol), further to PFOSA and finally to PFOS (Xu et al., 2004).

**Toxicology and mode of action**

In general, the knowledge about the toxicology of other polyfluorinated compounds than PFOS and PFOA is rather sparse, and although the perfluoroalkane sulfonic acids and perfluoroalkyl carbox-
ylac acids are closely related structurally, these chemicals elicit different biological responses in vitro and in vivo.

The acute lethal toxicities correspond moderately to a classification as Acute tox 3 or 4. PFOS is more toxic than PFOA, and the toxicity of perfluorinated chemicals increases generally with the length of the alkyl chain. Further, PFCAs with a branched alkyl chain seem to be less toxic than linear isomers.

The liver is the primary target organ for PFOS and PFOA both in rodents and humans, and because these PFAAs are analogue ligands to natural long-chain fatty acids, they may displace them in biochemical processes (Vanden Heuvel et al., 2006). This interference may contribute to the toxicity of these chemicals.

In the liver, polyfluorinated chemicals are mainly associated with either the peroxisome proliferator-activated receptor-α (PPARα) or the liver-fatty acid binding protein (L-FABP) receptor.

In an in vitro test of various perfluorinated chemicals PFOS had the most potent interference with L-FABP followed by EtFOSA, EtFOSE, and PFOA (Luebker et al., 2002).

The binding of fluorinated chemicals to PPARα, which is one of three isoforms of PPAR encoded by separate genes and differentially expressed in various tissues found in all mammalian species examined to date, induces peroxisome proliferation, which is a well-known toxicological mechanism.

The activation of PPARα by PFOA and PFOS is more selective but less potent than the fatty acids. PFOA is more capable than PFOS in activating PPARα, and rodents are more responsive than human in test systems (Takacs and Abbott 2007).

The liver toxicity and peroxisome proliferation potency in rats depends on the carbon chain length. The doses of PFBS required for producing similar increases in the enzyme hepatic acyl CoA oxidase activity (a measure of proliferation) was about 50 times higher than those of PFOS and PFHxS (Ehresman et al., 2007).

Ligands for PPARs have been widely developed for the treatment of various diseases, including dyslipidaemias and diabetes. Some hypolipidemic drugs, solvents and environmental chemicals are ligands for PPARα and can induce peroxisome proliferation; for example, clofibrate, phthalates, chloroform, perchloroethylene, trichloroethylene, HFC-123, and MTBE. Humans do not exhibit the same liver toxicities by these chemicals as found in rodent models (Peraza et al., 2006).

**Endocrine disruption**

The peroxisome proliferation in rodents may cause lipid accumulation in the liver and uncoupling of the mitochondrial oxidative phosphorylation process, as well as induction of various enzymes involved in lipid- and steroid metabolism with the results that serum cholesterol, thyroid hormones, and testosterone are reduced but levels of estradiol are increased. Thus PFOA, PFOS and other PFAS are likely to be endocrine disruptors (Jensen and Leffers, 2008).

The competitive binding of poly- and perfluorinated compounds to the thyroid hormone transport protein transthyretin has been studied by Weiss et al. (2009). In Table 19 some of the data are shown:
### TABLE 19

**COMPETITIVE BINDING TO TRANSTHYRETIN**

<table>
<thead>
<tr>
<th>Compound</th>
<th>T₄-TTR binding, %</th>
<th>IC₅₀ nM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBA</td>
<td>106</td>
<td>nd</td>
</tr>
<tr>
<td>PFHxA</td>
<td>43</td>
<td>8,220</td>
</tr>
<tr>
<td>PFHpA</td>
<td>7</td>
<td>1,565</td>
</tr>
<tr>
<td>PFOA</td>
<td>4</td>
<td>949</td>
</tr>
<tr>
<td>PFNA</td>
<td>18</td>
<td>2,737</td>
</tr>
<tr>
<td>PFDoA</td>
<td>46</td>
<td>8,954</td>
</tr>
<tr>
<td>PFUnA</td>
<td>74</td>
<td>21,560</td>
</tr>
<tr>
<td>PFBS</td>
<td>69</td>
<td>19,460</td>
</tr>
<tr>
<td>PFHxS</td>
<td>3</td>
<td>717</td>
</tr>
<tr>
<td>PFOS</td>
<td>1</td>
<td>940</td>
</tr>
<tr>
<td>8:2 FTOH</td>
<td>117</td>
<td>nd</td>
</tr>
<tr>
<td>FOSA</td>
<td>32</td>
<td>6,124</td>
</tr>
</tbody>
</table>

T₄-TTR binding (%) =% inhibition of T₄-TTR at max conc.  
IC₅₀ (nM) = conc. at 50% inhibition

It is clear that the binding potency decreased in the order of PFHxS>PFOS>PFOA>PFHpA>PFNA etc.

Some polyfluorinated chemicals have also estrogenic effects in cell cultures ("E-screen assay") (Soto et al., 1995). For example, the fluorotelomer alcohols 6:2 FTOH and 8:2 FTOH induce MCF-7 breast cancer cell proliferation and up-regulates the estrogenic receptor, but PFOS, PFOA and PFNA had no estrogenic effect in that test (Maras et al., 2006; Vanparys et al., 2006).

**Immunotoxicity**

The immunotoxicity potential of PFOS and PFOA have been shown and evaluated in an *in vitro* test system with cytokine release by immune cells (Corsini et al., 2011). It was shown that both PFOS and PFOA suppress cytokine secretion; of these, PFOS was the most potent. It was also shown that PFOA and PFOS have different mechanisms of action.

**Genotoxicity**

The genotoxicological potential to generate reactive oxygen species (ROS) and to induce oxidative DNA damage in human HepG2 cells has been studied for the perfluorinated chemicals PFOA, PFOS, PFBS, PFNA and PFHxA (Eriksen et al., 2010). PFOA was most active followed by PFOS and PFNA. Perfluorobutane sulfonate (PFBS) and perfluorohexanoic acid (PFHxA) did not generate ROS or DNA damage in that test.

**Effects on cell membranes and intercellular communication**

PFOS, PFOA and other PFAAs are substances attracted to surfaces, and PFOS and to a lesser extent PFOA can partition into model bilayers and cell membranes, where they cause changes in membrane structure, properties and function. An increased fluidity may change cell membrane surface potential and enhance calcium channels with the result of increased intracellular Ca²⁺ (Harada et al., 2005; Liao et al., 2008). That is the case for cultured hippocampal neurons where PFOS was most potent followed by PFTA, PFDA PFHxS and PFOA (Liao et al., 2009).

PFOS, PFOSA, PFHxS and PFCAs with carbon chain lengths of 7-10 can rapidly and reversibly inhibit gap junction intercellular communication (GJIC) in a dose-dependent manner in animals, with PFDA inhibiting more than PFOA. GJIC is the major pathway of intracellular signal transduc-
tion; it is therefore important for normal cell growth and function. Defects in this communication may lead to teratogenesis, neuropathy, infertility, diabetes, autoimmune disorders, cancer, and other diseases (Upham et al., 2009).

6.2 Toxicology of PFSA, including PFOS and derivatives

Acute toxicity
The acute lethal toxicity of PFOS moderately corresponds to a classification as Acute tox 4. The oral rat LD$_{50}$ for PFOS is 250 mg/kg bw (3M 1999); therefore, PFOS is a little more toxic than PFOA. The oral LD$_{50}$ in newborn mice was as low as 10 mg/kg bw/d (Lau et al., 2004).

Short-term exposures
Toxicological studies have demonstrated that the liver is the primary target organ for PFOS, and body weight loss, increased liver weight, liver cell hypertrophy and changed lipid metabolism with reduction in serum cholesterol are early responses in experimental animals (Seacat et al., 2003).

The no-observed-adverse-effect-level (NOAEL) for liver effects in male rats exposed for PFOS during 14 weeks feeding was 5 mg/kg/d (Seacat et al., 2003).

Rats seem to tolerate somewhat higher liver concentrations of PFOS than monkeys, because the NOAEL for changes in thyroid hormone values (T$_3$$\downarrow$ and TSH$\uparrow$) in a 6-month monkey study was 0.15 mg/kg/d (Seacat et al., 2002).

The sub-chronic toxicity of potassium perfluorobutanesulphonate (PFBS) has been studied in rats at doses of 60, 200, and 600 mg/kg-day bw for 90 days (Lieder et al., 2009a). No treatment-related mortality, bodyweight, or neurological effects were noted. Red blood cell counts, haemoglobin, and haematocrit values were reduced in males receiving 200 and 600 mg/kg-day. The NOAEL for the female rat in this study was 600 mg/kg-day (highest dose of study). The NOAEL for the male rat was 60 mg/kg-day based on haematological effects.

PFOS did affect the neuroendocrine system in rats, when female rats were injected intraperitoneally with 0, 1 and 10 mg PFOS/kg bw for two weeks (Austin et al., 2003). The oestrous cycle was affected, serum corticosterone level was increased, and serum leptin concentration and norepinephrine concentration in the paraventricular nucleus of the hypothalamus were decreased.

The immune system in mice seems to be highly sensitive to PFOS, and various immune parameters were affected at much lower levels than expected B-cells were identified as potential targets (Keil et al., 2008; Peden-Adams et al., 2008; Qazi et al., 2010; Fair et al., 2011). The lowest observed effect levels (LOAEL) in a 28 days' oral mouse study was 0.05 mg PFOS/kg total administered dose.

Reproductive and developmental effects
Many studies have shown that gestational exposure to PFOS may cause developmental toxicity in rats and mice, including reduction of foetal weight, cleft palate, oedema, delayed ossification of bones, and cardiac abnormalities (reviewed by Lau et al., 2004 and 2007), and the developmental toxicity of PFOS is higher than that of PFOA. Structural abnormalities were only found in the highest PFOS dose groups, where significant reductions of weight gain and food consumption were also observed in the pregnant dams. Thus the relevance of these effects may be questioned.

Exposure to PFOS during pregnancy in rats (1-10 mg PFOS/kg/d from gestation day 2-21) and mice (1-20 mg PFOS/kg/d from gestation day 1-18) indicated that in utero exposure to PFOS severely compromised postnatal survival and caused delay in growth and development accompanied by hypothyroxinemia in the surviving pups (Lau et al., 2003). In a two-generation reproduction study the NOAEL value in rats for PFOS was 0.1 mg/kg/d (Luebker et al., 2005). Concurrent exposure to
PFOS and restraint stress enhance effects (Fuentes et al., 2007). PFOS was associated with reduced epididymal sperm counts in mice (Wan et al., 2011).

High doses of EtFOSE (N-ethyl-N-(2-hydroxyethyl)perfluoroctane sulfonamide or N-ethyl perfluorooctane sulfonamidoethanol) also caused reduced maternal body weight and foetal weight in rodents and had effects quite similar to its metabolite PFOS. Both PFBS and PFHxS have been assessed for developmental and reproductive effects. Maternal exposure to PFBS potassium salt did not produce any adverse effect on embryo/foetal development, and no significant alterations were noted in a two-generation study in rats at doses of up to 1 mg/kg/d (NOAEL). PFHxS was only examined in a screening system at lower doses without any effect observed (Lau et al., 2003, 2004).

The potential reproductive and developmental toxicity of perfluorohexane sulfonate (PFHxS) was studied in an experiment with rats dosed by gavage at 0.3, 1, 3, and 10 mg/kg/d 14 days prior to cohabitation, during cohabitation, and until the day before sacrifice (21 days of lactation or presumed gestation day 25 (if not pregnant) for females and minimum of 42 days of treatment for males). Offspring were not dosed by gavage but were exposed by placental transfer in utero and potentially exposed via milk. At all doses reductions in serum total cholesterol and other biochemical changes in the blood but no reproductive or developmental effects were observed, and there were no treatment-related effects in dams or offspring (Butenhoff et al., 2009a).

In a more recent two-generation reproduction study with the potassium salt of perfluoro butanesulfonate the parental-generation (P) rats were dosed orally by gavage with 0, 30, 100, 300 and 1000 mg PFBS/kg/day for 10 weeks prior to and through mating (males and females), as well as during gestation and lactation (females only). First generation (F1) pups were dosed similarly, beginning at weaning (Lieder et al., 2009b). Second generation (F2) pups were not directly dosed but potentially exposed to PFBS through placental transfer and nursing, and the study was terminated 3 weeks after their birth. At the two high doses, increased liver weight and some effect on the kidneys were observed. NOAEL for the parental generations was 100 mg/kg bw/day.

Similar effects to what is mentioned for rodents happen in rabbits exposed to PFOS and EtFOSE during gestation. The no-observed-effect-level (NOEL) for PFOS in rabbits was 0.1 mg/kg/d (Case et al., 2001).

**Cancer and mutagenicity**

PFOS and derivatives are not mutagenic in various test systems but may increase the genotoxicity of other chemicals. An example is that the genotoxicity of cyclophosphamide in the micronucleus assay with hamster lung V79 cells was increased manifold by simultaneous exposure to PFOS (Jernbro et al., 2007).

In a two-year rat feeding study with PFOS, a modest liver tumour response (hepatocellular adenomas and one carcinoma) was observed in the high dose group of 20 ppm PFOS as potassium salt corresponding to an exposure of 1.5 mg PFOS/kg/d (Seacat et al., 2003).

A dietary exposure to 100 ppm EtFOSE over a two-year period caused an increase of hepatocellular adenomas (+ one carcinoma) in female rats and hepatocellular adenomas thyroid follicular cell adenomas in males rats (Thomford et al., 2002). It was estimated that 20% of an oral dose of EtFOSE was metabolised to PFOS.

### 6.3 Toxicology of PFCAs including PFOA and derivatives

The toxicology of PFOA has been reviewed by Kennedy et al. (2004), among others. The toxicological information about PFOA precursors and PFCAs with other chain lengths is sporadic.
Acute toxicity

The acute lethal toxicity of PFOA is moderate, corresponding to a classification as Acute tox 4; for instance, the oral LD$_{50}$ is reported to be between 430 and 1800 mg/kg for adult rats of both sexes with most data in the lower end (Kennedy et al., 2004). Newborns are twice as sensitive with oral LD$_{50}$ of about 250 mg/kg (The U.K. Committee on Toxicity 2006). In mice and guinea pigs the oral LD$_{50}$s are 457 and around 200 mg/kg, respectively. The dermal acute toxicity is lower with skin LD$_{50}$ of 7000 mg/kg in rats and 4300 mg/kg in rabbits probably because of limited uptake. PFOA is a mild skin- and eye irritant – maybe because of its acidity. PFOA is also moderately toxic by inhalation as dust with a $^{48}$LC$_{50}$ of 0.98 mg/L.

For PFOA and PFDA (perfluorodecanoic acid) the rat intraperitoneal LD$_{50}$s are 189 and 41 mg/kg, respectively. Thus PFDA with a longer alkyl chain is much more acutely toxic, and it also has delayed effects (Olson and Anderson, 1983). This is in accordance with the general finding that the toxicity of perfluorinated chemicals increases with the length of the fluoroalkyl chain.

Short-term exposures/repeated-dose toxicity

The liver is the target organ, and early responses in animals are dose-related body weight reduction, liver weight increase, hepatocellular hypertrophy and changed lipid metabolism with reduction in serum cholesterol (Kennedy et al., 2004).

The no-observable-adverse-effect-level (NOAEL) and lowest-observable-adverse-effect-level (LOAEL) for liver effects (weight reduction) by PFOA in male rats exposed by feeding in 13 weeks were estimated at 0.06 and 0.64 mg/kg bw/day, respectively (Perkins et al., 2004). Another repeated-dose study found a similar LOAEL of 0.3-1 mg/kg bw/day for PFOA in male rats, and the branched isomers of PFOA had lower toxicity than the linear forms (Loveless et al., 2006).

PFOA is less liver toxic in monkeys with a LOAEL of 3 mg/kg/d in a six month study. The only change in the monkey was liver enlargement (Butenhoff et al., 2002).

PFDA having a longer chain than PFOA was more toxic in rat, hamster, mouse and guinea pig (van Rafelgheim et al., 1987; Kawashima et al., 1995; Ohmori et al., 2003).

Sequential 28-day and 90-day oral toxicity studies were performed in male and female rats with ammonium perfluorobutyrate (PFBA) at doses up to 150 and 30 mg/kg-d, respectively, and ammonium perfluorooctanoate (PFOA) was used as a comparator at a dose of 30 mg/kg-d in the 28-days study (Butenhoff et al., 2012). Female rats were unaffected by PFBA. Effects in males included: increased liver weight, slight to minimal hepatocellular hypertrophy; decreased serum total cholesterol; and reduced serum thyroxin. The no-observable-adverse-effect-levels (NOAELs) were 6 and >150 mg/kg/d for male and female rats in the 28-day study and 6 and >30 mg/kg/d in the 90-day study, respectively. Unlike with PFBA, dosing with 30 mg/kg/d PFOA resulted in increased incidence of clinical signs of toxicity (e.g. hunched posture), increased liver weight in females as well as males, and a major (75%) reduction in body weight of males. Thus, the relative response of rats to dosing with PFBA as compared to PFOA was likely the result of both the more rapid pharmacokinetic clearance and lesser pharmacodynamic potency of PFBA.

For the sodium salt of perfluorohexanoic acid (PFHxA), a NOAEL for sub-chronic toxicity in rats after 90 days gavage exposure was determined at 20 mg/kg bw/day (Loveless et al., 2009). In another study based on liver effects, the NOAELs were estimated at 50 mg/kg bw/day and 200 mg/kg bw/day, respectively, for males and female rats (Chengelis et al., 2009).

Perfluorobutanoic acid (PFBA) has also been tested in a 90 days gavage study with rats (Foreman et al., 2009; Bjork and Wallace 2009). At the highest dose (30 mg/kg bw/day) there was an increase
in liver weight and reduced thyroid hormone in males indicating a higher toxicity than PFHxA but lower than PFOA. The toxicity was mediated by PPARα and not considered relevant for humans.

**Toxicological mechanism**

Polyfluorinated acids are analogue ligands to natural long-chain fatty acids and may displace them in biochemical processes and at receptors, such as PPARα and the liver-fatty acid binding protein (L-FABP).

Perfluoroalkanoates, particularly PFOA, PFNA and PFDA but not PFHxA, are highly potent peroxisome proliferators in rodent livers and affect mitochondrial, microsomal, and cytosolic enzymes and proteins involved in lipid metabolism (Ikeda et al., 1985; Vanden Heuvel 1996; Upham et. al., 1998; Kudo et al., 2000). PFBA has a slighter effect on indicators of peroxisome proliferation (Ikeda et al., 1985).

Kudo and co-workers (2001) studied PFCAs with different chain lengths (C7 - C10) in male rodent liver. Increase in hepatic fatty acid β-oxidation activity (acyl-CoA oxidase) was used as a biochemical measure of peroxisome proliferation. The result indicated that the liver concentration and not the chain length was decisive, but the longer the chain the more of the compound was accumulated in the liver.

In vitamin A deficient mice, PFOA had a stronger effect and caused a 3-6 times increase in the β-oxidation of fatty acids (Sohlenius et al., 1995).

The differences between animal species are significant for PFDA. Peroxisome proliferation was greatest in mice and almost absent in guinea pigs. However, accumulation of lipid droplets in liver cells was more pronounced in hamsters and guinea pigs than in rats and mice exposed to PFDA (van Rafelgheim et al., 1987).

**Immunotoxicology**

The potential of PFOA to be toxic for the immune system has been discussed by deWitt et al. (2009). PFOA is an immunosuppressant through induction of PPARs and enhances the IgE-mediated hypersensitivity response to ovalbumin, and in this way it may provoke asthma (Fairley et al., 2007). PFNA has also shown immunotoxicity (Fang et al., 2008; 2010).

**Reproductive and developmental effects**

Many studies have shown that gestational exposure to PFOA may cause developmental toxicity especially in mice (reviewed by Lau et al., 2004 and 2007).

Dose-dependent growth deficits and reduced birthweight were observed in offspring of pregnant mice which were exposed by gavage for PFOA during gestation days 1-17. At exposures ≥ 5 mg/kg/d postnatal survival was also reduced and eye-opening was delayed up to 2-3 days. The maternal LOAEL was determined at 1 mg/kg bw/day and the foetal NOAEL was maternal exposure to 3 mg/kg bw/day (Lau et al., 2006; Wolf et al., 2007).

A more recent mouse study observed higher body weight and increased insulin and leptin levels in post pubertal female offspring after low-dose in utero exposures to PFOA (Hines et al., 2009).

The mammary gland has, specifically, proven to be a sensitive tissue with respect to various developmental endpoints, including functional lactation, milk protein gene expression, and developing neonatal and peripubertal structures. Some animal studies have shown that gestational exposure of pregnant (female) mice to doses from 3 mg PFOA/kg bw/d may result in delayed mammary gland development for offspring, which persisted into adulthood. These impacts were both a matter of
doses and of exposure timing (White et al., 2009; Yang et al., 2009; Tan et al., 2007 and 2009; Zhao et al., 2010).

PFOA exposure in offspring either during lactation or through the intra-uterine route induces delayed mammary gland development. This delay was visible as early as birth and has been found to extend into adulthood. In a multigenerational mice study P0 dams were exposed by gavage to either up to 5 mg PFOA/kg/d on gestational days 1-17 or 1 mg/kg/d during gestation. The F1 and F2 offspring was exposed continuously to 5 ppm PFOA in their drinking water. The F1 dams exposed to PFOA exhibited diminished lactational morphology. All exposed F1 females and highest exposed P0 and F2 females had delayed mammary gland differentiation. It was concluded that gestational PFOA exposure of mice induced delay in mammary gland development and/or lactational differentiation across three generations (White et al., 2011). The exposure levels were similar to concentrations occasionally found in contaminated drinking water supplies in the USA.

For the sodium salt of perfluorohexanoic acid (PFHxA), a NOAEL for developmental toxicity in rats after 90 days gavage exposure was determined at 100 mg/kg bw/day (Loveless et al., 2009).

A study exposing pregnant mice to perfluorobutanoic acid (PFBA) in doses of 35, 175 and 350 mg/kg bw/day showed maternal liver effects at the two high doses but no significant effects on the offspring (Das et al., 2008). Thus PFBA has lower developmental toxicity than PFOA.

**Effects on fertility**

The effects on hormone levels in rodents are reflected in changes in the testis, where exposure to PFOA results in Leydig cell hyperplasia and eventually development of Leydig cell adenomas (Biegel et al., 1995).

A study of effects on testis in adult rats exposed to perfluorododecanoic acid (PFDoA) also showed a reduced gene expression of many genes involved in cholesterol transport and steroidogenesis and a reduced serum testosterone level (Shi et al., 2007). Thus, it seems that exposure to some PFAAs can severely affect proliferation and function of Leydig cells in the adult rat. Leydig cells in the testis are the main sites for testosterone biosynthesis.

This is of considerable concern, because Leydig cell hyperplasia is common among infertile men (Holm et al., 2003) who, as a group, also shows lower testosterone levels than comparable normal controls (Andersson et al., 2004). Reduced testis function has been linked to the testicular dysgenesis syndrome (TDS) (Skakkebæk et al., 2001). The TDS hypothesis states that in utero exposure to endocrine disruptors can damage testis development and lead to reduced testis function in the adult, with symptoms ranging from a moderately reduced semen quality to testis cancer. The best animal model for TDS consists of rats exposed to long-chain phthalates in a critical time window during development, which results in testis dysgenesis with Leydig cell hyperplasia and clustering of the Leydig cells in the centre of the testis, resulting in reduced testosterone levels and compromised fertility in the adults (Sharpe 2006; Hallmark et al., 2007).

The sodium salt of perfluorohexanoic acid (PFHxA) was not a reproductive or neurobehavioural toxicant in rats after 90 days gavage exposure at 500 mg/kg bw/day (Loveless et al., 2009).

**Cancer and mutagenicity**

PFOA was non-mutagenic in the Ames test using five strains of *Salmonella typhimurium* and in a single strain of Saccharomyces cerevisiae (Griffith and Long 1980). Several other mutagenicity studies of PFOA published by contract laboratories support the inactivity of PFOA (Kennedy et al., 2004). PFDA is also negative in the Ames-Test and various other test systems. However, PFDA was active in a chromosome aberration assay in the presence of S-9 mix and in an S-phase DNA synthesis assay (Godin et al., 1992). The sodium salt of perfluorohexanoic acid (PFHxA) was neither mu-
tagenic in the Ames test nor induced chromosome aberrations in human lymphocytes (Loveless et al., 2009).

Long-term animal bioassays have been conducted with CD rats belonging to a strain that has a low spontaneous incidence of relevant tumours. The rats were exposed to up to 300 ppm (corresponding to about 15 mg/kg/d) PFOA in the diet for two years; hyperplasia and a dose-dependent increase in testicular Leydig cell adenomas and increase of benign hepatocellular and pancreas tumours were observed (Cook et al., 1992; Biegel et al., 1995; Liu et al., 1996; Biegel et al., 2001). These tumours could be a result of peroxisome proliferation and endocrine changes, because reduced aromatase activity and a sustained increase in serum estradiol were observed. Nevertheless, US Environmental Protection Agency has classified PFOA as an animal carcinogen (US EPA 2002).

6.4 Toxicology of other polyfluorinated substances

These substances include for example fluorotelomers of various sorts and perfluoroalkyl phosphorous compounds. The toxicological data is limited.

Polyfluoroalkyl phosphate formulations are fluorotelomer-based commercial products with a high potential for human exposure, containing a mixture of fluorinated chain lengths as well as phosphate mono-esters (monoPAPs), di-esters (diPAPs) and tri-esters (triPAPs). Animal experiments with 4:2-, 6:2-, 8:2- and 10:2 monoPAPs and diPAPs showed that the diPAPs were bioavailable, with bioavailability decreasing as the chain length increased from 4 to 10 perfluorinated carbons (D’Eon & Mabury 2011). The monoPAPs were not absorbed from the gut; however, they found evidence to suggest phosphate-ester cleavage within the gut contents. Biotransformation to the PFCAs was observed for both monoPAPs and diPAPs congeners.

The mono- and di-substituted perfluorinated phosphonic acids (mono-PFPAs and di-PFPAs) are a new class of fluorinated acids, high volume chemicals (surfactants) used, as wetting agent in waxes and coatings and as defoaming additives in pesticides, among other uses, and found occasionally in the environment and in human blood in Canada. In rats these chemicals (with C6-C12 fluoroalkyl chains) are absorbed a little slower than PFCAs and the absorption decreases with chain length and di-PFPAs less than mono-PFPAs. The blood half-lives of a few days are similar to PFOA and PFOS but the renal clearance is much slower. The faecal excretion is lower than 10%. Preliminary data indicates that these chemicals are long-lived in humans (D’Eon & Mabury 2010).

The fluorotelomer alcohols 6:2 FTOH and 8:2 FTOH induce MCF-7 breast cancer cell proliferation and up-regulates the oestrogen receptor (Maras et al., 2006; Vanparys et al., 2006).

Various polyfluorinated alkyl iodides have been studied for estrogenic activity in some in vitro test systems (Wang et al., 2012). The perfluorohexyl- and perfluorooctyl iodides were the only tested substances promoting the proliferation of MCF-7 cells, induced luciferase activity in MVLN cells, and up-regulated the expression of two estrogen-responsive genes, TFF1 and EGR3. All tested substances showed estrogenic effects. The optimal chain length for estrogenic effect was C6-perfluoroalkyl iodides.

6.5 Human epidemiological studies of the effect of exposures to polyfluoroalkylated chemicals

Workplace exposures and cancer

The experience from the work environment has not indicated any important direct adverse health effects among workers exposed to either PFOS (Olsen et al., 1999) or PFOA (Olsen et al., 2000), besides the retrospective cohort mortality study of a cohort of 2083 workers potentially exposed to perfluorooctane sulfonyl fluoride (PFOSF) at least 1 year at the 3M Minnesota (Alexander et al., 2003). PFOSF can be metabolised into PFOS. A total of 145 deaths were identified, and that was less than expected for the general population and the total cancer deaths were also less than ex-
pected (healthy worker effect). However, for the highly exposed, two deaths of liver cancer (SMR 3.08) and three deaths of bladder cancer (SMR 12.77) were observed. For the whole cohort there was an increased mortality of bladder cancer (SMR 4.81).

These results have been dismissed by The U.K. Committee on Toxicity (2006) because of:

- inadequacy of exposure assessment using job categories;
- potential co-exposure to carcinogenic aromatic amines, and
- lack of evaluation across PFOS manufacturing sites.

However, an exposure assessment based on job categories is normal for occupational cohort studies, and in addition the U.K. Committee on Toxicity did not mention that blood concentrations were available for the various job categories. The potential exposures to aromatic amines are likely to have been insignificant compared to the larger PFOSF exposures but an additive effect or promotion cannot be excluded. Finally, the factory studied in Minnesota was the major (only?) production facility in the World in that period.

Cancer risk in non-occupational groups

In a Danish prospective cohort of about 57,000 healthy individuals aged 50-65 selected from 1993-1997 and followed until July 2006, no significant cancer risk related to PFOS and PFOA levels was indicated (Eriksen et al., 2009).

In Greenland the incidences of breast cancer have been increasing over recent years. A case-control study in Greenland compared serum levels of various environmental contaminants in breast cancer patients with levels in a control group (Bonefeld-Jørgensen et al., 2011). The following PFAAs were measured: PFSA (PFOS, PFHxS, and PFOSA), PFCAs (PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA and PPTrA) with PFOS and PFOA as the dominating species. Breast cancer cases had significantly higher serum levels of PFOS (medians: 45 ng/mL – 21.9 ng/mL) and ΣPFCA (medians: 8.0 ng/mL – 5.2 ng/mL) than controls.

Population studies with effect on lipid metabolism etc.

A recent review of epidemiological evidence on the health effects of PFOA was published by Steenland et al. (2010a). They reported that a positive association of PFOA with cholesterol levels in blood was observed in six occupational studies, three studies of a highly exposed community and one general population study. Several studies also showed an association between PFOS and lipids of a similar magnitude.

One study of a large population in mid-Ohio Valley exposed via contaminated drinking water and with mean serum concentration of 69 ng PFOA/mL and 23 ng PFOS/mL, respectively, showed that PFOA was significantly associated with increased total cholesterol and low density lipoproteins (Frisbee et al., 2010). PFOS was significantly associated with increased total cholesterol, low density lipoproteins and high density lipoproteins.

In the same population a later study showed a positive association between PFOS and PFOA serum levels and serum levels of alanine transferase (ALT) – a biomarker for liver damage (Gallo et al., 2012).

The population study used data for 860 individuals from the 2003-2004 National Health and Nutrition Examination Survey (NHANES) and found a positive association between total cholesterol and serum concentrations of PFOS (mean 25 ng/mL), PFOA (mean 4.6 ng/mL) and especially PFNA (mean 1.3 ng/mL) (Nelson et al., 2010a).
Three cross-sectional studies have reported positive association between PFOA and uric acid, a natural product of purine metabolism. In one study of adults with elevated community exposure to PFOA (Steenland et al., 2010b), both PFOA and PFOS were significantly associated with uric acid but PFOA more, and the concentrations in the blood of PFOA were also higher than PFOS.

A study of gene expression profiles in postmenopausal woman from Norway showed significant effects of PFOA on fatty acid metabolism and increased expression of CYP4A22 and on insulin signalling pathways (Rylander et al., 2011).

In a prospective cohort of 665 Danish pregnant women, it was found that their serum PFOA levels were positively associated with overweight/obesity at 20 years of age in their female offspring (Halldorsson et al., 2012). In addition, maternal PFOA concentrations were positively associated with serum insulin and leptin levels, and inversely associated with adiponectin levels in female and male offspring. In another study of a young hypertension cohort in Taiwan, serum PFNA concentrations were associated with elevated serum adiponectin (Lin et al., 2011).

**Population studies of reproductive effects**

In humans PFOS and PFOA are transferred from the pregnant mother to the foetus (Inoue et al., 2004; Needham et al., EST 2011; Beeson et al., 2011; Mondal et al., 2012; Gützkow et al., 2012).

A study was performed in the USA of the Danish National Birth Cohort, which included data from more than 90 000 pregnant Danish women obtained from March 1997 to November 2002 (Fei et al., 2007). This study found an inverse association between maternal plasma levels of PFOA - but not PFOS - and birth weight. The mean plasma concentrations were 35.3 ng PFOS/mL and 5.6 ng PFOA/mL.

An analysis of birth records linked to a survey from the PFOA drinking water contaminated mid-Ohio Valley showed some suggestion of an association with early preterm birth, and measures of growth restrictions showed weak and inconsistent association with PFOA (Savitz et al., 2012ab).

A cross-sectional study, which was conducted in 2004-2005 of about 300 mothers and their newborn from Baltimore in the USA, found a negative association between concentrations of PFOS and PFOA in the mothers’ serum and the birth weight and birth size of the newborn, although the serum concentrations were much lower in this study with medians of 5 ng PFOS/mL and 1.6 ng PFOA/mL (Apelberg et al., 2007ab). However, in a later study from Japan, where serum levels were similar with means of 5.6 ng PFOS/mL and 1.4 ng PFOA/mL, no such correlation was found (Washino et al., 2009).

A follow-up study of the Danish cohort found that maternal PFOA levels in early pregnancy were associated with smaller abdominal circumference and birth length. For each ng/mL increase of PFOA, birth length decreased by 0.069 cm and an abdominal circumference decreased by 0.059 cm (Fei et al., 2008).

A study of a large cohort from Avon in the UK with prenatal blood concentration (medians) of 19.2 ng/mL PFOS, 3.7 ng/mL PFOA and 1.6 ng/mL PFHxS showed that mothers from the upper tertile gave birth to girls weighing 140 gram less than for the lower tertile but at 20 months the girls with high PFOS exposure weighed 580 grams more (Maisonet et al., 2012). These results should be evaluated with the paper discussed above in mind (Halldorsson et al., 2012).

Another study discovered an association between PFOS and PFOA in maternal serum and decrease of duration of breast feeding in multiparous women (Fei et al., 2010).
Another follow-up reported an association between reported time to pregnancy and maternal plasma levels of PFOA and PFOS in 1400 pregnant women; therefore, these chemicals may cause reduced subfecundity (Fei et al., 2009). Another prospective cohort study of 222 Danish couples could not confirm that PFAAs may affect time-to pregnancy (Vestergaard et al., 2012).

That may not be a problem of the mother alone, because another Danish study found that high PFAA levels (medians: 24.5 ng PFOS/mL, 4.9 ng PFOA/mL and 6.6 ng PFHxS/mL) in blood serum were associated with fewer normal sperm in studied normal young men (Joensen et al., 2009).

Another more recent study of 256 American infertility patients reported no association between PFOS and PFOA levels (medians: 32.3 ng PFOS/mL and 49.2 ng PFOA/mL) and sperm quality (Raymer et al., 2011).

In an European study of the sperm quality of 588 partners to pregnant women from Greenland, Poland and Ukraine, a negative association was found between PFOS serum levels and sperm morphology in the two European populations but not in the Inuits from Greenland, who had the highest serum levels with a median of 44.7 ng PFOS/mL against 18.5 ng PFOS/mL in Poland and 7.6 ng PFOS/mL in Ukraine (Toft et al., 2012). It was suggested that PFOS interact with the sperm membrane function.

In a population of the contaminated area of mid-Ohio Valley, a study discovered that children showed a later age (3-6 months delay) of puberty correlated with PFOS/PFOA concentrations in the blood (Lopez-Espinosa et al., 2011).

A very recent study has discovered a significant association between serum PFOA and PFNA levels and endometriosis in the operative samples (Louis et al., 2012).

Kidney diseases
An association between serum PFAAs, insulin resistance and metabolic syndrome has been found indicating a possible diabetic effect and effect on the kidneys (Lin et al., 2009).

Chronic kidney Disease (CKD) is a major public health problem with increased prevalence in the USA and elsewhere (Coresh et al., 2011). Since, it is known that the kidneys are an important target organ for polyfluorinated chemicals a study from West Virginia of examined the relation between serum levels of PFOS and PFOA and CKD (Shankar et al., 2011). The population studied was 4500 adults of both sexes from NHANES surveys 1999-2008 for which there were serum PFAA measurements. For the fourth quartile (>29.5 ng PFOS/mL and >5.9 ng PFOA/mL) they found a positive association between these fluorinated chemicals and CKD which was independent of normal confounders.

Endocrine disruption
Data from the NHANES 1999-2006 surveys including almost 4000 individuals found that higher concentrations in serum of PFOS (>36.8 ng/mL) and PFOA (>5.7 ng/mL) were associated with current thyroid disease in the US general population (Melzer et al., 2010).

Effects on the immune system
An investigation of children aged 5 and 7 years from Faroe Island in the Atlantic showed that commonly prevalent exposures to PFOS, PFOA, PFHxS, PFNA and PFDA measured in blood serum were associated with lower antibody responses to childhood immunizations (vaccinations) and an increased risk of antibody concentrations below the level needed to provide long-term protection against diphtheria and tetanus (Grandjean et al., 2012).
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Children’s behaviour
Data from the NHANES 1999-2004 and the C8-Health Project in the USA surveys showed positive association between some serum PFAS levels and attention deficit-hyperactivity disorder (ADHD) in children (Hoffman et al., 2010; Stein and Savitz, 2011). The later study found an association with ADHD and PFHxS blood levels.

Higher blood levels of PFOS, PFNA, PFDA, PFHxS and PFOSA (but not PFOA) were associated with significantly shorter “Impaired Response Inhibition” (IRT) during the “differential reinforcement of low rates of responding” (DRL) tasks measuring children’s impulsivity (Gump et al. 2011).

6.6 Risk assessment
The risk characterisation for the general population exposed to PFOA shows a sufficient margin of exposure and safety for children adults and the elderly, according to Butenhoff et al. (2004).

The U.K. Committee on Toxicity (2006) has recommended a provisional Tolerable Daily Intake (TDI) for PFOA and PFOS of 3 µg/kg bw/d and 0.3 µg/kg bw/d, respectively, using an uncertainty factor of 100. They conclude that for some small children the TDI may already be exceeded.

In 2008 EFSA’s CONTAM Panel performed a risk assessment and established a tolerable daily intake (TDI) of 150 ng/kg bw per day for PFOS and 1,500 ng/kg bw per day for PFOA (EFSA 2008). EFSA has not suggested TDIs for other PFASs.

A 2012 report concluded that dietary exposures to PFOS and PFOA are highly unlikely to exceed the TDIs (EFSA, 2012).

These assessments have all been based on results of animal experiments, which may be highly arbitrary and unreliable because the renal clearances of PFOA and PFOS are almost insignificant in humans, contrary to a significant active excretion in experimental animals. These differences in excretion of PFASs are mentioned by EFSA but not taken into account in their assessment.

Therefore, these chemicals in humans leave the blood mainly by redistribution to internal organs and not by elimination from the body. This lack of elimination may considerably increase the inter-
nal exposure time in critical organs, and might be the explanation for the many effects found in lower exposed human populations.

6.7 Summary on human health effects

Information related to human health is available for only a few of the several hundreds of polyfluorinated chemicals (PFCs) used in industry and consumer products.

The perfluoroalkyl sulfonic acids (PFSAs) and the perfluoroalkyl carboxylic acids (PFCAs) are closely related structurally because of the perfluorinated chain. Nevertheless, these chemicals elicit different biological responses in vitro and in vivo. PFOS is more toxic than PFOA and the toxicity of perfluorinated chemicals increases generally with the length of the alkyl chain. PFCAs with a branched alkyl chain seem to be less toxic than linear isomers. Biological half-lives are much longer in humans compared to experimental animals.

PFOS and four of its derivatives have a harmonised classification as carcinogenic, toxic to reproduction, acute toxic and toxic to specific target organ by repeated exposure. A similar classification has been proposed for PFOA and APFO.

The precursors and functional derivatives of PFOS and PFOA will ultimately be transformed to the basic acids in the body and result in similar effects as the PFOS and PFOA. For example, the fluorotelomer alcohol 8:2 FTOH may be transformed in mice and rats to PFOA, PFNA and other metabolites. In the same way N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE) is metabolised to perfluorooctane sulfonamidoethanol (PFOSE), perfluorooctane sulfonamide (PFOSA) and finally to perfluorooctane sulfonate (PFOS).

Population studies have discovered positive associations between serum levels of perfluoroalkylated acids (PFAA) and uric acid levels, thyroid disease, overweight, insulin- and leptin levels, and Chronic Kidney Disease (CKD), which is a major public health problem with increased prevalence. An investigation of children from Faroe Island in the Atlantic showed that commonly prevalent exposures to PFAAs were associated with lower antibody responses to childhood immunizations (vaccinations). The immune system seems to be highly sensitive to PFAAs, and various immune parameters were affected at levels which are found in exposed human populations.

Human population studies have found associations between maternal PFAA exposure and reported time to pregnancy, preterm birth, and lower birth weight and birth size of newborns. Some population studies also indicate that PFAAs can have an adverse effect on semen quality.

The short-chain analogues have shorter half-live times in humans. The mean half-live in human blood of is about one month for PFBS and 2-4 days for PFBA as compared to half-lives of 5.4 years for PFOS, 8.5 years for PFHxS, and 3.8 years for PFOA.

The available information, mainly based on relatively few animal studies, indicates that the short-chain analogues to a lesser degree have less effect than the long-chain PFAAs are linked to adverse effects such as developmental toxicity and carcinogenic potential. In general the knowledge about the toxicology of most perfluorinated compounds is rather sparse, and it will take some years and much effort, before we will have sufficient information for evaluation of the full impact of the present levels in humans.

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* Hazard Class and Category Code(s) according to the CLP Regulation as concern human health: Carc. 2, Repr. 1B, STOT RE 1, Acute Tox. 4; see Table 4.
7. Monitoring data and exposure

7.1 PFASs in the environment

7.1.1 Monitoring of PFOS and other PFASs in the environment and releases from point sources

The Danish national environmental monitoring and assessment programme, NOVANA, includes measurements of seven PFAS in point sources and streams and PFOS in marine animals (Table 20). Occasionally screening surveys of a number of PFASs in more environmental compartments are undertaken.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Acronym</th>
<th>Point sources</th>
<th>Marine animals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorooctane sulfonic acid</td>
<td>PFOS</td>
<td>x (small and large sewage treatment plants)</td>
<td>x</td>
</tr>
<tr>
<td>Perfluorooctane sulfonamide</td>
<td>PFOSA</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Perfluorohexane sulfonic acid</td>
<td>PFHxS</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Perfluorooctanoic acid</td>
<td>PFOA</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Perfluorononanoic acid</td>
<td>PFNA</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Perfluorodecanoic acid</td>
<td>PFDA</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Perfluoroundecanoic acid</td>
<td>PFUnA</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

7.1.2 Results from the Danish NOVANA monitoring programme

A number of studies exist of the presence of PFOS and other perfluorinated substances in the environment in Denmark.

A NOVANA screening survey from 2007 of PFOS and other PFASs in the environment, as well as discharges from point sources, has identified the presence of a number of different PFAS compounds near point sources, and in freshwater and marine environments in Denmark (Strand J. et al., 2007). The survey included the following PFASs: PFOS, PFOSA, PFHxS, PFOA, PFNA, PFDA and PFUnA. PFOS and PFOA were generally the predominant components of the measured PFASs in both the point sources and in the aquatic environment as shown in Figure 6.
Increased concentrations of PFOS locally in eel, e.g. from the Silkeborg Lakes and Odense Fjord, indicated that local sources can impact the environment. PFASs were only detected in fish, not in sediments and mussels from freshwater and marine environments.

The survey assessed the level of PFOS to represent an environmental risk especially to fish-eating birds and mammals at the highest trophic levels of the food chain, as most of the fish samples exceed the PNEC value of 17 µg/kg (predicted no-effect concentration) for PFOS in animal food. It should, however, be noted that only the liver and not the entire fish was analysed in the survey (Strand et al., 2007). No conclusion was drawn for the other analysed FPASs.

The most recent data from the NOVANA programme is shown in the table below.
### TABLE 21
Most recent monitoring data for PFOS and other polyfluorinated substances in the environment from the National Novana Programme

<table>
<thead>
<tr>
<th>Substance</th>
<th>Point source</th>
<th>Number of samples *1</th>
<th>Median (maximum) concentration, mg/kg dw</th>
<th>Year</th>
<th>Source of information</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>Lake sediment</td>
<td>18 (18)</td>
<td>&lt;0.010 (&lt;0.010)</td>
<td>2009</td>
<td>Bjerring et al. 2010</td>
</tr>
<tr>
<td></td>
<td>Fish liver</td>
<td>15 (15)</td>
<td>44.4 (156.0)</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;1.0</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Marine sediment</td>
<td>0 (8)</td>
<td>&lt;1.0</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td>PFOSA</td>
<td>Lake sediment</td>
<td>18 (18)</td>
<td>&lt;0.010 (&lt;0.010)</td>
<td>2009</td>
<td>Bjerring et al. 2010</td>
</tr>
<tr>
<td></td>
<td>Fish liver</td>
<td>1 (15)</td>
<td>2.3 (2.3)</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;0.9</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;0.9</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td>PFHxS</td>
<td>Lake sediment</td>
<td>18 (18)</td>
<td>&lt;0.010 (&lt;0.010)</td>
<td>2009</td>
<td>Bjerring et al. 2010</td>
</tr>
<tr>
<td></td>
<td>Fish liver</td>
<td>3 (15)</td>
<td>1.4 (1.6)</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;0.7</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;0.7</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td>PFOA</td>
<td>Lake sediment</td>
<td>18 (18)</td>
<td>&lt;0.010 (&lt;0.010)</td>
<td>2009</td>
<td>Bjerring et al. 2010</td>
</tr>
<tr>
<td></td>
<td>Fish liver</td>
<td>12 (15)</td>
<td>6.18 (24.5)</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;0.4</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;0.4</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td>PFNA</td>
<td>Lake sediment</td>
<td>18 (18)</td>
<td>&lt;0.010 (&lt;0.010)</td>
<td>2009</td>
<td>Bjerring et al. 2010</td>
</tr>
<tr>
<td></td>
<td>Fish liver</td>
<td>6 (15)</td>
<td>2.45 (3.6)</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;0.7</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;0.7</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td>PFDA</td>
<td>Lake sediment</td>
<td>18 (18)</td>
<td>&lt;0.010 (&lt;0.010)</td>
<td>2009</td>
<td>Bjerring et al. 2010</td>
</tr>
<tr>
<td></td>
<td>Fish liver</td>
<td>9 (15)</td>
<td>3.64 (7.9)</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;1.0</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;1.0</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td>PFUnA</td>
<td>Lake sediment</td>
<td>18 (18)</td>
<td>&lt;0.010 (&lt;0.010)</td>
<td>2009</td>
<td>Bjerring et al. 2010</td>
</tr>
<tr>
<td></td>
<td>Fish liver</td>
<td>9 (15)</td>
<td>3.42 (9.4)</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;1.7</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Fresh water sediment</td>
<td>0 (8)</td>
<td>&lt;1.7</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
</tbody>
</table>

*1 Number of positive samples in bracket
7.1.3 The Baltic Sea and North Sea environments

HELCOM concluded in a 2010 assessment report that the PFOS levels in many fish species and sub-regions of the Baltic Sea are higher than the estimated PNEC (predicted no effect concentration) level for the protection of predators, such as mammals and predatory birds, via secondary poisoning (HELCOM, 2009). The risks and threats of PFOA on the Baltic marine environment are currently difficult to estimate due to the lack of ecotoxicological information (i.e. PNEC value has not been comprehensively assessed) according to the study.

The results demonstrate relatively high concentrations of PFOS in the Kattegat and inner Danish waters, compared with levels found in the Baltic Sea (HELCOM, 2009). The concentrations of PFOS in the liver of seals from Danish waters were in the range of 565 to 977 µg/kg while the range for PFOA was 0.3-1.3 µg/kg. For herring and other fish, levels were more uniform across the region. In the Danish waters the concentration of PFOS ranged from 10 to 60 µg/kg ww, while for PFOA it ranged from 1 to 10 µg/kg ww.

The assessment did not include data for other PFASs.

In a screening of perfluorinated substances in the Nordic environment (Kallenborn, 2004) found that lake water, seawater and rainwater (precipitation) samples were contaminated at relatively low levels. However, measurable amounts of PFAS were found in all samples. The Nordic biota samples showed signals of species-dependent distribution and levels. The highest PFAS levels were found in the top predator, the Danish harbour seal (*Phoca vitulina*) samples with PFOS as the predominant PFAS contaminant.

A study of the distribution of PFASs in sediments from the North Sea and the Baltic Sea analysed the spatial and temporal variation the concentrations of PFBS, PFHxA, PFHxS, PFHpA, PFOA, PFOS, PFNA, PFDA, and PFOSA (Theobald et al., 2011). PFASs could be detected in sediments from all 15 stations which had been sampled. In most samples from the German Bight and western Baltic Sea, PFOS had the highest concentrations (0.02 to 2.4 µg/kg dry weight), followed by PFOA at 0.06 to 1.6 µg/kg dry weight. Levels of the other PFASs were five to ten times lower. In order to assess the potential of sediments for the investigation of PFAS time trends, a segmented core from an accumulating area in the Skagerrak (northern North Sea) was analysed. PFOS and PFOA concentrations clearly increase from the lowest layers to the surface layer, indicating a steady increase in PFAS concentrations over the last years. The PFOS and PFOA curves show a nearly parallel temporal development. Similar trends were observed for the other PFCAs (PFHxA, PFHpA, PFNA, PFDA), though at lower concentration levels. The time trends of the PFASs differ fundamentally from those of the “classical” pollutants like PCBs, DDT and HCB, for which used ceased earlier. The data demonstrates that the increase in PFOS concentrations started in the mid-1980s and accelerated for both PFOA and PFOS since approximately 1995.

Ahrens et al. (2010) examined the spatial distribution of 15 PFCs in surface water in the North Sea, Baltic Sea and Norwegian Sea. In the North Sea, the highest concentration was found near the coast, whereas the PFC concentration decreased rapidly from 18.4 to 0.07 ng/L towards the open North Sea. The river Elbe could be identified as a local input source for PFCs into the North Sea, whereas perfluorobutanoicacid (PFBA) was transported into the sampling area with the easterly current. In contrast to the North Sea, the distribution of PFCs in the Baltic Sea was relatively homogeneous, where diffuse sources dominated. In general, the composition profile was influenced from local sources caused by human activities, whereas atmospheric deposition of PFCs were negligible, but according to the authors, the deposition could possibly have an influence on lesser-contaminated sites like the open North Sea or Norwegian Sea.

7.1.4 PFASs in the Arctic environment

PFASs have been detected in air, water, sediment, wildlife and human beings all around the world. Atmospheric transport and global ocean currents have been suggested as the pathways of the PFASs' global transport.
Volatile precursors, such as FTOHs, can undergo long-range atmospheric transport and can be degraded via abiotic and biotic mechanisms. The detection of FTOHs in the Arctic and Antarctic air agreed with the model prediction and conclusion, and supported the hypothesis of atmospheric transport toward remote regions. Dreyer et al. (2009) found that total gas-phase concentrations of ship-based samples ranged from 4.5 pg/m³ in the Southern Ocean to 335 pg/m³ in European source regions. Concentrations of 8:2 FTOH, the analyte that was usually observed in highest concentrations, were between 1.8 and 130 pg/m³. PFC concentrations decreased from continental regions toward marine regions and from Central Europe toward the Arctic and Antarctica. According to the authors, the study gives further evidence that volatile PFCs undergo long-range atmospheric transport to remote regions and may contribute to their contamination with persistent PFCAs and PFSAs.

The significance of precursors to the levels of PFASs found in the Arctic is not well understood for all substances. Most modelling results address transport of PFOA; these conclude that the degradation of FTOHs is likely to be a minor source of PFSAs in the Arctic.

Ionic PFCAs and perfluoroalkyl sulfonates (PFSAs), which have higher water solubility, are mainly distributed in surface waters. Global transport by marine ocean currents was indicated as the major pathway of PFASs' delivery to non-emission regions by both monitoring and modelling results (Zhao et al., 2012).

Stemmler and Lammel (2010) used a global multicompartment model, including fully coupled three-dimensional ocean and atmospheric general circulation models, to approximate the transport of PFOA to the Arctic. In addition to primary emissions, the formation of PFOA in the atmosphere from degradation of 8:2 FTOH was included as a PFOA source. According to the model Oceanic Transport, 8–23 t/y was delivered to the Arctic; this pathway constituted the dominant source of PFOA to the Arctic. Formation of PFOA in the atmosphere led to episodic transport events (time-scale of days) into the Arctic. The total atmospheric deposition of PFOA in the Arctic in the 1990s was estimated at about 1 t/y and was dominated by primary emissions of PFOA rather than secondary formation from FTOH.

In accordance with this work, Prevedouros et al. (2006) calculated the amount of perfluorooctanoic acid (PFOA) transported to the Arctic Ocean by water as 2–12 t/y.

Zhao et al. (2012) detected elevated levels of \( \sum \) PFASs in the North Atlantic Ocean with the concentrations ranging from 130 to 650 pg/L. In the Greenland Sea, the \( \sum \) PFAS concentrations ranged from 45 to 280 pg/L, and the five most frequently detected compounds were perfluorooctanoic acid (PFOA), perfluorohexanesulfonate (PFHxS), perfluoroheptanoic acid (PFHpA), perfluorooctane sulfonate (PFOS) and perfluorobutane sulfonate (PFBS).

The presence of PFASs in the Arctic environment has been extensively studied, among others as part of the Arctic Monitoring and Assessment Programme (AMAP). The available data have been reviewed by Butt et al. (2010) as part of the AMAP POPs assessment (2009) and by Houde et al. (2011).

According to Butt et al. (2010) "The bulk of the monitoring efforts in biological samples have focused on the perfluorinated carboxylates (PFCAs) and sulfonates (PFSAs), although there are very few measurements of PFC precursors. The marine food web has been well studied, particularly the top predators. In contrast, freshwater and terrestrial ecosystems have been poorly studied. Studies from show that in wildlife perfluorooctane sulfonate (PFOS) is generally measured in the highest concentration, followed by either perfluorononanoate (PFNA) or perfluoroundecanoate.
(PFUnA). However, some whale species show relatively high levels of perfluorooctane sulfonamide (PFOSA) and seabirds are typically characterized by high proportions of the C11–C15 PFCAs. PFOA is generally infrequently detected and is present in low concentrations in C11–C15 PFCAs. Food web studies show high bioaccumulation in the upper trophic-level animals, although the mechanism of PFC biomagnification is not understood. Spatial trend studies show some differences between populations, although there are inconsistencies between PFC trends. The majority of temporal trend studies are from the Northern American Arctic and Greenland. Studies show generally increasing levels of PFCs from the 1970s, although some studies from the Canadian Arctic show recent declines in PFOS levels. In contrast, ringed seals and polar bears from Greenland continue to show increasing PFOS concentrations. The inconsistent temporal trends between regions may be representative of differences in emissions from source regions.”

Houde et al. (2011) notes in a review of monitoring of PFCs in aquatic biota, that the most notable observation made was the preponderance of long-chain PFCAs found in organisms, particularly from East Asia and northern latitudes. PFCs detected in livers of tuna collected from the Pacific rim were predominantly PFOS and PFUnA, whereas PFDA and perfluorododecanoate (PFDoA) were also commonly identified (please find original references in the review). The predominance of PFUnA was also observed in livers of dolphins and porpoises, fish, and water bird eggs from several sites in Asia. In addition to Asian sites, the long-chain PFCA profile was also observed in Arctic regions. High proportion of C11-C15 PFCAs were found in Arctic seabirds and PFCA concentrations in polar bear liver were composed largely of C9-C11 with much lesser amounts of PFOA, PFDoA, and perfluorotridecanoate (PFTrA). The contamination profile may suggest specific sources of emission in East Asia dominated by long-chainPFCAs followed by long-range transport via ocean and atmospheric pathways to Northern regions of the globe, according to the authors. The overall observations made in aquatic wildlife worldwide seem to indicate that PFCA levels may surpass those of PFSAs in the future. However, this prediction also depends on trends in use and emissions (Houde et al., 2011).

A recent study supported by the Nordic Council of Ministers analysed 18 PFASs in tissues of different marine mammals from the Arctic (Dam et al., 2011). PFOS was generally found in the highest concentrations. A significant decrease in PFOS was found in hooded seals (1990–2007). On the other hand, increasing trends of one or more PFASs were found in samples of ringed seals, in pilot whales, white-sided dolphins and harbour porpoises. For PFUnA, a significantly increasing trend was found for ringed seals, pilot whales and white-sided dolphins, indicating that levels of the longer-chained PFASs are still increasing. The results are in accordance with the other results reviewed by Houde et al. (2011) and mentioned above.

**7.1.5 PFOS and other polyfluorinated substances in point sources**

In point sources such as wastewater treatment plants, industrial plants and landfills, significant differences in concentration levels have been observed among the different facilities.

The most recent monitoring data are shown in Table 22.

The available data suggests that wastewater treatment plants may be local sources of PFOS substances, as these substances were found not only in inlet water and sludge, but also in outlet water (Strand et al., 2007). By far the highest concentrations of PFOS were found in the outlet water from an industrial facility. However, it was concluded in the study that the concentrations of PFAS in the outlet water were below the critical value where a risk to aquatic organisms is presented.

For data on effluents from landfills please see section 4.2.1.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Point source</th>
<th>Number of samples</th>
<th>Median (maximum) concentration, mg/kg dw</th>
<th>Year</th>
<th>Source of information</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>Water WWT outlet</td>
<td>11 (13)</td>
<td>8,3 (18,1)</td>
<td>2006</td>
<td>Strand J. et al., 2007</td>
</tr>
<tr>
<td>PFOS</td>
<td>WWT sludge</td>
<td>7 (7)</td>
<td>21,7 (74,1)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFHxS</td>
<td>Water WWT outlet</td>
<td>7 (13)</td>
<td>1,4 (2,7)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFHxS</td>
<td>WWT sludge</td>
<td>7 (7)</td>
<td>3,8 (10,7)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFOSA</td>
<td>Water WWT outlet</td>
<td>4 (13)</td>
<td>1,6 (2,1)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFOSA</td>
<td>WWT sludge</td>
<td>1 (7)</td>
<td>3,6 (3,6)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFOA</td>
<td>Water WWT outlet</td>
<td>12 (13)</td>
<td>15,1 (24,4)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFOA</td>
<td>WWT sludge</td>
<td>7 (7)</td>
<td>4,2 (10,7)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFNA</td>
<td>Water WWT outlet</td>
<td>10 (13)</td>
<td>2,4 (3,1)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFNA</td>
<td>WWT sludge</td>
<td>7 (7)</td>
<td>1,7 (8)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFDA</td>
<td>Water WWT outlet</td>
<td>2 (13)</td>
<td>3,1 (3,6)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFDA</td>
<td>WWT sludge</td>
<td>7 (7)</td>
<td>8,7 (10,5)</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFUnA</td>
<td>Water WWT outlet</td>
<td>0 (13)</td>
<td>&lt;2,2</td>
<td>2006</td>
<td>- -</td>
</tr>
<tr>
<td>PFUnA</td>
<td>WWT sludge</td>
<td>3 (7)</td>
<td>2,2 (4,4)</td>
<td>2006</td>
<td>- -</td>
</tr>
</tbody>
</table>

As part of the COHIBA project, running from 2009 to 2012 and co-financed by European Union within the Baltic Sea Region Programme, PFOS and PFOA sources of emissions of PFOS and PFOA to the Baltic Sea were identified and measures for emission reduction evaluated (COHIBA, 2011a,b). The following paragraph is extracted from the report on emission reduction measures.

Within the project, sources of emissions of PFOS and PFOA to the Baltic Sea were assessed on the basis of substance flow analyses (SFA) and review of the literature. Total input of PFOS/PFOA to all environmental compartments in the Baltic Sea catchment was estimated at 300-600 kg/year (around year 2010). Approximately 40% of the total load was emitted to water. The contribution of emissions from municipal waste water treatment plants to the total load was estimated to be in the range of 30% for PFOS and 40% for PFOA. These amounts included direct emissions to water via treatment plant effluent, as well as emissions to (agricultural) land via sewage sludge. The load in municipal waste water originated from urban stock (products), as well as from indirect dischargers, for example metal plating facilities. PFOA releases due to transformation of fluorotelomer were estimated to account for 30% of all releases. The largest contribution to the total load of PFOS/PFOA came from the use of fire fighting foam containing PFOS (and PFOA as impurity). It was estimated that the fire-fighting foams accounted for 70% of the total emissions, while accounting for 20% of the emissions of PFOA. This emission estimate was subject to high uncertainty, since the load emitted to the environment (mainly to land) depends on the incidence of fires and the fate of used fire fighting foam. This use of PFOS has been banned in the EU since 2008; the remaining stocks had to be used or destroyed by mid 2011 (see Chapter 4). Therefore, emissions from this source would currently be expected to decline sharply.
7.1.6 FFASs in groundwater

PFASs are not monitored in groundwater in Denmark.

A pan-European survey of the occurrence of other selected polar organic persistent pollutants in groundwater from 2011 presents data for PFOS, PFOA and PFHxS, PFHpA. The survey includes groundwater samples from Denmark and 22 other EU Member States from a total of 164 locations, but the data are not presented by country.

The maximum and average concentrations of PFOS were higher than the concentration of the three other substances, whereas the median concentration is highest for PFOA. Median concentrations are presented without decimals which make the data difficult to interpret.

### TABLE 23

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Limit of detection, ng/L</th>
<th>Freq. of detection (%)</th>
<th>Max, ng/L</th>
<th>Average, ng/L</th>
<th>Median, ng/L</th>
<th>90th percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>0.4</td>
<td>48.2</td>
<td>135</td>
<td>4</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>PFOA</td>
<td>0.4</td>
<td>65.9</td>
<td>39</td>
<td>3</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>PFHxS</td>
<td>0.4</td>
<td>34.8</td>
<td>19</td>
<td>1</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>PFHpA</td>
<td>0.4</td>
<td>29.9</td>
<td>21</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

7.1.7 Environmental risk limits

The National Institute for Public Health (RIVM) in the Netherlands have developed environmental risk limits for PFOS and proposed water quality standards in accordance with the Water Framework Directive (RIVM, 2010).

### TABLE 24

<table>
<thead>
<tr>
<th>ERL</th>
<th>MPC (µg/L)</th>
<th>MACeco (µg/L)</th>
<th>NC (µg/L)</th>
<th>SRCeco (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater</td>
<td>6.5 x 10^-4</td>
<td>0.65</td>
<td>36</td>
<td>6.5 x 10^-6</td>
</tr>
<tr>
<td>Surface water</td>
<td>0.53</td>
<td>530</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>intended for drinking</td>
<td></td>
<td></td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>water abstraction</td>
<td></td>
<td></td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Marine water</td>
<td>5.3 x 10^-4</td>
<td>0.53</td>
<td>7.2</td>
<td>5.3 x 10^-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0053</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>930</td>
</tr>
</tbody>
</table>

n.a. = not applicable

7.2 Human exposure and biomonitoring

Human exposure to PFASs was reviewed in the 2008 survey of fluorinated substances in impregnated consumer products and impregnating agents (Poulsen et al. 2008). The following review focuses on newer findings.

7.2.1 PFAS in food and dietary exposure

EU

In 2010, the European food safety authority EFSA issued a call for data on PFASs in food with a closing date of 31 January 2012. Thirteen countries have submitted 56,862 analytical results on 27...
PFASs in food covering the sampling period 1998 to 2012. In addition, data on PFASs in food from a three-year EU research project (PERFOOD 8) were submitted to EFSA.

EFSA has summarised the information on the occurrence of perfluoroalkylated substances in food and estimated dietary exposure (EFSA, 2012). The following has been extracted from the report. Table 6 lists PFASs for which data were reported and to what extent quantified results were reported. For eleven of the substances, all analytical results were below the limit of detection or limit of quantification. A total of 54,195 analytical results were included in the assessment.

Most results were available for PFOS and PFOA, while results for PFPeDA, 8:2 FTOH, 8:2 monoPAP, 8:2 diPAP, EtFOSA, EtFOSE and FC-807 were very low. Across food groups, the highest number of data were available for 'Fish and other seafood' (n = 25,328) and 'Meat and meat products (including edible offal)' (n = 13,780).

Across food groups, PFASs were reported more frequently in fish and other seafood, in meat and meat products and to a lesser extent in other food groups. The highest concentrations for the different PFASs were found in edible offal and in particular in liver. Individually quantified values ranged from a low of 0.00034 µg/kg for drinking water to a high of 3480 µg/kg for wild boar liver. However, generally food with the highest concentrations does not have the greatest impact on exposure because the quantities consumed are low (e.g. liver from wild animals). Fish from fresh water were more highly contaminated than marine fish and diadromous fish (fish living in both salt and fresh water).
<table>
<thead>
<tr>
<th>PFAS family/substance</th>
<th>Acronyms</th>
<th>C atoms</th>
<th>Number of observations</th>
<th>Frequency quantified</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Perfluoroalkyl carboxylic acids</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluorobutanoic acid</td>
<td>PFBA</td>
<td>C4</td>
<td>1628</td>
<td>not detected</td>
</tr>
<tr>
<td>Perfluoropentanoic acid</td>
<td>PFPA</td>
<td>C5</td>
<td>2397</td>
<td>3%</td>
</tr>
<tr>
<td>Perfluorohexanoic acid</td>
<td>PFHxA</td>
<td>C6</td>
<td>3355</td>
<td>4%</td>
</tr>
<tr>
<td>Perfluoroheptanoic acid</td>
<td>PFHpA</td>
<td>C7</td>
<td>2486</td>
<td>2%</td>
</tr>
<tr>
<td>Perfluorooctanoic acid</td>
<td>PFOA</td>
<td>C8</td>
<td>7536</td>
<td>9%</td>
</tr>
<tr>
<td>Perfluorononanoic acid</td>
<td>PFNA</td>
<td>C9</td>
<td>3814</td>
<td>5%</td>
</tr>
<tr>
<td>Perfluorodecanoic acid</td>
<td>PFDA</td>
<td>C10</td>
<td>3715</td>
<td>6%</td>
</tr>
<tr>
<td>Perfluoroundecanoic acid</td>
<td>PFUnA</td>
<td>C11</td>
<td>2680</td>
<td>7%</td>
</tr>
<tr>
<td>Perfluorododecanoic acid</td>
<td>PFDoDA</td>
<td>C12</td>
<td>2693</td>
<td>6%</td>
</tr>
<tr>
<td>Perfluorotridecanoic acid</td>
<td>PFTeDA</td>
<td>C13</td>
<td>1495</td>
<td>6%</td>
</tr>
<tr>
<td>Perfluorotetradecanoic acid</td>
<td>PFTeDA</td>
<td>C14</td>
<td>1855</td>
<td>0.6%</td>
</tr>
<tr>
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<td>PFPeDA</td>
<td>C15</td>
<td>3</td>
<td>not detected</td>
</tr>
<tr>
<td>Perfluorohexadecanoic acid</td>
<td>PFHxDA</td>
<td>C16</td>
<td>968</td>
<td>not detected</td>
</tr>
<tr>
<td>Perfluoroheptadecanoic acid</td>
<td>PFHxDA</td>
<td>C16</td>
<td>968</td>
<td>not detected</td>
</tr>
<tr>
<td>Perfluoroundecanoic acid</td>
<td>PFUnA</td>
<td>C11</td>
<td>2680</td>
<td>7%</td>
</tr>
<tr>
<td>Perfluorodecanoic acid</td>
<td>PFDa</td>
<td>C12</td>
<td>2693</td>
<td>6%</td>
</tr>
<tr>
<td>Perfluorotridecanoic acid</td>
<td>PFTeDA</td>
<td>C13</td>
<td>1495</td>
<td>6%</td>
</tr>
<tr>
<td>Perfluorotetradecanoic acid</td>
<td>PFTeDA</td>
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<td>1855</td>
<td>0.6%</td>
</tr>
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<td>3</td>
<td>not detected</td>
</tr>
<tr>
<td>Perfluorohexadecanoic acid</td>
<td>PFHxDA</td>
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<td>968</td>
<td>not detected</td>
</tr>
<tr>
<td>Perfluoroheptadecanoic acid</td>
<td>PFHxDA</td>
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</tr>
<tr>
<td>Perfluorooctadecanoic acid</td>
<td>PFOA</td>
<td>C17</td>
<td>947</td>
<td>not detected</td>
</tr>
<tr>
<td><strong>Perfluoroalkane sulfonic acids</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluorobutane sulfonic acid</td>
<td>PFBS</td>
<td>C4</td>
<td>3197</td>
<td>2%</td>
</tr>
<tr>
<td>Perfluorohexane sulfonic acid</td>
<td>PFHxS</td>
<td>C6</td>
<td>3222</td>
<td>2%</td>
</tr>
<tr>
<td>Perfluoroheptane sulfonic acid</td>
<td>PFHpS</td>
<td>C7</td>
<td>761</td>
<td>0.1%</td>
</tr>
<tr>
<td>Perfluoroctane sulfonic acid</td>
<td>PFOS</td>
<td>C8</td>
<td>7523</td>
<td>29%</td>
</tr>
<tr>
<td>Perfluorodecane sulfonic acid</td>
<td>PFDS</td>
<td>C10</td>
<td>1851</td>
<td>0.7%</td>
</tr>
<tr>
<td>Perfluoroalkane sulfonic acid</td>
<td>PFSAs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluorobutane sulfonic acid</td>
<td>PFBS</td>
<td>C4</td>
<td>3197</td>
<td>2%</td>
</tr>
<tr>
<td>Perfluorohexane sulfonic acid</td>
<td>PFHxS</td>
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<td>3222</td>
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<tr>
<td>Perfluoroheptane sulfonic acid</td>
<td>PFHpS</td>
<td>C7</td>
<td>761</td>
<td>0.1%</td>
</tr>
<tr>
<td>Perfluoroctane sulfonic acid</td>
<td>PFOS</td>
<td>C8</td>
<td>7523</td>
<td>29%</td>
</tr>
<tr>
<td>Perfluorodecane sulfonic acid</td>
<td>PFDS</td>
<td>C10</td>
<td>1851</td>
<td>0.7%</td>
</tr>
<tr>
<td>Perfluoroalkane sulfonic acid</td>
<td>PFSAs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluoroctane sulfonic acid</td>
<td>PFOS</td>
<td>C8</td>
<td>136</td>
<td>not detected</td>
</tr>
<tr>
<td>(n:2) Fluorotelomer alcohols</td>
<td>(n:2) FTOHs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8:2 Fluorotelomer alcohol</td>
<td>8:2 FTOH</td>
<td>C8</td>
<td>18</td>
<td>not detected</td>
</tr>
<tr>
<td>Polyfluoroalkyl phosphoric acid esters</td>
<td>PAPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8:2 Fluorotelomer phosphate monoester</td>
<td>8:2 monoPAP</td>
<td>C8</td>
<td>13</td>
<td>not detected</td>
</tr>
<tr>
<td>8:2 Fluorotelomer phosphate diesters</td>
<td>8:2 diPAP</td>
<td>C8</td>
<td>3</td>
<td>not detected</td>
</tr>
<tr>
<td>Perfluoroalkane sulfonamides</td>
<td>FASAs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluoroctane sulfonamide</td>
<td>PFOSA</td>
<td>C8</td>
<td>1930</td>
<td>7%</td>
</tr>
<tr>
<td>N-ethyl perfluoroalkane sulfonamides</td>
<td>EtFASAs</td>
<td>C8</td>
<td>1930</td>
<td>7%</td>
</tr>
<tr>
<td>N-ethylperfluoroctane sulfonamide</td>
<td>EtFOSA</td>
<td>C8</td>
<td>28</td>
<td>not detected</td>
</tr>
<tr>
<td>N-Ethyl perfluoroalkane sulfonamidoethanol</td>
<td>EtFASEs</td>
<td>C8</td>
<td>28</td>
<td>not detected</td>
</tr>
<tr>
<td>N-Ethyl perfluoroctane sulfonamidoethanol</td>
<td>EtFOSE</td>
<td>C8</td>
<td>28</td>
<td>not detected</td>
</tr>
<tr>
<td>Perfluoroalkyl phosphate</td>
<td>FC-807</td>
<td>C8</td>
<td>3</td>
<td>not detected</td>
</tr>
</tbody>
</table>
The contributions from the different food groups to the total dietary exposure varied among the substances. The figures below show the contributions from different food groups to the total dietary exposure for PFOS and PFOA respectively.

The highest contributors to dietary PFOS exposure across all age classes were “Fish and other seafood”, whereas for PFOA, the exposure was more evenly distributed between food groups.

Based on the available occurrence data for 16 PFASs in fish, a comparison of the lower-boundary mean concentrations found in fresh water fish, marine fish and diadromous fish was performed.
The results showed consistently higher mean concentrations in fish from fresh water. Diadromous fish had mean concentrations slightly higher or similar to the marine fish. PFOS had a markedly higher mean concentration in all three fish categories than the other PFASs, whereas the concentration of PFOA was in the same range as most of the other PFASs.

Dietary exposure was calculated using the overall European lower and upper boundary mean occurrence of PFASs. The low proportion of quantified results prevented calculation of a more realistic dietary exposure. The upper boundary results are highly overestimated, but still the exposure estimates in all age classes and for both the mean and the 95th percentile consumers were well below the TDIs for PFOS (150 ng/kg bw per day) and PFOA (1500 ng/kg bw per day) set by the EFSA Scientific Panel on Contaminants in the Food Chain (EFSA, 2008).

The TDI is based on animal studies and is discussed in Chapter 0.

For PFOS, the highest upper boundary mean exposure estimate for the adult population (5.2 ng/kg bw per day) represented 3.5 % of the TDI while the highest 95th percentile estimate (10 ng/kg bw per day) represented 6.7 % of the TDI. In toddlers, the age class having the highest exposure, the same parameters represented 9.3 % and 19 % of the TDI, respectively.

The highest contributors to dietary PFOS exposure across all age classes were ‘Fish and other seafood’ (50 to 80 %) followed by ‘Fruits and fruit products’ (8 to 27 %) and ‘Meat and meat products’ (5 to 8 %).

For PFOA, the chronic dietary exposure (long-term exposure over the entire lifetime) in all age classes and for both average and high consumers was also far below the TDI. For adults, the highest upper boundary mean estimate (4.3 ng/kg bw per day) represented 0.3 % of the TDI while the highest 95th percentile estimate (7.7 ng/kg bw per day) represented 0.5 % of the TDI. In toddlers, the age class having the highest exposure, the highest mean and 95th percentile estimates would represent 1.1 % and 2.1 % of the TDI, respectively. The most important contributors to PFOA exposure in all age classes were ‘Fruits and fruit products’ (18 to 39 %) and ‘Fish and other seafood’ (7.6 to 27 %) but high variations were observed in relation to dietary habits.
For children younger than 1 year, EFSA notes that the uncertainty is particular high due to a lack of dietary surveys reporting consumption data for this age group.

Based on the available data with a low proportion of quantified results, the chronic dietary exposure to the other 25 single PFASs is expected to be in the low ng/kg bw per day range or even lower. Since no TDIs are available for these PFASs, it was not possible to evaluate the relevance of the dietary exposure for human health.

EFSA concludes that, based on further results from toxicological evaluations, the relevance of various PFASs to human health could be better established, thus allowing for the definition of a set of priority PFASs for future monitoring. The use of analytical methods with improved sensitivity would be required to monitor such priority PFASs in order to increase the proportion of quantified results and thereby the reliability of exposure assessments.

**Denmark**

The chronic dietary exposure to PFOS and PFOA in Denmark as compared to the EU average is shown in the table below. The exposures are calculated with relatively high uncertainties and the available data did not indicate significant differences between the exposure in Denmark and the EU average. Estimates of dietary exposure to other PFASs in Denmark are not available.

**TABLE 26**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Other children *1</th>
<th>Adolescents</th>
<th>Adults</th>
<th>Elderly</th>
<th>Very elderly</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean P95</td>
<td>Mean P95</td>
<td>Mean P95</td>
<td>Mean P95</td>
<td>Mean P95</td>
</tr>
<tr>
<td>PFOS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Denmark</td>
<td>1.8-7.2 [5-14]</td>
<td>0.8-3.9 [2.4-7.3]</td>
<td>0.8-3.0 [2.1-5.6]</td>
<td>1.0-3.7 [2.2-6.5]</td>
<td>1.2-4.1 [2.2-8.0]</td>
</tr>
<tr>
<td>PFOA</td>
<td>0.3-8.3 [0.5-14]</td>
<td>0.1-4.7 [0.3-8.0]</td>
<td>0.2-3.4 [0.3-5.7]</td>
<td>0.2-3.7 [0.3-6.2]</td>
<td>0.2-4.1 [0.3-6.9]</td>
</tr>
</tbody>
</table>

*1 The report include data for infants, toddlers and “other children”; for Denmark only data for “other children” is calculated.

*2 P95 estimates for dietary surveys/age classes with less than 60 observations are not statistically robust and therefore not presented in the table.

Until 2011, analyses of PFOS in food were not included in the Danish monitoring programme for organic pollutants in food from environment and industrial processes.

In 2011, the Danish Veterinary and Food Administration (DVFA, 2012) has analysed for PFOS and PFOA in 43 samples, of which eight were samples of farmed fish (four from land-based trout farms, and four from marine trout farms) and 35 were other samples of animal origin (four beef, three chicken and 28 pork). No concentrations of PFOS or PFOA above the detection limit of 0.5 ng/g wet weight were found in the 35 samples of animal meat (DVFA, 2012a). PFOS was found in a concentration of 0.53 ng/g wet weight (just above the detection limit) in one sample of farmed trout (from a marine fish farm); however, the other samples from fish did not reveal any PFOS contents. Samples were also taken from wild fish, where PFOS was detected in all samples at mean concentrations of 1.3-3.3 ng/g (2012b.) PFOA was not detected in any of the samples.
7.2.2 PFASs in drinking water

PFASs are not covered by any monitoring programmes for groundwater or drinking water in Denmark.

PFASs in drinking water have recently been reviewed by Fromme et al. (2009) and D’Hollander et al. (2010). Data from Japan, Germany, Spain and Italy varies considerably. Particularly high levels are reported from contaminated areas in Germany.

**TABLE 27**

OBSERVED RANGE OF PERFLUORINATED CHEMICALS IN DRINKING WATER, ng/L (D’HOLLANDER ET AL., 2010)

<table>
<thead>
<tr>
<th>Sampling sites (n)</th>
<th>Country, sampling date</th>
<th>PFHxA*</th>
<th>PFHpA</th>
<th>PFOA</th>
<th>PFBS</th>
<th>PFHxS</th>
<th>PFOS</th>
<th>PFNA</th>
<th>PFDA</th>
<th>PFUnA</th>
<th>PFDoA</th>
<th>References **</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tokyo, Kyoto</td>
<td>Japan, not given</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.1-12</td>
<td></td>
<td>0.1-51</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Harada et al. (2003)</td>
</tr>
<tr>
<td>Osaka and Toboku</td>
<td>Area, Japan 2003</td>
<td>-</td>
<td>-</td>
<td>0.7-50</td>
<td>&lt;0.1-12</td>
<td></td>
<td>0.1-51</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Saito et al. (2004a)</td>
</tr>
<tr>
<td>Ruhr, Ruhr River</td>
<td>Moehne area, Germany 2006</td>
<td>&lt;1-56</td>
<td>&lt;1-23</td>
<td>&lt;1-59</td>
<td>&lt;1-26</td>
<td></td>
<td>0.1-22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Skutlarek et al. (2006)b</td>
</tr>
<tr>
<td>Area of Lake Maggiore</td>
<td>(n = 6) Italy 2007</td>
<td>0.3-0.8</td>
<td>1.0-2.9</td>
<td>2.6-9.7</td>
<td>0.3-0.7</td>
<td>0.1-0.3</td>
<td>0.1-0.4</td>
<td>0.1-2.8</td>
<td></td>
<td></td>
<td>Loos et al. (2007)</td>
<td></td>
</tr>
<tr>
<td>Catalonia (n = 4)</td>
<td>Spain 2007</td>
<td>&lt;0.9</td>
<td>&lt;0.6-3.0</td>
<td>0.3-6.3</td>
<td>&lt;0.3</td>
<td>&lt;0.2-0.3</td>
<td>0.4-0.9</td>
<td>&lt;0.4-0.5</td>
<td>&lt;0.8</td>
<td>&lt;0.4</td>
<td>&lt;0.3</td>
<td>Ericson et al. (2008b)b</td>
</tr>
<tr>
<td>Catalonia (n = 4)</td>
<td>Spain 2007</td>
<td>&lt;0.9</td>
<td>&lt;0.6-0.4</td>
<td>0.2-0.7</td>
<td>&lt;0.3</td>
<td>&lt;0.2</td>
<td>&lt;0.24</td>
<td>&lt;0.4-0.2</td>
<td>&lt;0.8-0.6</td>
<td>&lt;0.4</td>
<td>&lt;0.3</td>
<td>Ericson et al. (2008b)c</td>
</tr>
<tr>
<td>Osaka (n = 14)</td>
<td>Japan 2006-2007</td>
<td>2.3-84</td>
<td>&lt;0.1-22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Takagi et al. (2008)</td>
<td></td>
</tr>
</tbody>
</table>

*PFHxA: perfluorohexanoic acid; PFHpA: perfluoroheptanoic acid; PFOA: perfluorooctanoic acid; PFBS: perfluorobutane sulfonate; PFHxS: perfluorohexane sulfonate; PFOS: perfluorooctane sulfonate; PFNA: perfluorononanoic acid; PFDA: perfluorodecanoic acid; PFUnA: perfluoroundecanoic acid; PFDoA: perfluorododecanoic acid

**See original source for full references

Guidelines for PFOS and PFOA in drinking water have been issued by the authorities in several EU Member States. The Health Protection Agency (HPA) in the UK, for example, advises that the maximum acceptable concentration of perfluorooctane sulfonate (PFOS) in drinking water is 0.3 µg/L, and that the maximum acceptable concentration of perfluorooctanoic acid (PFOA) in drinking water is 10 µg/L (Health Protection Agency, 2012). These concentrations are well above the maximum concentration of PFOS found in ground water in Table 23.

7.2.3 Consumer products as sources of PFASs

Releases of PFASs from consumer products may be a source of exposure to PFASs in the home.

In order to make an estimation of exposure, Washburn et al. (2005) determined concentrations of PFOA in the consumer articles from extraction tests and product formulation information. Potential exposures during consumer use of the articles were quantified based on an assessment of behaviour patterns and regulatory guidance. For each of the population groups addressed, exposures were quantified for mill-treated carpeting, solution-treated carpeting (including home application of carpet-care solution), apparel (treated with fluorotelomer-based product, sometimes containing a fluoropolymer membrane), treated nonwoven medical garments, non-stick cookware, and thread seal tape. For the Reasonable Maximum Exposure (RME) Scenarios the treated carpeting accounted for the highest contribution to the hypothetical annual average intake. The RME value for infants due to exposure to PFOS in the carpeting was one to two orders of magnitude higher than the RME values for adult residents.
Guo et al. (2009) analysed the PFCA content of 116 consumer products (“articles of commerce”) and estimated the quantities which could be present in a “typical” American home. Given the quantities of articles found in typical homes, it was concluded that professional carpet-care liquids, pretreated carpeting, treated floor waxes and sealants, and treated home textile products and upholstery are likely to be the most important PFCA sources in non-occupational indoor environments. According to the study, limited data suggest that the PFCA content in consumer products has shown a downward trend overall; however, definitive confirmation of such a trend will require long-term monitoring.

**Food packaging and cookware as sources of PFASs in the food**

A report from EFSA with results of the monitoring of PFASs in food in the period 2000 – 2009 (EFSA, 2011) includes a brief discussion of the significance of packaging and cookware as a source of the substances in the food. According to the report, Jogsten et al. (2009, as cited by EFSA, 2011) evaluated the exposure to PFASs from consumption of various raw and cooked foodstuffs, including packaged food. It was not sufficiently clear as to whether cooking with non-stick cookware or packaged foods, could contribute to a higher human exposure to PFASs. Nelson et al. (2010, as cited by EFSA, 2011) found a positive association between the serum concentration of PFOA and PFNA and fast food consumption. The authors suggest that PFASs may enter the food chain both through bioaccumulation and contact with packaging.

The French Food Safety Agency evaluated the potential human health risks related to the residual presence of PFOA in non-stick coatings for cookware in 2009 (AFSSA, 2009 as cited by EFSA, 2011). It has been concluded that the consumer health risk related to residues of PFOA in non-stick coating for cookware is negligible.

A study by the Norwegian Institute of Public Health (2007, as cited by Posner et al., 2007) examined the significance of exposure to PFOA from PTFE cookware. The study showed that in a worst case scenario an adult human would be exposed to 66 ng PFOA /kg bw, when drinking 100 ml of water cooked in a PTFE-coated pan. It was concluded that, even at an assumption of 100% uptake of PFOA, these low levels would not constitute an essential intake route for humans (Posner et al., 2007).

Stahl et al. (2012), on the basis of a review of the existing literature, reach the conclusion that given the present state of knowledge, it is not possible to say whether the use of nonstick-coated cooking utensils or packaging materials with PFC-based coating lead to a significant increase in dietary intake.

PFASs in packaging on the Danish market and migration from the packaging are described in section 3.3.2. The significance of the migration as regards the human exposure was not estimated.

**Clothing as a source of PFAS exposure**

According to the German Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR) it has not been shown that consumers are significantly exposed to PFOA and FTOH from clothing fabrics (Umweltbundesamt, 2009). The BfR estimates that the maximum quantity amounts to 20 ng/kg gram of body weight. A recently published report came to the conclusion that less than one per cent of the daily uptake of PFOS and PFOA occurs through the skin (Kudo et al., 2002 as cited by Umweltbundesamt, 2009).

**7.2.4 Total human exposure**

The total human exposure to PFOS and PFOA was reviewed in a Scientific Opinion of the Panel on Contaminants in the Food Chain in 2008 (EFSA, 2008). The EFSA Scientific reached the conclusion that for PFOA, the total contribution from the non-food sources, mainly indoor exposure, could be as high as 50% of the estimated average dietary exposure to PFOA (EFSA, 2008).
Fromme et al. (2009) and Trudel et al. (2008) have reviewed the current knowledge of PFAS monitoring data in environmental media relevant for human exposure. In this context, PFAS concentrations in indoor and ambient air, house dust, drinking water and food were outlined. Furthermore, the papers summarized human biomonitoring data of PFAS levels in blood, breast milk, and human tissues.

The estimated adult daily intake of PFOS, PFOA, \( \sum_{\text{FTOH}} \) and \( \sum_{\text{FOSE/FOSA}} \) for the general population is shown in Table 28 (Fromme et al., 2009).

As seen from the table, dietary exposure is the dominant intake pathway for PFOS and PFOA \( \sum_{\text{FOSE/FOSA}} \), responsible for 91% and 99%, respectively, of the total intake of the general adult population using mean intake data. Using high daily intake data, house dust may be a significant source of PFOA exposure. A scoring by the authors using a simple one-compartment toxicokinetic model showed that the dietary intake corresponds well with the blood plasma level of the same population. The total estimated intake of PFOS and PFOA were well below the TDI values recommended by the EFSA Scientific Panel on Contaminants in the Food Chain of 150 ng/kg body weight for PFOS and 1500 ng/kg bw per day for PFOA.

For \( \sum_{\text{FTOH}} \) and \( \sum_{\text{FOSE/FOSA}} \), in the mean exposure scenario, house dust is the main source of exposure while in the high exposure scenario the diet may be the major exposure source for \( \sum_{\text{FOSE/FOSA}} \).

The study did not specifically estimate the exposure of children. According to the Fromme et al. (2009), it is obvious from biomonitoring data that the internal exposure of children is comparable to that of adults, but the exposure situation of children is not well understood, and therefore the authors do not make any statements on the risks of children’s exposure to PFAS using the data available. Trudel et al. (2008) notes that children tend to experience higher total uptake doses (on a body weight basis) than teenagers and adults because of higher relative uptake via food consumption and hand-to-mouth transfer of chemical from treated carpets and ingestion of dust.

Furthermore the authors conclude that besides this background exposure of the general population, a specific additional exposure may occur which causes an increased PFAS body burden. This has been observed in populations living near PFAS production facilities or in areas with environmental contamination of PFASs. The consumption of highly contaminated fish products may also cause an increase in PFAS body burdens.

In accordance with the results of Fromme et al. (2009), Trudel et al. (2008) concludes that the greatest portion of the chronic exposure to PFOS and PFOA is likely to result from the intake of contaminated foods, including drinking water. Consumer products cause a minor portion of the consumer exposure to PFOS and PFOA. Of these, it is mainly impregnation sprays, treated carpets in homes, and coated food contact materials that may lead to consumer exposure to PFOS and PFOA.

Haug et al. (2011) estimated individual PFC intakes from multiple exposure sources for a study group of 41 Norwegian women using measured PFC concentrations in indoor air and house dust as well as information from food frequency questionnaires and PFC concentrations in Norwegian food. Food was generally the major exposure source, representing 67-84% of the median total intake for PFOA and 88-99% for PFOS using different dust ingestion rates and biotransformation factors of ‘precursor’ compounds. However, on an individual basis, the indoor environment accounted for up to 50% of the total intake for several women. Significant positive associations between concentrations of PFCs in house dust and the corresponding serum concentrations underline the importance
of indoor environment as an exposure pathway for PFCs. For breast-fed infants, breast milk was calculated to be the single most important source to PFCs by far (Haug et al., 2011).

Several authors have emphasized that there may be additional sources of human exposure to PFOS and PFOA from precursor compounds including fluorotelomer alcohols (FTOHs), perfluoroalkyl sulfonamides (PFOSAs) and amido alcohols (PFOSEs) that are metabolized to form PFOA and PFOS, respectively. Considering the potential routes of human exposure, Fromme et al. (2009) estimated the overall mean and high daily intake for a non-occupationally exposed adult population to two groups of potential precursors of PFCAs and PFAS: $\Sigma$FTOH, AND $\Sigma$FOSE/FOSA (Table 28).

Using some rough estimates regarding the percentage of the precursors converted in the human body to PFOS and PFOA, the authors conclude that FTOHs have only a negligible contribution (<1%) to the total mean and high intake PFOA exposures of adults. Moreover, the contribution of the converted $\Sigma$FOSAs/FOSEs to total PFOS exposure of the general population was estimated to reach only 10%.

### TABLE 28
ESTIMATED ADULT DAILY INTAKE OF PFOS, PFOA, $\Sigma$FTOH, AND $\Sigma$FOSE/FOSA FOR THE GENERAL POPULATION. MEAN INTAKE BASED ON MEAN OR MEDIAN CONCENTRATIONS; HIGH INTAKE BASED ON UPPER PERCENTILE OR MAXIMUM CONCENTRATIONS (FROMME ET AL., 2009)

<table>
<thead>
<tr>
<th>Source</th>
<th>Daily intake pg/kg bw</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PFOS</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>Indoor air</td>
<td>0.9</td>
</tr>
<tr>
<td>Outdoor air</td>
<td>1.3</td>
</tr>
<tr>
<td>House dust</td>
<td>16.4</td>
</tr>
<tr>
<td>Diet</td>
<td>2,816.7</td>
</tr>
<tr>
<td>Drinking water</td>
<td>21.7</td>
</tr>
<tr>
<td>Overall intake</td>
<td>2,857</td>
</tr>
</tbody>
</table>

Vestergren et al. (2008) estimated the relative importance of precursor-based doses of PFOS and PFOA to be 2–5% and 2–8% in an intermediate scenario and 60–80% and 28–55% in a high-exposure scenario. Compared to the data of Fromme et al. (2009) the results of Vestergren et al. (2008) indicate that subgroups of the population may receive a substantial part of the PFOS and PFOA doses from precursor compounds, even though they are of low importance for the general population.

### 7.2.5 Human biomonitoring data

PFAS concentrations in the serum of exposed workers have been a subject of study since 1993, whereas data on serum concentrations in the general population have only been available since 1998 (Stahl et al., 2011). Since then PFOS and PFOA in particular have been measured in human blood (including cord blood) and in human milk in many countries, while measurements in other specimen types are few. The data have been reviewed by several authors (e.g. Jensen et al., 2008; Fromme et al., 2009, Stahl et al., 2011). Data up to 2008 were reviewed in the previous Danish survey of PFCs (Jensen et al., 2008). The following focuses on the overall trend, in particular the temporal trends and the levels of other PFCs as compared with PFOS and PFOA, as well as data from Denmark.
Human blood

Poulsen et al. (2008) reviewed existing information on PFOS and PFOA in blood. As mentioned in the review, in blood the perfluorinated chemicals are mainly bound to serum proteins, especially albumin. In most studies blood serum is analysed but other studies analyse whole blood or blood plasma. When comparing such studies it is important to take into account that results will depend on what medium is analysed. The levels in serum or plasma are approximately two to three times the levels in whole blood. A summary of the PFOS and PFOA levels in serum/plasma samples across the world showed a wide range in concentration, with PFOS typically three to ten times higher than the concentration of PFOA (Figure 10). In a similar figure summarising the data on whole blood samples, the difference between PFOS and PFOA was less distinctive.

The levels shown are well in accordance with an overview prepared by OECD (2002) of PFOS and PFOA levels in human blood sampled in various countries from 1998-2000. The average levels ranged from 17 to 53 ng/mL for PFOS and 3 to 17 ng/mL for PFOA (OECD, 2002, as cited by Jensen et al., 2008).

Mean and median concentrations for some PFASs, such as PFOS, from North American populations appear to be slightly higher than European, Asian, and Australian populations studied (Fromme et al., 2009). Another commonly found substance that appeared to vary amongst populations was PFHxS. Concentrations reported were <0.4–40.0 mg/L for Europe, 0.1–20.9 mg/L for Asia and 0.4–712 mg/L for North America (Fromme et al., 2009).

Vestergren and Cousins (2009) have reviewed a wide range of studies of PFOA in human blood sera from all over the world. The data show that the background-exposed population in the industrialized countries worldwide exhibits a narrow concentration range; arithmetic means of published studies range between 2 and 8 µg/L PFOA, with the exception of a few outlier studies. Significantly higher concentrations were found in ammonium perfluorooctanoate (APFO) production workers and elevated serum concentrations of PFOA (mean 27.4–423 µg/L) in non-occupationally exposed populations have been reported from areas where use of contaminated soil conditioner and a fluoropolymer production site, respectively, were identified as sources of contamination. The authors conclude that food intake is the major contemporary exposure pathway for the background popula-
Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances

tion, whereas drinking water exposure is dominant for populations near sources of contaminated drinking water.

Compared to the PFOS, PFOA and PFHxS, less information is available on other PFASs. In some recent studies, mean PFNA concentrations of 0.3–1.1 µg/L have been estimated, as summarised by Fromme et al. (2009). Other PFASs, such as PFDA or PFUnA, were found at only very low concentrations, if at all.

EFSA (2008) concludes that most studies did not find clear gender or age related differences in the concentrations of PFOS in blood, but also quotes data from the USA demonstrating significantly higher levels in males than in females. Fromme et al. (2009) state, contrary to the conclusion of EFSA, that in the majority of the studies, differences in blood levels of PFOS between sexes have been observed with higher levels in male donors.

Since PFASs are highly persistent contaminants that do not undergo metabolism, it might be expected that PFAS body levels would increase with age. However, most studies that have examined the association of age with PFAS concentrations in blood (including plasma and serum) have not observed significant age effects (Fromme et al., 2009).

**Denmark**

As reported in Jensen et al. (2008), a study by Fei et al. (2007) reports the results of PFOS and PFOA in 1399 blood plasma samples collected during March 1996 - November 2002 among a cohort of pregnant women in Denmark. The average levels of PFOS and PFOA were 35.3 ng/mL (range: 6.4-106.7 ng/mL) and 5.6 ng/mL (range: <1.0-41.5 ng/mL), respectively.

Surveys of the 1,076 Danish pregnant women published in 2008 (as part of studies into the effect of PFOS and PFOA on the foetus) showed an average mean concentration of PFOS in blood plasma, at the start of the pregnancy, of 35 ng/mL (Halldorsson et al., 2008). The level of PFOS in the blood was relatively stable throughout the pregnancy and correlated positively with the intake of red meat, animal fats, and snacks (e.g. popcorn and crisps), whereas the level correlated negatively with the intake of vegetables and poultry. This suggests that intake from food, at least in the past, has been a significant source of PFOS intake in Denmark.

A study from 2011 of 652 Danish males addressing the connection between exposure to PFOS and PFOA and the risk of cancer, found only intake of eggs to correlate positively with the level of PFOS in the blood plasma (Eriksen et al., 2011). However, in overall terms, these results did not suggest that diet is the primary source of exposure in Denmark. The results also suggested a geographical variation in the source of exposure in Denmark, in that people residing in Aarhus had significantly higher levels of PFOS in their blood plasma than people residing in Copenhagen. The paper gave no explanation for that difference.

As reported in Jensen et al. (2008), serum concentrations of 9 perfluorinated compounds (PFOS, PFOA, PFOSA, MeFOSA-AcOH, EtFOSA-AcOH, PFHxS, PFNA, PFDA and PFDoA) have been measured in two groups of Faroe Island residents (Kato et al., 2007). The first group included 12 mothers sampled in 2000 and their 5 year old children sampled in 2005. The median concentrations for PFOS were 23.7 and 16.3 ng/mL respectively. The children had the lower levels. Levels of the other contaminants were much lower: 2.4 and 4.5 ng/mL, respectively, for PFOA. The second group consisted of 103 children of 7 years of age with samples collected in 1993-1994. The median concentration for PFOS was 29 ng/mL and for PFOA 5.5 ng/mL.

**Sweden – temporal trends**

Glynn et al. (2012) have recently investigated temporal trends of blood serum levels of 13 perfluorinated alkyl acids (PFAAs) and perfluorooctane sulfonamide (FOSA) in primiparous women (N =
Levels of PFBS and PFHxS increased 11%/y and 8.3%/y, respectively, during the period and levels of the long-chain perfluorododecanoate (PFDA) increased 4.3%/y and 3.8%/y, respectively. Concomitantly, levels of FOSA (22%/y), perfluoroctane sulfonate (PFOS, 8.4%/y), perfluorodecanoate (PFDA) increased 4.3%/y and 3.8%/y, respectively. Therefore, one or several sources of exposure to the latter compounds have been reduced or eliminated, whereas exposure to the former compounds has recently increased. PFAA levels in maternal serum sampled during pregnancy and the nursing period as well as in cord blood were strongly correlated. The strongest correlations between cord blood levels and maternal levels were observed for maternal serum sampled shortly before or after the delivery.

Norway – temporal trends
Fifty-seven pooled archived human serum samples were analyzed to assess the time trends in the period 1976 to 2007 as well as the influence of age and gender of 19 PFCs in Norwegian residents (Haug et al., 2009). A 9-fold increase in the serum concentrations of PFOS, PFOA, and PFHpS was measured for men (40-50 years) from 1977 to the mid 1990s where the concentrations reached a plateau before starting to decrease around year 2000. A similar trend was also seen for PFHxS, PFNA, PFDA and PFUnA, but no clear decline was observed for these PFCs in recent years. The highest concentrations were found for PFOS and PFOA, with levels around 30 ng/mL and 5 ng/mL, when the concentrations peaked around year 2000 for men of the age group 40-50 years. In 2006 the concentrations in pooled serum samples from men, age 40-50 years were in decreasing order: PFOS (12 ng/mL), PFOA (2.7 ng/mL), PFHxS (1.4 ng/mL), PFNA (0.55 ng/mL), PFDA (0.22 ng/mL), PFPeDA (0.11), PFHpA (0.078 ng/mL), ng/mL), PFTrDA (0.071 ng/mL), and PFHpS (0.055 ng/mL). Other analysed PFCs were below the detection level.

Germany - temporal trends
From the PFC-affected area in the Sauerland, Germany time trend analysis of PFOS and PFOA samples of young adults (20–31 years old) indicated a slight, but not significant, increase in concentrations from 1977 to about 1990, which was then followed by a decreasing tendency of the concentration (Wilhelm et al., 2008 as cited by Fromme et al., 2009). The sampling time period covered 1977–2004. In contrast, there was a clear linear increase of PFHxS plasma concentrations up to 2004.

USA – temporal trends
Based on 7876 serum samples collected from a representative sample of the general U.S. population 12 years of age during NHANES (National Health and Nutrition Examination Survey) 1999-2008, Kato et al. (2011) concluded that PFOS concentrations in the USA showed a significant downward trend, because of discontinuing industrial production of PFOS, but PFNA concentrations showed a significant upward trend. PFOA concentrations during 1999-2000 were significantly higher than during any other time period examined, but PFOA concentrations have remained essentially unchanged during 2003-2008. PFHxS concentrations showed a downward trend from 1999 to 2006, but concentrations increased during 2007-2008.

Olsen et al. (2012) analysed eleven PFASs in plasma from a total of 600 American Red Cross adult blood donors from six locations in 2010. Findings were compared to results from different donor samples analyzed at the same locations collected in 2000-2001 (N = 645 serum samples) and 2006 (N = 600 plasma samples). Most measurements in 2010 were below the lower limit of quantification for PFBS, PFPA, PFHxA, and PFDoA. For the remaining analytes, the geometric mean concentrations are shown in Table 29.

The decline in PFOS suggested a population half-life of 4.3 years. According to the authors this estimate is comparable to the geometric mean serum elimination half-life of 4.8 years reported in
individuals. This similarity supports the conclusion that the dominant PFOS-related exposures to humans in the United States were greatly mitigated during the phase-out period.

The concentration of PFOS in the blood was significantly higher than the concentration of any other of the analysed PFASs, with PFOA and PFHxA ranking second and third.

### TABLE 29
**GEOMETRIC MEAN CONCENTRATIONS OF PFASs IN BLOOD PLASMA FROM AMERICAN BLOOD DONORS (OLSEN ET AL., 2012)**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Geometric mean concentrations, ng/mL</th>
<th>Decline, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2000/2001</td>
<td>2006</td>
</tr>
<tr>
<td>PFOS</td>
<td>34.9</td>
<td>14.5</td>
</tr>
<tr>
<td>PFOA</td>
<td>4.7</td>
<td>3.4</td>
</tr>
<tr>
<td>PFHxS</td>
<td>2.25</td>
<td>1.52</td>
</tr>
<tr>
<td>PFNA</td>
<td>0.57</td>
<td>0.97</td>
</tr>
<tr>
<td>PFDA</td>
<td>0.16</td>
<td>0.34</td>
</tr>
<tr>
<td>PFHpA</td>
<td>0.13</td>
<td>0.09</td>
</tr>
<tr>
<td>PFUnA</td>
<td>0.10</td>
<td>0.18</td>
</tr>
</tbody>
</table>

### PFAS in breast milk

No Danish data on PFASs in breast milk have been obtained.

EFSA (2008) states that few data are available for PFAS in human milk. The results of local measurements in Sweden and China found that PFOS was present at similar concentrations in the milk from either country: 0.060–0.470 (mean, 0.201) ng/mL in Sweden and 0.045–0.360 (mean, 0.121) ng/mL in China.

Based on the results of German samples, Vörkel et al. (2008) estimated an intake of 0.10 mg PFOS/day (using median) or 0.27 PFOS g/day (using maximum value) via breast milk for an infant of 5 kg body weight. The concentration ranged between 28 and 309 pg/mL (median: 119 pg/mL). The data suggested that fully breastfed infants are unlikely to exceed the recommended tolerable daily intake of PFOS and PFOA, according to the authors.

More recently, based on data on the concentrations of PFOS, PFHxS, and PFOA in pooled human milk samples obtained in Sweden between 1972 and 2008 (a period representing the most significant period of PFAS production) Sundström et al. (2011) investigated whether the time trend of these substances in human milk parallels that indicated in human serum. PFOS was the predominant analyte present in the breast milk and all three analytes showed statistically significant increasing trends from 1972 to 2000, with concentrations reaching a plateau in the 1990s. In the last part of the 1990s, the measured concentrations of PFOS, PFHxS, and PFOA were at 212-237 pg/mL, 16-28 pg/mL, and 120-139 pg/mL, respectively. PFOA and PFOS showed statistically significant decreasing trends during 2001–2008. At the end of the study, in 2008, the measured concentrations of PFOS, PFHxS, and PFOA in pooled human milk were 75 pg/mL, 14 pg/mL, and 74 pg/mL, respectively. The temporal concentration trends of PFOS, PFHxS, and PFOA observed in human milk are parallel to those reported in the general population serum concentrations.
Summary on monitoring and exposure

Environmental monitoring and exposure
Seven PFASs are included in the NOVANA monitoring programme for point sources while only PFOS is included in the programme for marine animals. PFOS and PFOA are generally the predominant components of the measured PFASs in both effluent from point sources and in the aquatic environment in Denmark. An assessment from the Danish NOVANA programme and a HELCOM assessment concluded that the level of PFOS in fish may represent an environmental risk, especially to fish-eating birds and mammals at the highest trophic levels of the food chain, as most of the fish samples exceed the PNEC value. No conclusion was drawn for the other analysed FPASs. Data from EFSA demonstrates that the concentration of PFOS in freshwater fish is typically about 10 times higher than the concentration of each of the fourteen other analysed PFASs.

The risks and threats of PFOA to the Baltic marine environment are currently difficult to estimate due to the lack of ecotoxicological information according to a HELCOM assessment (i.e. PNEC value has not been comprehensively assessed). The assessment does not include other PFASs.

In a recent study of sediment from the German Bight and western Baltic Sea, PFOS had the highest concentrations followed by PFOA. The levels of seven other analysed PFASs were five to ten times lower.

In a study of 18 PFASs in tissues of different marine mammals from the Arctic, PFOS was generally found in the highest concentrations. A significant decrease in PFOS was found in hooded seals (1990–2007). Increasing trends of one or more PFASs were found in samples of ringed seals, in pilot whales, white-sided dolphins and harbour porpoises. For PFUnDA a significantly increasing trend was found for ringed seals, pilot whales and white-sided dolphins, indicating that levels of the larger PFASs are still increasing.

The maximum and average concentrations of PFOS in groundwater across the EU were higher than the concentration of the three other analysed substances (PFOA, PFHxS and PFHpA).

In all environmental compartments the concentration of PFOS exceeds the concentration of other PFASs. As expected, a decreasing trend has been demonstrated for PFOS while the concentration of other PFASs increase, although the concentrations are still well below the concentration of PFOS. The data confirm that the PFOS and PFOA are of the highest concern, but it would still be relevant to follow the trend of other PFASs and more specifically assess the potential risk of some of the newer PFASs.

Human biomonitoring and exposure
The dietary intake of PFOS and PFOA in the EU seems to be well below the established tolerable daily intake (TDI). According to a recent EFSA assessment for PFOS, the highest upper boundary mean exposure estimate for the adult population (5.2 ng/kg bw per day) represented 3.5 % of the TDI while the 95th percentile estimate (10 ng/kg bw per day) represented 6.7 % of the TDI. In toddlers, the age class having the highest exposure, the same parameters represented 9.3 % and 19 % of the TDI, respectively. For PFOA, the chronic dietary exposure in all age classes and for both average and high intake consumers was also far below the TDI. Based on the available data with a very low proportion of quantified results, EFSA expects the chronic dietary exposure to 25 other single PFASs to be in the low ng/kg bw per day range or even lower. Since no TDIs are available for these PFASs, it was not possible for EFSA to evaluate the relevance of the dietary exposure for human health.

EFSA concludes that the relevance of various PFASs to human health could be better established on the basis of further results from toxicological evaluations, thus allowing for the definition of a set of priority PFASs for future monitoring. The use of analytical methods with improved sensitivity
would be required to monitor such priority PFASs in order to increase the proportion of quantified results and thereby the reliability of exposure assessments.

The French Food Safety Agency and the Norwegian Institute of Public Health have evaluated the potential human health risks related to the residual presence of PFOA in non-stick coatings for cookware and concluded that the consumer health risk related to residues of PFOA in non-stick coating for cookware is negligible. According to the German Federal Institute for Risk Assessment, it has not been shown that consumers are significantly exposed to PFOA and FTOH from clothing fabrics. However, some authors conclude that given the present state of knowledge, it is not possible to say whether the use of nonstick-coated cooking utensils or packaging materials with PFC-based coating lead to a significant increase in dietary internal PFC contamination in humans.

The EFSA Scientific Panel on Contaminants in the Food Chain reached the conclusion that for PFOA, the total contribution from the non-food sources, mainly indoor exposure, could be as high as 50% compared to the estimated average dietary exposure to PFOA (EFSA, 2008). For the adult population, reviews show that dietary exposure is the dominant intake pathway, responsible for 91% (PFOS) and 99% (PFOA) of the total intake of the general adult population, when mean intake data are used for the estimate. Using high-intake data (based on maximum concentrations), the intake with house dust may be of the same size as dietary exposure as reported by the EFSA Scientific Panel. The total estimated intake of PFOS and PFOA were still when using high-intake data below the TDI values recommended by EFSA. Biomonitoring data indicate that the internal exposure of children is comparable to that of adults, but the exposure situation of children is not well understood, and therefore the authors do not make any statements on the risks of children’s exposure to PFAS using the data available.

On the basis of reviews of the literature of the potential direct exposure from precursors, it has been concluded that FTOHs have only a negligible contribution (<1%) to the total mean and high intake PFOA exposure of adults. Moreover, the contribution of the converted $\sum$ FOSAs/FOSEs to total PFOS exposure of the general population was estimated to reach only 10%.

A wealth of data on PFOS, PFOA and PFHxS in human blood exists from all over the world demonstrating elevated concentrations in workers with occupational exposure and populations in contaminated areas. Compared to the PFOS, PFOA and PFHxS, less information is available on other PFASs. The available data demonstrate that the concentration of PFOS, even though it has decreased in recent years, is significantly higher than the concentration of the other PFASs.

The general change from PFOS and PFOA substances to other PFASs is reflected in changes in human blood levels. Investigations of temporal trends of blood serum levels of PFAS in Sweden have demonstrated that the levels of the short-chain PFBS and levels of the long-chain PFHxS, PFNA and PFDA increased over the period 1996-2010. Concomitantly, levels of FOSA, PFOS, PFDS, and PFOA decreased. Similar trends have been demonstrated in Norway.

A decreasing trend in the concentrations of PFOS and PFOA has also been demonstrated in the USA, but one study from the USA also indicates a decline in the concentration of PFHpA, PFNA, PFDA, and PFUnA, while other studies indicate increases for some substances. However, even though the concentration of PFOS has decreased from 34.9 ng/mL in 2000 to 8.3 ng/mL in 2010, the mean PFOS concentration was still significantly higher than the concentration of the other analysed PFASs.

The concentration in breast milk has also been demonstrated to follow the trend in the use of the substances. Analysis of breast milk in Sweden showed statistically significant increasing trends in the concentration of PFOS, PFHxS, and PFOA from 1972 to 2000, with concentrations reaching a plateau in the 1990s. PFOA and PFOS showed statistically significant decreasing trends during
2001–2008. In 2008 the concentration of PFOS and PFOA were both around 75 pg/mL, while the concentration of PFHxS was 14 pg/mL.
8. Information on alternatives

Three extensive reports are available on alternatives to PFOS for the different traditional application areas:

- Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid in open applications. Prepared for the Persistent Organic Pollutants Review Committee, Eighth meeting, Geneva, 15–19 October 2012 (UNEP, 2012);
- Guidance on alternatives to perfluorooctane sulfonate and its derivatives. Prepared for the Persistent Organic Pollutants Review Committee Sixth meeting, Geneva, 11–15. October 2010. (UNEP, 2010), and
- More environmentally friendly alternatives to PFOS-compounds and PFOA (Poulsen et al., 2005).

Furthermore, a few reports are available on more specific applications; among these, a recent report on alternatives to PFOS in non-decorative hard crome plating (Poulsen et al., 2011) is available (see section 3.3.2).

The US EPA is reviewing substitutes for PFOA, PFOS and other long-chain perfluorinated substances as part of its review process for new chemicals under EPA’s New Chemicals Program. Over 150 alternatives of various types have been received and reviewed by EPA. It has not been possible to identify any public assessments or reviews on these substances.

As part of the data collection FluoroCouncil has been contacted and the Council has forwarded some comments prepared by the Council to the first draft of the technical paper on the identification and assessment of alternatives to the use of PFOS in open applications (UNEP, 2012). No further information was received.

8.1 Main alternatives to PFOS and PFOS-related substances

An overview of the status of the use of PFOS-related substances and the main alternatives is shown in Table 30 from the guidance on alternatives to perfluorooctane sulfonate and its derivatives from 2010, prepared under the auspices of the Stockholm Convention.
<table>
<thead>
<tr>
<th>Use area</th>
<th>Use status for PFOS-related substances</th>
<th>Alternatives used</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aviation hydraulic oils</td>
<td>PFOS-related compounds may still be used.</td>
<td>Other fluorinated substances and non-fluorinated phosphate compounds other fluorinated substances and non-fluorinated phosphate compounds could be used after considering hazards/risk characteristics</td>
<td>Considerable information gaps though there are several products established on the market for years.</td>
</tr>
<tr>
<td>Fire-fighting foams</td>
<td>The use of PFOS-related substances in new products has been phased out in most OECD countries. Stocks are still being used up.</td>
<td>C6– fluorotelomers are used as substitutes in new products; fluorine-free alternatives are used for training exercises and possibly in other settings than offshore.</td>
<td>Alternatives to PFOS are widely used and easily accessible on several markets in North America, Europe and Asia (China). Costs for the alternatives are assessed as equal to PFOS with the exception of China that states that the alternative is slightly more expensive than PFOS.</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Sulfluoramid is used in some countries as an active substance and surfactant in pesticide products for termites, cockroaches and other insects. Other fluorosurfactants may be used as “inert” surfactants in other pesticide products.</td>
<td>Synthetic insecticides such as S-Methoprene, Pyriproxyfen, Fipronil, Imidacloprid, Chlorpyrifos, Cypermethrin, Deltamethrin, Fenitrothion, Abamectin (commercial mixture) and their mixtures are alternative active substances, sometimes used in combination. Alternative surfactants may exist. There are also a number of alternative nonchemical methods, mainly biological controls</td>
<td>Some or all chemical alternatives to PFOS are easily available in South America (Argentina, Brazil) and Asia (China). These substances are mostly systemic insecticides that are in the range from highly toxic to humans and environment to less toxic to humans” and moderately or highly toxic to environment. Some of the alternatives are considered as less effective than PFOS by Brazil. Biological control agents are available in a number of countries including South America, USA, and China (Taiwan).</td>
</tr>
<tr>
<td>Metal plating</td>
<td>PFOS-compounds are still used in hard chrome plating. Cr-III has replaced Cr-VI in decorative chrome plating.</td>
<td>Some non-fluorinated alternatives are marketed but they are not considered equally effective in hard chrome plating. A C6-fluorotelomer is used as a substitute and may be effective. PFBS derivatives may also be used. Physical barriers may also apply.</td>
<td>Only Canada and China report that alternatives to PFOS are used for years with success. They are easily available on their markets. There is little or no health environmental data available for the chemical alternatives from the parties. Costs for the alternatives are slightly higher than PFOS.</td>
</tr>
</tbody>
</table>
| Electrical and electronic parts | PFOS-based chemicals are or have been used in the manufacturing of digital cameras, mobile phones, printers, scanners, satellite communication and radar systems, etc. | For most of these uses, alternatives are available or are under development.                                                                                                                                                                                                                   | Considerable information gaps                                                                CLUDING
<table>
<thead>
<tr>
<th>Use area</th>
<th>Use status for PFOS-related substances</th>
<th>Alternatives used</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically driven oil production (Oil production and mining)</td>
<td>PFOS derivatives may occasionally be used as surfactants in the oil and mining industries.</td>
<td>PFBS, telomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids and thioether</td>
<td>Considerable information gaps.</td>
</tr>
<tr>
<td>Carpets, leather and apparel, textiles and upholstery (Impregnation of textiles, leather and carpets)</td>
<td>PFOS-related substances have been phased out in most OECD countries.</td>
<td>Other fluorinated compounds, like C6-fluorotelomers and PFBS, silicone-based products, stearamidomethyl pyridine chloride, perfluorobutane sulfonate for leather. Dendrimers.</td>
<td>Both USA and China describe short chain alternatives used on their markets on a regular basis as alternatives to PFOS. Perfluorohexane sulfonyle fluoride (PFHxSF) and its derivatives, which are not feasible alternatives to PFOS and related substances, exist on the Chinese market and are commercialized with a production volume of 20 tons per year. The Chinese full production capacity of perfluorohexane sulfonyle fluoride (PFHxSF) and its derivatives is up to 50 tons per year that is in line with production of PFOS. Perfluorohexane sulfonyle fluoride (PFHxSF) and its derivatives used as textile finishing agents with waterproof, anti-fouling effect equals with that of PFOS, but its grease-proof is lower than that of PFOS. There are concerns over the persistence of C6 compounds and the increased ability of C6 and C4 compounds to contaminate water. Dendrimers are used as non-fluorine alternatives to PFOS as water proofing agents on textiles and leather. There are considerations concerning health since cytotoxicity studies have shown dendrimers able to cross cell membranes, disrupt platelet function, and cause hemolysis.</td>
</tr>
<tr>
<td>Paper and packaging (Impregnation of paper and cardboard)</td>
<td>PFOS-related substances have been phased out in most OECD countries.</td>
<td>Fluorotelomer-based substances and phosphates, mechanical processes</td>
<td>Considerable information gaps.</td>
</tr>
<tr>
<td>Coatings and coating additives (Surface coatings, paint and varnish)</td>
<td>PFOS-related substances have been phased out in most OECD countries</td>
<td>Telomer-based compounds, fluorinated polyethers, PFBS, propylated aromatics, silicone surfactants, sulfosuccinates, polypropylene glycol ethers. Dendrimers.</td>
<td>Considerable information gaps. PFOS-related substances are no longer used on coatings and coating additives, although such articles may still be imported.</td>
</tr>
<tr>
<td>Photographic industry *2</td>
<td>A shift to digital techniques has reduced the use drastically.</td>
<td>Telomer-based surfactants products, hydrocarbon surfactants, silicone products, C3-C4-fluorinated chemicals</td>
<td>-</td>
</tr>
<tr>
<td>Use area</td>
<td>Use status for PFOS-related substances</td>
<td>Alternatives used</td>
<td>Remarks</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------------------</td>
<td>-------------------</td>
<td>---------</td>
</tr>
<tr>
<td>*<em>Semiconductor industry <em>2</em></em></td>
<td>PFOS is still used but in lower concentrations.</td>
<td>No substitutes with comparable effectiveness have been identified, and doing so may take up to 5 years, according to the industry. It should be possible to use PFBS, fluorinated polyethers or telomers.</td>
<td>-</td>
</tr>
<tr>
<td>*<em>Medical devices <em>2</em></em></td>
<td>Old video endoscopes at hospitals contain a CCD colour filter that contains a small amount of PFOS. PFOS is also used as an effective dispersant for contrast agents in radio-opaque catheters.</td>
<td>Repairing such video endoscopes requires a CCD colour filter containing PFOS. New CCD filters are PFOS-free. For radio-opaque ethylene tetrafluoroethylene, PFBS can replace PFOS.</td>
<td>-</td>
</tr>
<tr>
<td><strong>Others (Cleaning agents, waxes and polishes for cars and floors)</strong></td>
<td>PFOS-related substances have been phased out in most OECD countries.</td>
<td>Fluorotelomer-based substances, fluorinated polyethers, C4-perfluorinated compounds</td>
<td>Note that these applications are banned.</td>
</tr>
</tbody>
</table>

*1 The majority of table is derived from UNEP, 2012. Applications marked with *2 are derived from UNEP, 2010.

8.2 **Non-fluoro or low-fluoro alternatives to long-chain PFAA substances**

The technological best alternatives to the long-chain (≥ C8) fluorinated chemicals are most often other less hazardous fluorinated chemicals with a fluorinated alkyl chain length of ≤ C6 or fluoropolymers. Most of these substances have been discussed above.

The others, which are fluoroalkyl polyether, fluorinated ethers, ketones etc., will be discussed in the following paragraphs together with some non-fluorinated alternatives, such as silicone polymers, siloxanes, propylated aromatics, sulfosuccinates, etc.

Where PFOS derivatives had very broad application areas, many of the non-fluorinated alternatives only can be used to specific applications. The following review of substitutes to long-chain polyfluorinated chemicals not already discussed in the paper is based on the “Draft Guidance document on Alternatives to perfluorooctane sulfonic acid (PFOS) and its derivatives” as drafted by Allan Astrup Jensen for the Stockholm Convention in 2010 (UNEP, 2010).
### TABLE 31
MAIN ALTERNATIVES TO LONG-CHAIN POLYFLUORINATED COMPOUNDS (UNEP, 2010)

<table>
<thead>
<tr>
<th>Alternative compound</th>
<th>Product trade name</th>
<th>Company</th>
<th>Used in / used for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorobutane sulfonate (PFBS) or based on different C4-perfluorocompounds</td>
<td>Novec™</td>
<td>3M</td>
<td>Paint and coatings industry, electronic coating; industrial and commercial cleaning; stain protectors for carpets, leather, furniture, automotive, hard surfaces and other apparels</td>
</tr>
<tr>
<td>C6 fluorotelomer sulfonamide compounds (80%)</td>
<td></td>
<td>DuPont</td>
<td>Fire-fighting foam</td>
</tr>
<tr>
<td>C4-C6 Fluorotelomer alcohols and esters</td>
<td>Scotchgard™</td>
<td>DuPont</td>
<td>Surfactant, coating, printing, textile and chemical industries</td>
</tr>
<tr>
<td>Fluorinated co-polymers.</td>
<td>FORAFAC™ 1157; 1183</td>
<td>DuPont</td>
<td>Impregnation of leather and indoor car upholstery</td>
</tr>
<tr>
<td>CF3 or C3F3 fluoroalkyl polyethers</td>
<td>Zonyl®</td>
<td>OMNOVA Solutions Inc.</td>
<td>Surfactant and flow-, level-, and wetting additive for coating formulations, floor polish.</td>
</tr>
<tr>
<td>Dodecafluoro-2-methylpentane-3-one</td>
<td>Capstone®</td>
<td>3M</td>
<td>Fire-fighting foam</td>
</tr>
<tr>
<td>Perfluorobutyl methyl ethers</td>
<td>Foraperle 225 etc.</td>
<td>3M</td>
<td>Industrial cleaning</td>
</tr>
<tr>
<td>Propylated naphthalenes or biphenyls</td>
<td>Ruetasolv™</td>
<td>Rütgers Kureha Solvents Gmbh</td>
<td>Water repelling agents for rust protection systems, marine paints, coatings, etc.</td>
</tr>
<tr>
<td>Fatty alcohol polyglycol ether sulfate</td>
<td>Emulphor™</td>
<td>BASF</td>
<td>Levelling and wetting agents</td>
</tr>
<tr>
<td>Silicone polymers</td>
<td>WorléeAdd™</td>
<td>Worlée-Chemie</td>
<td>Wetting agents in the paint and ink industry</td>
</tr>
<tr>
<td>Sulfosuccinate</td>
<td>Lutensit™</td>
<td>BASF</td>
<td>Levelling and wetting agents</td>
</tr>
<tr>
<td></td>
<td>EDAPLAN™ LA 451</td>
<td>Münzing Chemie</td>
<td>Paint and coating industry: Wetting and dispersing agents for water based applications e.g. wood primers</td>
</tr>
<tr>
<td></td>
<td>HYDROPALAT™ 875</td>
<td>Cognis</td>
<td></td>
</tr>
</tbody>
</table>

### Fluorinated ethers and ketones
The fluorinated ethers and ketones are used for industrial cleaning and fire-fighting foams, respectively. There is no available information about the properties of these chemicals. Among the polyfluorodialkyl ether sulfonates, FC-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate) and FC-53B (potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate) are used in hard chrome plating in China⁷. The structure of FC-53 is an analogue of PFOS with a CF₂-group substituted by oxygen.

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Fluorinated polyethers
The company OMNOVA Solutions Inc. produces a family of short-chain fluorosurfactants based on fluorinated polyethers with a molecular weight greater than 1,000 and with C₂F₅- or CF₃- perfluoroalkyl side chain structures, under the trade name PolyFox™. The PolyFox product line includes anionic and non-ionic surfactants, UV-radiation curable acrylic monomer derivatives and polyols. It seems that these surfactants have a moderate surface tension, which is not quite as low as the conventional fluorinated surfactants. The new surfactants are claimed to have a broad processing window, where less interference with other compounds is experienced. Coating quality is improved as reduced foaming is achieved. The last item is an important factor in producing and processing water-based coatings. PolyFox fluorosurfactants have found use in aqueous and solvent-borne semiconductor coating formulations. In a number of examples, excellent wetting, flow and leveling properties have been afforded to semiconductor coatings. In addition, the poly(alkylene oxide) chain of all PolyFox materials has an inherently low refractive index compared to other commercial polymers such as acrylics. The presence of even very short (-CF₃, -C₂F₅) side chains additionally reduces the refractive index, and PolyFox materials are also used as antireflection layers in photore sist and LCD screen applications. The PolyFox formulation is currently being used as a surfactant in floor polish products in the USA, Europe and Asia.

The acute toxicities of PolyFox formulations are low (oral rat LD₅₀ > 2 g/kg bw) but the fluorinated polyether may irritate skin and the respiratory system. Generally, there is a lack of data. Fluorinated polyethers do have a high molecular weight, making them less available for transport across biomembranes and therefore less biologically available. Furthermore, the polymer backbone linkage of the PolyFox molecules is an ether link, which is more environmentally stable than e.g. the ester/amide linkages of PFOS and telomer-based fluorosurfactants. This makes the PolyFox molecule more resistant to degradation to lower molecular carboxylic acids. PolyFox has low acute toxicity to aquatic organisms and will not bioaccumulate. PolyFox products seem to have reduced environmental impacts versus most other fluorosurfactants commercially available.

Siloxanes
Siloxanes are chemical substances containing units with the general formula R₂SiO, where "R" represents either hydrogen or a hydrocarbon group. They may be straight-chain or cyclic compounds and vary in weight from a few hundred to several hundred thousand g/mol for the polymers. Siloxanes are building blocks for silicone products. The siloxanes of main interest from an environmental perspective are the volatile methyl siloxanes, having a short SiO backbone, in particular the cyclic siloxanes known as D₄, D₅ and D₆ and the linear siloxanes, MM (or HMDS), MDM, MD₂M and MD₃M. Out of these commercially used siloxanes, D₄, D₅, and MM are chemicals of high production volume within the European Union. The first two are the most commonly used siloxanes in the Nordic countries (Kaj et al., 2005).8 Recent activities within the Nordic area have focused on investigating the environmental occurrence of the above-mentioned siloxanes, which are used in a large number of industrial and consumer products such as sealants, fuel, car polish, cleaners, anti-foam ing agents, car waxes, personal care and biomedical products (Lassen C et al. 2005).9 The widespread use of siloxanes, their broad application, high volatility and potential for toxic effects have raised concerns about these compounds within various disciplines of environmental science. Recent studies indicate that they may be widespread in the environment (Cousins AP et al. 2009).10

Silicone polyethers are another class of silicone derivatives which have special surfactant properties. The leading manufacturers are Bluestar, Dow Corning, Evonik-Goldschmidt, Momentive and Wacker. Other companies sell specially formulated mixtures for specific applications. The company

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“Bluestar Silicones” markets some PFOS alternatives based on silicone for textile applications with the trade name Advantex™.

Worlée-Chemie produces silicone polymers, which in the paint and ink industry can be used as alternative wetting agents to fluorosurfactants in several cases. WorléeAdd® 340 is a low viscosity, non-ionic special modified silicone polyether (contains 3-(polyoxyethylene) propylheptamethyltrisiloxane, CAS no. 67674-67-3) which can improve surface wetting of aqueous systems on difficult substrates like polyethylene and polypropylene or contaminated substrates. It has a low surface tension and is claimed to be highly efficient in improving wetting, spreading and leveling of water-borne coatings and eliminating surface defects without foam stabilizing. It is further claimed that the compound normally has no negative effect on recoating. Another product, WorléeAdd® 345, is a mixture of a silicone polyether (10-15%) and a diocetyl sulfosuccinate (50-55%) in ethanol and water. This surfactant can be used to improve wetting properties of aqueous coatings for different substrates, where the penetration into absorbing surfaces also is improved.

A study carried out by the National Food Institute at the Technical University of Denmark investigated the toxic effects of siloxanes as a group in order to set a health-based quality criterion for ambient air (Greve K et al., 2008). Toxic effects of D3, D4, D5, D6, and HMDS were studied using a ‘read-across’ method, which is based on structural similarity and its relation to toxicity. The linear siloxane HMDS appeared to have lower potential for liver toxicity, but higher potential for lung toxicity, than the cyclic substances. Decreasing toxicity with increasing chain length was also indicated. An ambient quality criterion of 0.01 mg/m³ was derived, based on lung toxicity, and including a safety factor of 250. The silicone industry disagrees with the conclusions of this study.

Low molecular weight polydimethylsiloxanes have been studied extensively by industry to define their safety profile. These studies demonstrated that the polydimethylsiloxanes studied all possess a very low potential for toxicity (ECETOC, 1994). However, other studies of siloxanes indicate that these substances may be harmful by inhalation, and that exposure may induce serious damage to eyes. Prolonged and frequent skin contact to WorléeAdd 340 may cause skin irritation. Thus, knowledge on the toxicity of siloxanes is still incomplete.

The Scientific Committee for Consumer Products in the EU has published an Opinion on D4 in which the safety of D4’s use as a cosmetic ingredient has not been questioned. In the United States, the Cosmetic Ingredients Review panel is about to publish its final assessment of the safety of cyclomethicone, D3, D4, D5, D6 and D7. The panel has concluded that D4, D5, D6 and D7 are safe for use in cosmetics. D3 will be taken off the INCI list of cosmetic ingredients, because D3 is not a commercial product.

Perfluoroalkyl derivatives of siloxanes also exist, e.g. 1H,1H,2H,2H-perfluoroalkyl-triethoxysilane, which is effective for glass and surface treatment. A particular compound, polyfluoroethyl triethoxysilane (1H,1H,2H,2H-perfluoroethyl triethoxysilane), has been banned in Denmark, because of lung damage in experimental mice (Nørgaard et al. 2010).

Siloxanes are widely distributed in the Nordic environment and diffuse sources via the dominant emission pathway of the sewage system to the aquatic environment are the dominant emission pathways. In general, the siloxanes are highly stable and persistent compounds without degradation in the environment. The cyclic- and short-chained linear siloxanes are bioconcentrated in aquatic organisms. These siloxanes may be toxic to aquatic organisms and are bioaccumulative; however, there are still gaps in our knowledge.

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In a MSDS the silicone polymer in WorléeAddTM 340 was classified as environmentally dangerous with the R-phrases R51/53 (“Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment”). The R-phrase R53 indicates that the substance is bioaccumulative. Canada has identified decamethyl cyclopentasiloxane (D5) and octamethyl cyclotetrasiloxane (D4) as “inherently toxic to wildlife”. The cyclic siloxanes D4, D5 and D6 have been subjected to an environmental risk assessment by the United Kingdom Environment Agency applying the EU Technical Guidance. In 2009 the silicone industry submitted extensive monitoring data to the UK as the EU Rapporteur demonstrating that none of these substances biomagnifies in the environment.

Propylated aromatics

The company “Rütgers Kureha Solvents” produces different aromatic surfactants with the trade name Ruetasolv®, based on propylated naphthalenes and biphenyls, which can be used as water repelling agents for different applications, such as corrosion protection systems, marine paints, resins, printing inks, coatings, electrical, electronically and mechanical applications. They may also act as plasticizers and film forming aids in emulsion paints and adhesives. The various isopropyl naphthalenes and isopropyl biphenyls are highly hydrophobic substances that are compatible with almost all raw materials as follows: Epoxy resins, polyurethane resins, resin esters, hydrocarbon resins, polystyrene, elastomers, dispersions, emulsions, styrene-acrylate-copolymers, vinyl acetate and ethylene vinyl acetate polymers, mineral oils, bitumen, etc.

The propylated aromatic products are all colourless liquids with a boiling point of about 300˚C and have a very low solubility in water. The substances p-isopropyl-1,1’-biphenyl (Ruetasolv BP 4103,) and p,p'-diisopropyl-1,1'-biphenyl (Ruetasolv BP 4201,) can cause skin sensitization or dermatitis at repeated skin contact, and long-term exposures cause irritation of the eyes, nose, throat, mucous membranes and the respiratory tract. p-Isopropyl-1,1'-biphenyl has a very low acute toxicity with an oral LD50 value for rats of > 4 g/kg. Central nervous system (CNS) damage, liver and kidney damage have, however, been reported as chronic effects of this chemical in animals. The isopropylated naphthalenes are also irritating substances. The acute toxicity of diisopropyl naphthalene (Ruetasolv DI) is very low with an oral rat LD50 of 3900 mg/kg.

The biphenyls and the naphthalenes have high octanol/water partition coefficients (log Ko/w) and the bioconcentration factor (BCF) for the substances is greater than 100. Therefore, these chemicals are potentially bioaccumulative. The biphenyl moiety appears to be easily biodegradable, whereas the naphthalene moiety only slowly biodegrades. The sparse information available suggests that the biphenyls are acutely toxic to aquatic organisms, whereas the naphthalenes have no acute toxic effects in the investigated fish species.

Sulfosuccinates

Several companies produce surfactants based on 50-75% of the sodium salt of di(2-ethylhexyl) sulfosuccinate, which can be used as a wetting agent for aqueous systems of detergents, cleaners, paints and coatings. It is also used in pesticides. In a product from BASF (Lutensit®-A-BO) the sulfosuccinate is mixed with water and ethanol, and in a product from Cognis (Hydropalat® 875) the sulfosuccinate is mixed with water and 2,2-dimethylpropane-1,3-diol. The product from Cognis can be used as a wetting agent in aqueous coating systems and is particularly suitable for difficult-to-wet substrates like plastics, metal, cellulose film, silicone treated papers and glass. This surfactant may also be used as an emulsifier for emulsion polymerization. Another area where it can be used as an alternative to fluorinated surfactants is in optimizing the color acceptance of aqueous pigment concentrates in different coatings. The product has a medium foam formation. Münzing Chemie produces a surfactant (Edaplan® LA 451) based on a sulfosuccinate derivative in ethanol and water, which also can be used as a wetting agent for aqueous paints and coatings. The identity of the sulfosuccinate was not disclosed. The product is claimed to have good wetting properties, no increase in foam and good re-coatability. The surface tension is moderate. Application areas are decorative
paint, wood and furniture coatings, automotive and repair coating, industrial coatings, printing inks and overprint varnishes.

Toxicological information is scarce. Sulfosuccinates are irritants to eyes, skin and the respiratory system, especially for prolonged or repeated contact. Dermatitis has been observed as a long-term effect as well as CNS depression and injury to heart, liver and blood-forming organs. The substance di(2-ethylhexyl) sulfosuccinate has low acute toxicity if swallowed (LD₅₀ (oral, rat) = 1.9 g/kg). Information found in the HSDB database suggests that di(2-ethylhexyl) sulfosuccinate is mildly toxic (by ingestion) to humans with a probable oral lethal dose (human) of 0.5–5 g/kg. A possible metabolite is the branched 2-ethylhexanol, which may have reproductive effects. Di(2-ethylhexyl) sulfosuccinate is easily biodegradable and not likely to bioaccumulate; however, a 96hLC₅₀ value of 10–100 mg/l for *Leuciscus idus* (small fresh-water cyprinoid fish) shows that this sulfosuccinate may be harmful to aquatic organisms.

**Stearamidomethyl pyridine chloride**

A classic cationic textile surfactant is 1-(stearamidomethyl) pyridinium chloride, earlier marketed by ICI as Velan PF. The substance is reacted with cellulose at elevated temperatures to form a durable water-repellent finish on cotton. It was later found that the reaction was restricted to the surface of the fibers and the high cure temperature weakened the fabric. Sodium acetate had to be added to prevent the decomposition of the cellulose by the hydrogen chloride formed. Also, the pyridine liberated during the reaction has an unpleasant odour, and the fabric had to be scoured after the cure. The toxicological properties of pyridine ended its use in the 1970s when government regulations on such substances were introduced. It may be evaluated differently at present. Further information about properties is lacking. There is a lack of public data on this chemical.

**Polypropylene glycol ether, amines, and sulfates**

Possible replacements of fluorosurfactants in some applications are anionic surfactants based on aliphatic alcohols. The BASF product Emulphor® FAS 30 is the sodium salt of fatty alcohol polyglycol ether sulfate, which are preferentially used in the emulsion polymerization of acrylate and methacrylate esters, styrene and vinyl esters. These anionic emulsifiers are also combined with non-ionic Emulan® grades in order to achieve the desired properties such as particle size or emulsion stability (BASF). Because of its foaming properties, it is also used in cosmetics and fire-fighting foams. A fatty alcohol polyglycol ether sulfate has the general formula:

\[
R_1-O-(CH_2CH_2O)_n\text{SO}_3X
\]

wherein \( R_1 \) represents a linear or branched alkyl and/or alkenyl group having e.g. 12 to 16 carbon atoms, \( n \) represents a number usually from 2 to 4, and \( X \) represents a cation selected from the group consisting of \( \text{Na}^+ \), ammonium, or substituted ammonium.

A related non-fluorosurfactant is Enthone® (ethoxylated oleyl amine, CAS no. 26635-93-8) used in decorative chrome plating but also in many other applications. Its general formula is:

\[
R-N(CH_2CH_2O)_{H_m}(CH_2CH_2O)_{H_n}.
\]

The Emulphor FAS 30 has low acute toxicity by ingestion (oral LD₅₀ > 2 g/kg bw) and it is not considered to be irritating. There is a lack of data on this chemical. Enthone and other polyethylene glycol amines are non-toxic and non-irritating, non-ionic emulsifiers. The Emulphor FAS 30 is readily biodegradable (>70% elimination according to OECD 301E) and does not seem to be acutely toxic to aquatic organisms as the reported 96hLC₅₀ value for fish (*Leuciscus idus*) is > 100 mg/L. Enthone is readily degradable with low toxicity. There is, however, a lack of data on these chemicals.
8.3 Summary on alternatives
There are alternatives to long-chain fluorinated chemicals for most applications. The technologically best alternatives to hazardous fluorinated chemicals are short-chain and less hazardous fluorinated chemicals with a fluorocarbon length of ≤C6 or fluoropolymers. In addition some non-fluorinated alternatives, such as siloxanes, propylated aromatics, and sulfosuccinates, can be used for specific applications.

The fluorinated alternatives are still rather persistent but much less bioaccumulative and toxic than the long-chain homologues.

The non-fluorinated alternatives are not very persistent and bioaccumulative, but some of the substances are more toxic. In general, there is a lack of public data on the properties of the alternatives, which often are protected by commercial secrecy, and because most academic research has been on the polyfluorinated chemicals.

In TABLE 32 an overview is shown of the properties of the discussed alternatives based on the screening system developed by US EPA in their “Design for the Environment Programme” (http://www.epa.gov/dfe/alternative_assessments.html).

### TABLE 32
OVERVIEW OF THE PROPERTIES OF THE DISCUSSED ALTERNATIVES

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CAS No</th>
<th>Persistence</th>
<th>Degradation products of concern</th>
<th>Bioaccumulation</th>
<th>Animal toxicity</th>
<th>Degradation</th>
<th>Aquatic toxicity</th>
<th>Application</th>
<th>Other info</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluorinated ethers and ketones</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecafluoro-2-methylpentan-3-one</td>
<td>756-13-8</td>
<td><em>H</em></td>
<td><em>H</em></td>
<td><em>VL</em></td>
<td>n.d.</td>
<td>n.d.</td>
<td>Fire-fighting foam</td>
<td>Novec™ 1230</td>
<td></td>
</tr>
<tr>
<td>Methyl nonafluorobutyl ether</td>
<td>163702-07-6</td>
<td><em>H</em></td>
<td><em>M</em></td>
<td><em>VL</em></td>
<td>n.d.</td>
<td>n.d.</td>
<td>Commercial and industrial cleaning</td>
<td>Novec™</td>
<td></td>
</tr>
<tr>
<td>Methyl nonafluoro isobutyl ether</td>
<td>163702-08-7</td>
<td><em>H</em></td>
<td><em>M</em></td>
<td><em>VL</em></td>
<td>n.d.</td>
<td>n.d.</td>
<td>Commercial and industrial cleaning</td>
<td>Novec™</td>
<td></td>
</tr>
<tr>
<td>Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy) ethane sulfonate</td>
<td>not available</td>
<td><em>VH</em></td>
<td><em>H</em></td>
<td><em>H</em></td>
<td>n.d.</td>
<td>n.d.</td>
<td>Hard chrome plating</td>
<td>FC-53</td>
<td></td>
</tr>
<tr>
<td>Potassium 2-(6-chloro-1,1,2,2,3,4,4,5,5,6,6-dodecafluoro-hexyloxy)-1,1,2,2-tetrafluoroethane sulfonate</td>
<td>not available</td>
<td><em>VH</em></td>
<td><em>VH</em></td>
<td><em>H</em></td>
<td>n.d.</td>
<td>n.d.</td>
<td>Hard chrome plating</td>
<td>FC-53B</td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td>CAS No</td>
<td>Persistance</td>
<td>Degradation products of concern</td>
<td>Bioaccumulation</td>
<td>Animal toxicity</td>
<td>Degradation Aquatic toxicity</td>
<td>Application</td>
<td>Other info</td>
<td></td>
</tr>
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<td>------------</td>
<td></td>
</tr>
<tr>
<td>Fluorinated polymers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecyl methacrylate polymer with α-fluoro-ω-[2-{(1-oxo-octadecyl)-oxy}ethyl]-poly(difluoro-methylene)</td>
<td>65530-65-6</td>
<td>M</td>
<td>M</td>
<td>VL</td>
<td>VL</td>
<td>VL</td>
<td>Finishing and protection of leathers and car upholstery</td>
<td>Foraperle®</td>
<td></td>
</tr>
<tr>
<td>Fluoroalkyl polyethers</td>
<td>not available</td>
<td>M</td>
<td>M</td>
<td>VL</td>
<td>n.d.</td>
<td>n.d.</td>
<td>Surfactant, semiconductor coating formulations, antireflection layers, floor polish</td>
<td>PolyFox™ 656</td>
<td></td>
</tr>
<tr>
<td>Siloxanes and silicone polymers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexamethyl disiloxane</td>
<td>107-46-0</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>H</td>
<td>Industrial and consumer products such as sealants, fuel, car polish, cleaners, anti-foaming agents, car waxes, personal care and biomedical products</td>
<td>MM</td>
<td></td>
</tr>
<tr>
<td>Octamethyl trisiloxane</td>
<td>107-51-7</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>H</td>
<td></td>
<td>MDM</td>
<td></td>
</tr>
<tr>
<td>Decamethyl tetrasiloxane</td>
<td>141-62-8</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>H</td>
<td></td>
<td>MD2M</td>
<td></td>
</tr>
<tr>
<td>Dodecamethyl cyclohexasiloxane</td>
<td>540-97-6</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>VH</td>
<td></td>
<td>D6</td>
<td></td>
</tr>
<tr>
<td>Decamethyl cyclopentasiloxane</td>
<td>541-02-6</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>H</td>
<td></td>
<td>D5</td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td>CAS No</td>
<td>Persistence</td>
<td>Degradation products of concern</td>
<td>Bioaccumulation</td>
<td>Animal toxicity</td>
<td>Degradate</td>
<td>Aquatic toxicity</td>
<td>Application</td>
<td>Other info</td>
</tr>
<tr>
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<td>------------</td>
</tr>
<tr>
<td>Octamethyl cyclotetrasiloxane</td>
<td>556-67-2</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>H</td>
<td>H</td>
<td></td>
<td>D₄</td>
<td></td>
</tr>
<tr>
<td>3-(Polyoxyethylene) propyl heptamethyl trisiloxane</td>
<td>67674-67-3</td>
<td>H</td>
<td>H</td>
<td>M</td>
<td>H</td>
<td>H</td>
<td>WorléeAdd® 340</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bis(1-methylethyl) 1,1′-biphenyl</td>
<td>69009-90-1</td>
<td>M</td>
<td>n.d.</td>
<td>M</td>
<td>M</td>
<td>n.d.</td>
<td></td>
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<td>M</td>
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<td>577-11-7</td>
<td>VL</td>
<td>VL</td>
<td>VL</td>
<td>L</td>
<td>H</td>
<td>Wetting agent for aqueous systems of detergents, cleaners, paints and coatings, pesticides.</td>
<td>Lutensit® A-BO</td>
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<td>VL</td>
<td>n.d.</td>
<td>n.d.</td>
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<td>n.d.</td>
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<td>Velan PF</td>
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<td>Persistance</td>
<td>Degradation products of concern</td>
<td>Bioaccumulation</td>
<td>Animal toxicity</td>
<td>Degradate Aquatic toxicity</td>
<td>Application</td>
<td>Other info</td>
<td></td>
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<tr>
<td>Sodium salt of fatty alcohol polyglycol ether sulfate R-O- ((CH_2CH_2O)_n- SO_3X)</td>
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<td>VL</td>
<td>VL</td>
<td>L</td>
<td>L</td>
<td></td>
<td></td>
<td>Emulphor FAS 30</td>
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<td>VL</td>
<td>VL</td>
<td>L</td>
<td>M</td>
<td></td>
<td>Decorative chrome plating</td>
<td>Enthone</td>
<td></td>
</tr>
</tbody>
</table>

**VL** = Very low hazard  
**L** = Low hazard  
**M** = Moderate hazard  
**H** = High hazard  
**VH** = Very high hazard  
Endpoints in colored text (**VL**, **L**, **M**, **H**, and **VH**) were assigned based on experimental data.  
Endpoints in black italics (**VL**, **L**, **M**, **H**, and **VH**) were assigned using estimated values and professional judgment (Structure Activity Relationships).  
Y=Yes…N=No; n.d = no data
9. Overall conclusions

9.1 Main issues

PFOS and other long-chain perfluoroalkyl sulfonates
The use of PFOS and substances that may degrade to PFOS is today restricted by the EU POPs regulation. The main issues concern management of PFOS-containing waste (solid waste and sewage sludge), remaining exempted uses of the PFOS and PFOS-contaminated soil. These issues are addressed by the action plan for reduction of PFOS is Denmark.

PFOA and other long-chain perfluoroalkyl carboxylic acids
PFOA, precursor chemicals and higher homologue chemicals are addressed by the US EPA PFOA Stewardship Program and the major global manufacturers (representing more than 90% of the global production) have agreed to work toward eliminating emissions and product content of these chemicals by 2015. Expectedly this will result in significantly lower environmental concentrations and human exposure to these chemicals in the future, even some manufactures e.g. in China are not participating in the stewardship program. Human biomonitoring studies have demonstrated a decrease in concentration of PFOA in blood and breast milk for the period 2000-2010.

Annex XV dossiers have been prepared for APFO and three longer chained PFCAs and an Annex XV dossier for PFOA is on its way. The dossiers do not address possible precursors. The pathways and substance flows that lead to the presence of PFOA and longer homologues in the environment and human exposure is, however still not fully understood and it is not clear to what extent precursors are present in articles produced in the EU or imported from countries outside the EU.

Short-chain perfluoroalkyl acids
According to information from the industry the current trend is to replace the long-chain PFASs with short-chain homologues. The short-chain homologues have a better toxicological profile and do not bioaccumulate to the same extent as the long-chain substance as they are excreted more rapidly from both humans and organisms in the environment, but they are still persistent in the environment. The short-chain homologues and their precursors (e.g. fluorotelomers base on short-chain fluorochemistry) generally seems to have a better human health and environmental profile than the substances based on long-chain fluorochemistry, but it is difficult on the current knowledge to assess to what extent non-fluorinated substances could be alternatives of less concern to the long-chain PFASs for some applications.

Fluorotelomers and side-chain-fluorinated polymers
Fluorotelomers and fluorotelomer-based side-chain-fluorinated polymers account for the major part of the use of PFCs. The formation of hazardous transformation products has traditionally been a major concern related to these substances.

The side-chain fluorinated polymers are exempt from registration under REACH and do not appear to have been pre-registered. The status of these polymers under REACH and particularly side-chain-fluorinated polymers imported from countries outside the EU is not clear. More information on how the use of these substances can be assessed and regulated under REACH would be advantageous.
It has been demonstrated in many studies that a wide range of perfluorinated substances at low concentrations can be extracted from e.g. textiles and packaging treated with side-chain-fluorinated polymers. The releases of substances from the different parts of the life cycle of the substances and the significance of the exposure of humans and the environment from substances released from articles treated with the side-chain-fluorinated polymers is still not fully understood and again, more information would be of advantage.

**Exposure across substance groups**

Recently published data from EFSA indicates that the total dietary intake of PFOS and PFOA is well below the established TDI. On the other hand have population studies discovered positive associations between a number of adverse effects at commonly prevalent exposures.

### 9.2 Data gaps

The PFCs is a large and diverse group of substances and for most of the substances limited information on their use, fate and possible effects exists. The main data gaps indentified in this report are summarised below.

The action plan for reduction of PFOS in Denmark addresses some data gaps for PFOS and PFOS-related substances:

- Limited information is available on the possible sources of contamination of soil and groundwater with PFOA/PFOS, and it is not clear whether contamination of soil and groundwater in connection with fire drill sites is a generally occurring phenomenon.
- Limited data are available on the destruction efficiency of PFOS under the actual conditions in the municipal solid waste incinerators, and more studies are necessary to clarify whether it would be necessary to dispose of PFOS-containing waste to hazardous waste incinerators in order to comply with the requirements of the Stockholm Convention

For substances other than PFOS and PFOA, the link between the use of the substances and the environmental and human exposure is poorly understood. It is not clear to what extent perfluorinated side-chains of the side-chain-fluorinated polymers are released from the articles and at what stage of the lifecycle of the substances releases occur. Analysis of e.g. packaging and textiles demonstrates that a range of substances can be extracted at low levels from the articles, but the significance of this as regards possible human exposure and releases to the environment is not known.

Long-chain homologues to PFOA (C9-C12 or longer) are found in relatively high concentrations in the environment, but hardly any information on the use of these substances and their possible precursors is available.

Public available data on the ecotoxicity of the short-chain PFASs is very limited. The short-chain PFASs (e.g. butane-based) appear to be persistent but not to bioaccumulate to the same extent as the long-chain homologues, as they are excreted rapidly from the organisms studied. The ecotoxicity may not be a critical issue, but data are not available.

A recent Danish risk evaluation of perfluorinated compounds in sewage concludes that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystems where the sludge is applied and that more information on the fate and effects of PFASs is needed.

The risks and threats of PFOA and long-chain homologues to the marine environment are currently difficult to estimate due to the lack of ecotoxicological information e.g. PNEC value has not been comprehensively assessed.

In general the knowledge about the human toxicology of most perfluorinated compounds is rather sparse, and it will take some years and much effort, before sufficient information for evaluation of
the full impact of the present levels in humans is available. EFSA concludes that, based on further results from toxicological evaluations, the relevance of various PFASs to human health could be better established, thus allowing for the definition of a set of priority PFASs for future monitoring. The use of analytical methods with improved sensitivity would be required to monitor such priority PFASs in order to increase the proportion of quantified results and thereby the reliability of exposure assessments.

Population studies have discovered positive associations between a number of adverse effects at commonly prevalent exposures to the PFCs. More knowledge on adverse effects at actual exposure levels and a better understanding of which substances contribute to the effects is needed.

Many of the non-fluorinated alternatives are not very persistent and bioaccumulative, but are some of them are more toxic than the PFCs. However, there is a lack of public data on the properties of the non-fluorine alternatives to the PFCs, which often are protected by commercial secrecy, and because most academic research has been on the polyfluorinated chemicals.
10. Abbreviations and acronyms

10:2 monoPAP  10:2 Fluorotelomer phosphate monoester
4:2 FTOH  4:2 Fluorotelomer alcohol
6:2 FTAC  6:2 Fluorotelomer acrylate
6:2 FTMAC  6:2 Fluorotelomer methacrylate
6:2 FTO  6:2 Fluorotelomer olefin
6:2 FTS  6:2 Fluorotelomer sulfonate
6:2 FTSA  6:2 Fluorotelomer sulfonic acid ()
8:2 diPAP  8:2 Fluorotelomer phosphate diesters
8:2 FTAL  8:2 Fluorotelomer aldehyde
8:2 FTCA  8:2 Fluorotelomer carboxylic acid
8:2 FTI  8:2 Fluorotelomer iodide
8:2 FTOH  8:2 Fluorotelomer alcohol
8:2 FTUOH  8:2 Unsaturated fluorotelomer alcohol
8:2 monoPAP  8:2 Fluorotelomer phosphate monoester
AMAP  Arctic Monitoring and Assessment Programme
APFN  Ammonium perfluorononanoate
APFO  Ammonium perfluorooctanoate
BAT  Best available techniques
BCF  Bioconcentration factor
BMF  Biomagnification factor
BEP  Best environmental practice
BSAF  Biota-to-soil accumulation factor
BfR  German Federal Institute for Risk Assessment
BuFASAs  N-butyl perfluoroalkane sulfonamides
C4-PFSAs  Perfluoroalkyl sulfonic acids with a chain length of four
C6/C6-PFPIA  Bis(perfluorohexyl) phosphinic acid
C6-PFSAs  Perfluoroalkyl sulfonic acids with a chain length of six
C8-PFPA  Perfluorooctyl phosphonic acid
CKD  Chronic kidney Disease
CLP  Classification, Labelling and Packaging (Regulation)
C&L  Classification and Labelling
CMR  Carcinogenic, mutagenic or toxic to reproduction
CN  Combined nomenclature
DDD  Dichlorodiphenyldichloroethane
diPAPS  polyfluoroalkyl-diester phosphates
d.l.  Detection limite
d.w.  dry weight
ECn  Effect concentration where n % of the species tested show the effect
ECF  Electrochemical fluorination
EFSA  European Food Safety Authority
EPA  Environmental Protection Agency
ESWI  European Scientific Working group on Influenza
EtFASAs  N-ethyl perfluorooctane sulfonamides
EtFASEs  N-Ethyl perfluoroalkane sulfonamidoethanol
EtFBSE  N-Ethyl perfluoro-butane sulfonamidoethanol
EtFBSE  N-Ethyl perfluoro-butane sulfonamidoethanol
EtFOSA  N-ethylperfluorooctane sulfonamide
EtFOSAA  N-Ethyl perfluorooc-tane sulfonamidoacetic acid
EtFOSAC  N-Ethyl perfluoro-octane sulfonamidoethyl acrylate
EtFOSE  N-ethylperfluorooctane sulfonamidoethanol
FASAAs Perfluoroalkane sulfonamidoacetic acids
FASEs Perfluoroalkane sulfonamidoethanols
FASe  Perfluoroalkane sulfonamidoethanol
FC-807 Perfluoroalkyl phosphate
FOSA Perfluorooctane sulfonamide
FTBP Fluorotelomer based polymer
FTCA Fluorotelomer carboxylates
PTO Fluorotelomer olefin
FTOH Fluorotelomer alcohols
FTS Fluorotelomer sulfonates
FTUCA Fluorotelomer unsaturated carboxylic acids
GJIC Gap junction intercellular communication
HCB Hexachlorobenzene
HFP Hexafluoropropylene
HMDS Hexamethyldisiloxane
HPA Health Protection Agency
ICCM International Conference on Chemicals Management
MeFASA N-methyl perfluorooctane sulfonamides
MPC Maximum permissible concentration
KPFO PFOA potassium salt
Kd Soil/water distribution coefficient
LC Lethal effect concentration
L-FABP Liver-fatty acid binding protein
LOAEEL Lowest observable adverse effect level
LOUS List of Undesirable Substances
MACeco: Maximum Acceptable Concentration for ecosystems
monoPAPS polyfluoroalkyl-mono phosphates
NHANES National Health and Nutrition Examination Survey (in the USA)
NOAEEL No observable adverse effect level
NOEC No observable effect concentration
NOVANA Danish national surveillance programme for the aquatic environment
MCF-7 Michigan Cancer Foundation – 7 breast cancer cell line
MSWI Municipal solid waste incinerator
MTBE Methyl tertiary butyl ether
MWWTP Municipal waste water treatment plant
n:2 FTIs n:2 Fluorotelomer iodides
n:2 FTOHs n:2 Fluorotelomer alcohols
NC Negligible Concentration
NCP New Chemicals Program
NEt4-PFOS Tetraethylammonium perfluorooctane sulfonate
OECD Organisation for Economic Co-operation and Development
OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic
PAFs Perfluoroalkanoyl fluorides
PAPs Polyfluoroalkyl phosphoric acid esters
PASFs Perfluoroalkane sulfonyle fluoride
PBT Persistent, bioaccumulative and toxic (in the environment)
PCBs Polychlorinated biphenyls
PFAA Perfluoroalkyl acids
PFAIs Perfluoroalkyl iodides
PFALH$_2$Os Perfluoroalkyl aldehyde hydrates
PFALs Perfluoroalkyl aldehydes
PFASs entire group of perfluoroalkyl and polyfluoroalkyl substances
PFBA Perfluorobutanoic acid
PFBS Perfluorobutane sulfonic acid
PFCAs Perfluoroalkyl carboxylic acids
PFCAs Perfluoroalkyl carboxylates
PFCs Collective designation of perfluoroalkyl substances, polyfluoroalkyl substances and side-chain fluorinated polymers
PFDA Perfluorodecanoic acid
PFDoDA Perfluorododecanoic acid
PFDS Perfluorodecane sulfonic acid
PFHpA Perfluorohexanoic acid
PFHpS Perfluorohexane sulfonic acid
PFHxDA Perfluorohexadecanoic acid
PFHxI Perfluorohexyl iodide
PFHxS Perfluorohexane sulfonic acid
PFNAPerfluorononanoic acid
PFNA Perfluorononanal
PFOA Perfluorooctanoic acid
PFODA Perfluorooctadecanoic acid
PFOS Perfluorooctane sulfonate
PFOS Perfluorooctane sulfonic acid
PFOSA Perfluorooctane sulphonamide
PFOSF Perfluorooctane sulfonyl fluoride
PFOSI Perfluorooctane sulfinic acid
PFOSI Perfluorooctane sulfinic acid
PFPA Perfluoropentanoic acid
PFPPAs Perfluoroalkyl phosphonic acids
PFPeDA Perfluoropentadecanoic acid
PFPEs Perfluoropolyethers
PFPIAs Perfluoroalkyl phosphinic acids
PFSAs Perfluoroalkyl sulfonic acids
PFSAs Perfluoroalkane sulfonates
PFSAs Perfluoroalkane sulfonic acids
PF_SIAs Perfluoroalkane sulfinic acids
PFTE Polytetrafluoroethylene
PFTrDA Perfluorotridecanoic acid
PFUnDA Perfluoroundecanoic acid = PFUnA
PNEC Predicted No Effect Concentration
POF Perfluoroocantoyl fluoride
POPs Persistent organic pollutants
POSF Perfluorooctane sulfonic acid
PPARα Peroxisome proliferator-activated receptor-α
PTFE  Polytetrafluoroethylene
PVDF  Polyvinylidene fluoride
PVF  Polyvinylfluoride
RME  Reasonable Maximum Exposure
ROS  Reactive oxygen species
SAICM  Strategic Approach to International Chemicals Management
SRCEco  Serious Risk Concentration for ecosystems
SFAenes  Semifluorinated n-alkenes
SFAs  Semifluorinated n-alkanes
SVHC  Substances of Very High Concern
TDI  Tolerable daily intake
TDS  Testicular dysgenesis syndrome
TFE  Copolymers of tetrafluoroethylene
TSCA  Toxic Substances Control Act
UNEP  The United Nations Environment Programme
UNIDO  The United Nations Industrial Development Organization
USEPA  United States Environmental Protection Agency
vPvB  Very persistent and very bioaccumulative
w.w.  Wet weight
WWTP  Waste water treatment plant
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### Annex 1: List of specific substance abbreviations used in the report

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<th>Abb.</th>
<th>Chemical name</th>
<th>CAS No</th>
<th>Chain length</th>
<th>Group name</th>
<th>Group abb.</th>
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<td>10:2 Fluorotelomer phosphate monoester</td>
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<td>n:2 Polyfluoroalkyl phosphoric acid esters</td>
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<td>Tetraethylammonium perfluorooctane sulfonate</td>
<td>56773-42-3</td>
<td>C8</td>
<td>Perfluoroalkane sulfonic acids</td>
<td>PFSAs</td>
</tr>
<tr>
<td>PBSF</td>
<td>Perfluorobutane sulfonyl fluoride</td>
<td>375-72-4</td>
<td>C4</td>
<td>Perfluoroalkane sulfonyl fluorides</td>
<td>PASFs</td>
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<tr>
<td>PFBA</td>
<td>Perfluorobutanoic acid</td>
<td>375-22-4</td>
<td>C4</td>
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<tr>
<td>PFBS</td>
<td>Perfluorobutane sulfonic acid</td>
<td>375-73-5</td>
<td>C4</td>
<td>Perfluoroalkane sulfonic acids</td>
<td>PFSAs</td>
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<tr>
<td>PFDA</td>
<td>Perfluorodecanoic acid</td>
<td>335-76-2</td>
<td>C10</td>
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<td>PFCAs</td>
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<tr>
<td>PFDoDA</td>
<td>Perfluorododecanoic acid</td>
<td>307-55-1</td>
<td>C12</td>
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<td>PFCAs</td>
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<td>PFDS</td>
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<td>335-77-3</td>
<td>C10</td>
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<td>PFHpA</td>
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<td>PFHpS</td>
<td>Perfluoroheptane sulfonic acid</td>
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<td>PFHxA</td>
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<td>PFHxDA</td>
<td>Perfluorohexadecanoic acid</td>
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<td>PFHxI</td>
<td>Perfluorohexyl iodide</td>
<td>355-43-1</td>
<td>C6</td>
<td>Perfluoroalkyl iodides (Telomer A)</td>
<td>PFAIs</td>
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<td>PFHxS</td>
<td>Perfluorohexane sulfonic acid</td>
<td>355-46-4</td>
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<td>63967-40-8</td>
<td>C8</td>
<td>Perfluoroalkyl aldehydes</td>
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<tr>
<td>PFOA</td>
<td>Perfluorooctanoic acid</td>
<td>335-67-1</td>
<td>C8</td>
<td>perfluoroalkyl carboxylic acids and salts</td>
<td>PFCAs</td>
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<tr>
<td>PFODA</td>
<td>Perfluorooctadecanoic acid</td>
<td>16517-11-6</td>
<td>C17</td>
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<td>PFOS</td>
<td>Perfluorooctane sulfonic acid</td>
<td>1763-23-1</td>
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<td>Perfluoroalkane sulfonic acids</td>
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<td>PFOSA</td>
<td>Perfluorooctane sulfonamide</td>
<td>754-91-6</td>
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<td>Perfluoroalkane sulfonamides</td>
<td>FASAs</td>
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<td>PFOSI</td>
<td>Perfluorooctane sulfinic acid</td>
<td>-</td>
<td>C8</td>
<td>Perfluoroalkane sulfinic acids</td>
<td>PFSIAs</td>
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<td>PFPDA</td>
<td>Perfluoropentanoic acid</td>
<td>2706-90-3</td>
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<td>PFCAs</td>
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<td>PFPedA</td>
<td>Perfluoropentadecanoic acid</td>
<td>141074-63-7</td>
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<td>Perfluoroalkyl carboxylic acids</td>
<td>PFCAs</td>
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<td>PFTeDA</td>
<td>Perfluorotetradecanoic acid</td>
<td>376-06-7</td>
<td>C14</td>
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<td>PFCAs</td>
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<tr>
<td>PFTrDA</td>
<td>Perfluorotridecanoic acid</td>
<td>72629-94-8</td>
<td>C13</td>
<td>Perfluoroalkyl carboxylic acids</td>
<td>PFCAs</td>
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<tr>
<td>PFUnA</td>
<td>Perfluoroundecanoic acid</td>
<td>4234-23-5</td>
<td>C11</td>
<td>Perfluoroalkyl carboxylic acids</td>
<td>PFCAs</td>
</tr>
</tbody>
</table>
Abb. | Chemical name | CAS No | Chain length | Group name | Group abb. |
--- | --- | --- | --- | --- | --- |
PFUnDA | Perfluoroundecanoic acid = PFUnA | 4234-23-5 | C11 | Perfluoroalkyl carboxylic acids | PFCAs |
PFOF | Perfluorooctanoyl fluoride | 335-66-0 | C8 | Perfluoroalkanoyl fluorides | PAFs |
POSF | Perfluorooctane sulfonyl fluoride | 307-35-7 | C8 | Perfluoroalkane sulfonyl fluorides | PASFs |
Annex 2: OECD 2007 substance groups

Grouping of PFCs used in the OECD surveys (OECD, 2007). Annex 1, 2 and 3 include substances that may be potentially degrade to PFOS, other PFASs and PFOA, respectively.

<table>
<thead>
<tr>
<th>Annex 1</th>
<th>Perfluorooctane sulfonate (PFOS) and related compounds.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annex 2</td>
<td>Perfluoroalkyl sulfonate (PFAS) and related compounds (other than the substances included in Annex 1)</td>
</tr>
<tr>
<td>Annex 3</td>
<td>List of perfluorooctanoic acid (PFOA) and related compounds.</td>
</tr>
<tr>
<td>Annex 4</td>
<td>Fluorinated chemicals that potentially degrade to PFCA</td>
</tr>
<tr>
<td>P1: Perfluoro alcohol compounds</td>
<td></td>
</tr>
<tr>
<td>P2: Perfluoro amine compounds</td>
<td></td>
</tr>
<tr>
<td>P3: Perfluoro carboxylic compounds (some overlap with annex 3)</td>
<td></td>
</tr>
<tr>
<td>P4: Perfluoro ester compounds</td>
<td></td>
</tr>
<tr>
<td>P5: Perfluoro ether compounds</td>
<td></td>
</tr>
<tr>
<td>P6: Perfluoro iodide compounds</td>
<td></td>
</tr>
<tr>
<td>P7: Perfluoro phosphonic/phosphinic compounds</td>
<td></td>
</tr>
<tr>
<td>P8: Partial perfluoro &amp; miscellaneous perfluoro compounds</td>
<td></td>
</tr>
<tr>
<td>F1: Fluoro alcohol compounds</td>
<td></td>
</tr>
<tr>
<td>F2: Fluoro ammonium compounds</td>
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<tr>
<td>F3: Fluoro amine compounds</td>
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<tr>
<td>F4: Fluoro carboxylic compounds</td>
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<tr>
<td>F5: Fluoro ester compounds</td>
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</tr>
<tr>
<td>F6: Fluoro ether compounds</td>
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</tr>
<tr>
<td>F7: Fluoro iodide compounds</td>
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</tr>
<tr>
<td>F8: Fluoro phosphate compounds</td>
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</tr>
<tr>
<td>F9: Fluoro sulfate compounds</td>
<td></td>
</tr>
<tr>
<td>F10: Fluoroalkyl silicate compounds</td>
<td></td>
</tr>
<tr>
<td>F11: Fluoro sulfonate/sulfonamide/sulfonyl compounds</td>
<td></td>
</tr>
<tr>
<td>F12: Fluoro siloxane/silicone/silane compounds</td>
<td></td>
</tr>
<tr>
<td>F13: Fluoro thiols compounds</td>
<td></td>
</tr>
<tr>
<td>F14: Fluoro thioether compounds</td>
<td></td>
</tr>
<tr>
<td>F15: Fluoro thioester compounds</td>
<td></td>
</tr>
<tr>
<td>F16: Fluoro urethane compounds</td>
<td></td>
</tr>
<tr>
<td>F17: Partial fluoro &amp; miscellaneous fluoro compounds</td>
<td></td>
</tr>
</tbody>
</table>
Annex 3: Data from the Danish Product Register

The PFAFs and fluorinated polymer substances identified by the data retrievals from the Danish Product Register in 2006 (Jensen et al., 2008), and 2012 are listed in the table below. The substances are ranked by quantity in 2012.

For the 2006 data for confidentiality reasons no exact figures are given, but the amounts are instead listed as uses over 5 tonnes in total, below 1 tonne, below 0.1 tonne and as 0.00/0.000 tonne which indicate that no amount have been reported to the Danish Product Register. The 2012 data are indicated slightly differently in accordance with the current confidentiality policy. Total quantities and total number of products are considered confidential if the substance is registered by less than 3 companies. For the majority of substances, the quantity is confidential.

For substances not on the 2006 list chemical names from preregistrations are indicated; for substances not preregistered the name used in the Product Register is indicated.

The 2012 data include:
- Substances on the OECD 2007 list
- Substances from the 2006 list of substances registered in the Product Register, but not on the OECD list (10 substances)
- Additional substances identified by Poulsen et al. (2008) (3 substances).
- Substances in the database of registered substances or the list of 2013 intentions which are not on the OECD 2007 list (xx substances). However, none of these substances were registered in the Product Register.

Three substances indentified in the 2006 survey were included in the data retrieval, but turned out to be mixtures based in fluoropolymers which are beyond the scope of this study:
- Tetrafluorethen polymer (CAS No 9002-84-0), constituent of PFTE polymer-based waxes. This substances was registered in 168 products with a total of 12 tonnes.
- Poly[oxy(trifluorotrifluoromethyl)-1,2-ethanediyl|1α-(1,1,2,2,2-pentafluoroethyl)ω-[tetrafluoro(trifluoromethyl)ethoxy]| (CAS No 60164-51-4) is a FPPE polymer. Data confidential.
- Poly(difluoromethylene), .alpha.-fluoro-.omega.- (2-iodoethyl) (CAS No 71215-70-8). Fluoro polymer. Data confidential.

<table>
<thead>
<tr>
<th>CAS No.</th>
<th>Substance name</th>
<th>OECD class</th>
<th>Chain length</th>
<th>Total amount in tonnes</th>
<th>Number of preparations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>2006</td>
<td>2012</td>
<td>confidential</td>
</tr>
<tr>
<td>26655-00-5</td>
<td>Propane, 1,1,2,2,3,3-heptafluoro-3-[(trifluoroethenyl)oxy]-, polymer with tetrafluoroethene</td>
<td>None / miscellaneous perfluoroalkyl</td>
<td>5</td>
<td>&gt; 5</td>
<td>confidential</td>
</tr>
<tr>
<td>65545-80-4</td>
<td>Poly(oxy-1,2-ethanediyl), α-hydro-ω-hydroxy-, ether with α-fluoro-ω-(2-hydroxyethyl) poly(difluoromethylene) (1:1) (TSCA, DSL, AICS)</td>
<td>Fluoro ether (F6)</td>
<td>n</td>
<td>&gt; 1</td>
<td>0.9</td>
</tr>
<tr>
<td>143372-54-7</td>
<td>Siloxanes and silicones, (3,3,4,4,5,6,6,6,6,7,7,7,7,7,7,7,8,8,9,9,9,9,10,10,10-heptadecafluoroctyl)oxy Me, hydroxy Me, Me, octyl, ethers with polyethylene glycol mono-Me ether (TSCA, NDSL)</td>
<td>Fluorosiloxane/silicone/silanes (F12)</td>
<td>8</td>
<td>&gt; 1</td>
<td>0.6</td>
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<tr>
<td>CAS No.</td>
<td>Substance name</td>
<td>OECD class</td>
<td>Chain length</td>
<td>Total amount in tonnes 2006</td>
<td>Number of preparations</td>
</tr>
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<td>-----------------------------</td>
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<tr>
<td>24448-09-7</td>
<td>1-Octanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-N-methyl-(TSCA, DSL, AICS) (MeFOSE)</td>
<td>PFOS</td>
<td>8</td>
<td>&gt; 1</td>
<td>21</td>
</tr>
<tr>
<td>65530-70-3</td>
<td>Poly(difluoromethylene), α, α’-[phosphinicobis(oxy-2,1-ethanediyl)]bis(ω-fluoro-, ammonium salt (TSCA, DSL)</td>
<td>Fluoro phosphate (F8)</td>
<td>n</td>
<td>&lt; 1</td>
<td>19</td>
</tr>
<tr>
<td>68298-62-4</td>
<td>2-Propenoic acid, 2- [butyl [[(heptadecafluorooctyl)sulfonyl]amino]ethyl ester, telomer with 2-[butyl[(pentadecafluorooctyl)sulfonyl]amino]ethyl 2-propenoate, methylxirane polymer with oxirane di-2-propenoate, methylxirane polymer with oxirane mono-2-propenoate and 1-octanethiol (TSCA, DSL, AICS)</td>
<td>PFOS, PFAS</td>
<td>7-8</td>
<td>&lt; 0.1</td>
<td>32</td>
</tr>
<tr>
<td>65530-74-7</td>
<td>Ethanol, 2,2’-iminobis-, compd. With α-fluoro-ω-[2-(phosphonoxy)ethyl] poly(difluoromethylene) (1:1) (TSCA, DSL)</td>
<td>Fluoro phosphate (F8)</td>
<td>n</td>
<td>&lt; 0.1</td>
<td>8</td>
</tr>
<tr>
<td>65530-69-0</td>
<td>Poly(difluoromethylene), α-[2-{2-[carboxyethyl]thio}ethyl]-ω-fluoro-, lithium salt (TSCA, DSL, AICS)</td>
<td>Fluoro thi-oether (F14)</td>
<td>n</td>
<td>&lt; 0.1</td>
<td>17</td>
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<tr>
<td>68391-08-2</td>
<td>Alcohols, C8-14, g-ω-perfluoro (TSCA, DSL, EINECS, AICS)</td>
<td>Fluoro alcohols (F1)</td>
<td>6-12</td>
<td>&lt; 0.1</td>
<td>8</td>
</tr>
<tr>
<td>68391-08-2</td>
<td>Alcohols, C8-14, γ-ω-perfluoro</td>
<td>Fluoro alcohols (F1)</td>
<td>8-14</td>
<td>n.i.</td>
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<tr>
<td>65530-72-5</td>
<td>Poly(difluoromethylene), α-fluoro-ω-[2-(phosphonoxy)ethyl]-, diammonium salt (TSCA,DSL)</td>
<td>Fluoro phosphate</td>
<td>n</td>
<td>&lt; 1</td>
<td>19</td>
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<tr>
<td>2991-51-7</td>
<td>Glycine, N-ethyl-N-[(heptadecafluoroctyl)sulfonyl]-, potassium salt (TSCA, DSL, ENCS, AICS)</td>
<td>PFOS</td>
<td>8</td>
<td>&lt; 0.1</td>
<td>11</td>
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<tr>
<td>65530-71-4</td>
<td>Poly(difluoromethylene), α-fluoro-ω-[2-(phosphonoxy)ethyl]-, monoammonium salt (TSCA, DSL)</td>
<td>Fluoro phosphate (F8)</td>
<td>n</td>
<td>&lt; 0.1</td>
<td>18</td>
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<tr>
<td>65530-74-7</td>
<td>Ethanol, 2,2’-iminobis-, compd. With α-fluoro-ω-[2-(phosphonoxy)ethyl] poly(difluoromethylene) (1:1) (TSCA, DSL)</td>
<td>Fluoro phosphate (F8)</td>
<td>n</td>
<td>&lt; 0.1</td>
<td>8</td>
</tr>
<tr>
<td>54950-09-5</td>
<td>Butanedioic acid, sulfo-, 1,4- bis(3,3,4,4,5,5,6,7,7,8,8,8-tridecafluoroctyl) ester, sodium salt (TSCA, NDSL, AICS)</td>
<td>Fluoro ester (F5)</td>
<td>6</td>
<td>&lt; 0.1</td>
<td>11</td>
</tr>
<tr>
<td>65530-63-4</td>
<td>Ethanol, 2,2’-iminobis-, compd. With α-fluoro-ω-[2-(phosphonoxy)ethyl] poly (difluoromethylene) (2:1) (TSCA, DSL)</td>
<td>Fluoro phosphate (F8)</td>
<td>n</td>
<td>&lt; 0.1</td>
<td>7</td>
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<tr>
<td>65530-64-5</td>
<td>Ethanol, 2,2’-iminobis-, compd. With α, α’-[phosphinicobis(oxy-2,1-ethanediyl)] bis(ω-fluoro(poly(difluoromethylene)) (1:1) (TSCA, DSL)</td>
<td>Fluoro phosphate (F8)</td>
<td>n</td>
<td>&lt; 0.1</td>
<td>7</td>
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<tr>
<td>65530-64-5</td>
<td>Ethanol, 2,2’-iminobis-, compd. With α, α’-[phosphinicobis(oxy-2,1-ethanediyl)] bis(ω-fluoro(poly(difluoromethylene)) (1:1) (TSCA, DSL)</td>
<td>Fluoro phosphate (F8)</td>
<td>n</td>
<td>&lt; 0.1</td>
<td>7</td>
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<tr>
<td>CAS No.</td>
<td>Substance name</td>
<td>OECD class</td>
<td>Chain length</td>
<td>Total amount in tonnes</td>
<td>Number of preparations</td>
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<td>------------------------</td>
</tr>
<tr>
<td>65530-64-5</td>
<td>Ethanol, 2,2’-iminobis-, compd. With α, α’-[phosphinicobis(oxo-2,1-ethanediyl)] bis[ω-fluoropoly(difluoromethylene)] (1:1) (TSCA, DSL)</td>
<td>Fluoro phosphate (F8)</td>
<td>n</td>
<td>&lt; 0.1  0.001</td>
<td>7</td>
</tr>
<tr>
<td>67584-51-4</td>
<td>Glycine, N-ethyl-N-[(nonafluorobutyl)sulfonyl]-, potassium salt (TSCA, DSL, AICS)</td>
<td>PFAS</td>
<td>4</td>
<td>&lt; 0.1  0.001</td>
<td>7</td>
</tr>
<tr>
<td>67584-62-7</td>
<td>Glycine, N-ethyl-N-[(pentadecafluoroheptyl)sulfonyl]-, potassium salt (TSCA, DSL, ENCS, AICS)</td>
<td>PFAS</td>
<td>7</td>
<td>&lt; 0.1  0.001</td>
<td>7</td>
</tr>
<tr>
<td>67584-53-6</td>
<td>Glycine, N-ethyl-N-[(tridecafluorohexyl)sulfonyl]-, potassium salt (TSCA, DSL, ENCS, AICS)</td>
<td>PFAS</td>
<td>6</td>
<td>&lt; 0.1  0.001</td>
<td>11</td>
</tr>
<tr>
<td>65530-83-8</td>
<td>Poly(difluoromethylene), α-[2-{2-carboxyethyl]thio[ethyl]-ω-fluo- (TSCA, DSL, AICS)</td>
<td>Fluoro thioether (F14)</td>
<td>n</td>
<td>0.00 &lt;0.000</td>
<td>13</td>
</tr>
<tr>
<td>67584-52-5</td>
<td>Glycine, N-ethyl-N-[(undecafluoropentyl)sulfonyl]-, potassium salt (TSCA, DSL, AICS)</td>
<td>PFAS</td>
<td>5</td>
<td>0.000 &lt;0.000</td>
<td>7</td>
</tr>
<tr>
<td>68412-68-0</td>
<td>Phosphonic acid, perfluoro-C6-12-alkyl derivatives (TSCA, DSL, EINECS)</td>
<td>Perfluoro phosphonic/phosphinic (P7)</td>
<td>6-12</td>
<td>&gt; 1 conf.</td>
<td>-</td>
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<tr>
<td>68412-69-1</td>
<td>Phosphinic acid, bis(perfluoro-C6-12-alkyl) derivatives (TSCA, DSL, EINECS)</td>
<td>Perfluoro phosphonic/phosphinic (P7)</td>
<td>6-12</td>
<td>&gt; 1 conf.</td>
<td>-</td>
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<tr>
<td>56773-42-3</td>
<td>Ethanaminium, N,N,N-triethyl-, salt with 1,1,2,2,3,3,4,4,5,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (1:1) (TSCA, DSL, AICS, SWISS)</td>
<td>PFOS</td>
<td>8</td>
<td>&lt; 1 conf.</td>
<td>-</td>
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<tr>
<td>69991-67-9</td>
<td>1-Propene, 1,1,2,3,3,3-hexafluoro-, oxidized, polymerized</td>
<td>None / miscellaneous perfluoroalkyl</td>
<td>5</td>
<td>&lt; 1 conf.</td>
<td>-</td>
</tr>
<tr>
<td>174125-96-3</td>
<td>2-Propenoic acid, 2-methyl-, 2-(dimethylamino)ethyl ester, polymers with d-perfluoro-Cto-16-alkyl acrylate and vinyl acetate (TSCA, NDSL, AICS)</td>
<td>Fluoro ester (F5)</td>
<td>7-13</td>
<td>&lt; 0.1 conf.</td>
<td>-</td>
</tr>
<tr>
<td>CAS No.</td>
<td>Substance name</td>
<td>OECD class</td>
<td>Chain length</td>
<td>Total amount in tonnes 2006</td>
<td>Total amount in tonnes 2012</td>
</tr>
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<td>--------------</td>
<td>-------------------------------</td>
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</table>
| 17741-60-5 | 2-Propenoic acid, 3,3,4,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-
|          | heneicosafluorododecyl ester (TSCA, DSL, ENCS)                                 | Fluoro ester (F5)                 | 10           | < 0.1                         | conf.                 | -                      |
| 27905-45-9 | 2-Propenoic acid, 3,3,4,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-
|          | heptadecfluorododecyl ester (TSCA, DSL, ENCS)                                 | Fluoro ester (F5)                 | 8            | < 0.1                         | conf.                 | -                      |
| 2795-39-3  | 1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,4,5,5,6,6,7,7,8,8,8-
|          | heptadecafluoro-, potassium salt (TSCA, DSL, AICS)                            | PFOS                             | 8            | < 0.1                         | conf.                 | -                      |
| 1652-63-7  | 1-Propanaminium, 3-
|          | [(heptadecfluoro(octyl)sulfonyl]amino]-N,N,Ntrimethyl-, iodide (TSCA, DSL, AICS) | PFOS                             | 8            | < 0.1                         | conf.                 | -                      |
| 647-42-7   | 1-Octanol, 3,3,4,4,4,5,5,6,6,7,7,8,8,8-
|          | tridecafluoro- (TSCA, DSL, ENCS, AICS) 6:2 FTOH                              | Fluoro alcohols (F1)             | 6            | 0.00                          | conf.                 | -                      |
| 79070-11-4 | Poly(difluoromethylene), alpha.-chloro-.omega.- (2,2-
|          | dichloro-1,1,2-trifluorooctyl)-                                               | None (PFAS)                      | 8            | < 0.1                         | conf.                 | -                      |
| 3825-26-1  | Ammonium pentadecafluoroctanoate (EINECS)                                     | PFOA                             | 7            | < 0.1                         | conf.                 | -                      |
| 72276-08-5 | 2-Propenoic acid, 2-[methyl[(3,3,4,4,4,5,5,6,6,7,7,8,8,8-
|          | tridecafluorooctadecyl]sulfonyl]amino[ethyl ester (TSCA, NDSL)                | Fluoro sulfonate/sulfonamide/    | 16           | 0.00                          | conf.                 | -                      |
| 91032-01-8 | Fatty acids, C7-19, perfluoro (EINECS)                                        | PFOA, Perfluorocarboxyls (P3)    | 6-18         | 0.00                          | conf.                 | -                      |
| 678-39-7   | heptadecafluoro- (TSCA, DSL, AICS) 8:2 FTOH                                   | Fluoro alcohols (F1)             | 8            | 0.000                         | conf.                 | -                      |
| 65530-66-7 | Poly(difluoromethylene), alpha.-fluoro-ω-[2-[(2-methyl-1-
|          | oxo-2-propenyl)oxy]ethyl]- (TSCA, DSL)                                      | Fluoro ester (F5)                | n            | 0.000                         | conf.                 | -                      |
| 865-86-1   | 1-Dodecanol, 3,3,4,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-
|          | heneicosafluoro- (TSCA, DSL, AICS) 10:2 FTOH                                  | Fluoro alcohols (F1)             | 10           | 0.000                         | conf.                 | -                      |
| 67584-58-1 | 1-Propanaminium, N,N,N-trimethyl-3-
|          | [(pentadecafluoroheptyl)sulfonyl]amino]-, iodide (TSCA, DSL, AICS)          | PFAS                             | 7            | 0.000                         | conf.                 | -                      |
| 67939-95-1 | 1-Propanaminium, N,N,N-trimethyl-3-
|          | [(nonafluorobutyl)sulfonyl]amino]-, iodide (TSCA, DSL, AICS)                | PFAS                             | 4            | 0.000                         | conf.                 | -                      |
| 68957-57-3 | 1-Propanaminium, N,N,N-trimethyl-3-
|          | [(undecafluoropentyl)sulfonyl]amino]-, iodide (TSCA, DSL, AICS)              | PFAS                             | 5            | 0.000                         | conf.                 | -                      |
| 68957-58-4 | 1-Propanaminium, N,N,N-trimethyl-3-
<p>|          | [(tridecafluoroxy]sulfonyl]amino]-, iodide (TSCA, DSL, ENCS)                | PFAS                             | 6            | 0.000                         | conf.                 | -                      |</p>
<table>
<thead>
<tr>
<th>CAS No.</th>
<th>Substance name</th>
<th>OECD class</th>
<th>Chain length</th>
<th>Total amount in tonnes 2006</th>
<th>Number of preparations</th>
</tr>
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<tbody>
<tr>
<td>27619-97-2</td>
<td>3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoroctanesulfonic acid</td>
<td>Fluoro sulfonate/sulfonamide/sulfonyl compounds (F1)</td>
<td>6</td>
<td>n.i.</td>
<td>conf</td>
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<tr>
<td>70969-47-0</td>
<td>Thiols, C8-20, gamma-.omega.-perfluoro, telomers with acrylamide</td>
<td>Fluoro amine compounds (F3)</td>
<td>6-18</td>
<td>n.i.</td>
<td>conf</td>
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<tr>
<td>203743-03-7</td>
<td>2-Propanoic acid, 2-methyl-, hexadecyl ester, polymers with 2-hydroxyethyl methacrylate, gamma-.omega.-perfluoro-C10-16-alkyl acrylate and stearyl methacrylate</td>
<td>Fluoro ester compounds (F5)</td>
<td>8-14</td>
<td>n.i.</td>
<td>conf</td>
</tr>
<tr>
<td>196316-34-4</td>
<td>2-Propanoic acid, 2-methyl-, 2-(dimethylamino)ethyl ester, polymers with gamma-.omega.-perfluoro-C10-16-alkyl acrylate and vinyl acetate, acetates</td>
<td>Fluoro ester compounds (F5)</td>
<td>8-14</td>
<td>n.i.</td>
<td>conf</td>
</tr>
<tr>
<td>68187-47-3</td>
<td>1-Propanesulfonic acid, 2-methyl-, 2-[[1-oxo-3-[[γ-ω-perfluoro-C4-16-alkyl]thio]propyl]amino] derivs., sodium salts</td>
<td>Fluoro amine compounds (F3)</td>
<td>2-14</td>
<td>n.i.</td>
<td>conf</td>
</tr>
<tr>
<td>142636-88-2</td>
<td>Octadecylmethacrylat/2-propenoic acid, 3,3,4,4,5,5,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl ester/2-propenoic acid, 3,3,4,4,5,5,6,7,7,8,8,9,9,10,10,11,12,12-beneicosafuorodecyl ester/2-propenoic acid, 3,3,4,4,5,5,6,7,7,8,8,9,9,10,10,11,12,12-beneicosafuorodecyl ester/2-propenoic acid</td>
<td>Fluoro carboxylic compounds (F4)</td>
<td>8, 10 &amp; 12</td>
<td>n.i.</td>
<td>conf</td>
</tr>
<tr>
<td>70983-60-7</td>
<td>1-Propanaminium, 2-hydroxy-N,N,N-trimethyl-, 3-[[γ-ω-perfluoro-C6-20-alkyl]thio] derivs., chlorides</td>
<td>Fluoro thioether compounds (F14)</td>
<td>4-18</td>
<td>n.i.</td>
<td>conf</td>
</tr>
<tr>
<td>70969-47-0</td>
<td>Thiols, C8-20, gamma-.omega.-perfluoro, telomers with acrylamide</td>
<td>Fluoro amine compounds (F3)</td>
<td>6-18</td>
<td>n.i.</td>
<td>conf</td>
</tr>
<tr>
<td>39239-77-5</td>
<td>3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,12,12,13,13,14,14,14-Pentacosafluorotetradecanol</td>
<td>Fluoro alcohol compounds (F1)</td>
<td>12</td>
<td>n.i.</td>
<td>conf</td>
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<tr>
<td>60699-51-6</td>
<td>3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Nonacosafluorohexadecanol</td>
<td>Fluoro alcohol compounds (F1)</td>
<td>14</td>
<td>n.i.</td>
<td>conf</td>
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<tr>
<td>65104-67-8</td>
<td>Poly(difluoromethylene), alpha-.fluoro-.omega.-((2-(2-methyl-1-oxooctadecy)ethyl)-</td>
<td>Fluoro alcohol compounds (F1)</td>
<td>16</td>
<td>n.i.</td>
<td>conf</td>
</tr>
<tr>
<td>65530-66-7</td>
<td>Poly(difluoromethylene), alpha-.fluoro-.omega.-((2-(2-methyl-1-oxooctadecy)ethyl)-</td>
<td>Fluoro ester compounds (F5)</td>
<td>n</td>
<td>n.i.</td>
<td>conf</td>
</tr>
<tr>
<td>1652-63-7</td>
<td>[3-[(heptadecafluoroctyl)sulfonyl]amino]propyltrimethylammonium iodide</td>
<td>PFOS</td>
<td>8</td>
<td>n.i.</td>
<td>conf</td>
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<td>CAS No.</td>
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<td>Total amount in tonnes 2006</td>
<td>Total amount in tonnes 2012</td>
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<tr>
<td>14650-24-9</td>
<td>2-Propenoic acid, 2-methyl-, 2-((Heptadecafluorooctyl)sulfonyl)methylamino)-ethyl ester</td>
<td>None (PFAS precursors)</td>
<td>15</td>
<td>&lt; 0.1</td>
<td>Conf</td>
</tr>
<tr>
<td>119973-85-2</td>
<td>2-Propenoic acid, 2-methyl-, 3-chloro-2-hydroxypropyl ester, polymer with 3,3,4,4, 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluorodecyl 2-propenoate, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl 2-propenoate, N-(hydroxymethyl)-2-propenamide, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16-nonacosafluoro-hexadecyl 2-propenoate, octadecyl 2-propenoate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,1 4,14-pentacosa-fluorotetradecyl 2-propenoate (AICS)</td>
<td>Fluoro ester (F5)</td>
<td>8-14</td>
<td>&lt; 1</td>
<td>N.R.</td>
</tr>
<tr>
<td>163702-08-7</td>
<td>Propane, 2-(difluoromethoxymethyl)-1,1,2,3,3,3-heptafluoro- (approximately 70% by weight of mixture)</td>
<td>Perfluoro ethers (P5)</td>
<td>4</td>
<td>&lt; 0.1</td>
<td>N.R.</td>
</tr>
<tr>
<td>34455-29-3</td>
<td>1-Propanaminium, N-(carboxymethyl)-N,Ndimethyl-3-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-, inner salt (TSCA)</td>
<td>Fluoro sulfonyl/sulfonamide/sulfonyl (F11)</td>
<td>6</td>
<td>&lt; 0.1</td>
<td>N.R.</td>
</tr>
<tr>
<td>67584-42-3</td>
<td>Cyclohexanesulfonic acid, decafluoro(pentafluoroethyl)-, potassium salt</td>
<td>None (PFAS)</td>
<td>8</td>
<td>&lt; 0.1</td>
<td>N.R.</td>
</tr>
<tr>
<td>65530-85-0</td>
<td>Poly(difluoromethylene), alpha-(cyclohexylmethyl)-omega-hydro-</td>
<td>None (miscellaneous perfluoroalkyl)</td>
<td>n</td>
<td>&lt; 0.1</td>
<td>N.R.</td>
</tr>
<tr>
<td>34395-24-9</td>
<td>2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,1 4,14-pentacosafluorotetradecyl ester (TSCA, NDSL, ENCS)</td>
<td>Fluoro ester (F5)</td>
<td>12</td>
<td>&lt; 0.1</td>
<td>N.R.</td>
</tr>
<tr>
<td>163702-07-6</td>
<td>Butane, 1,1,1,2,3,3,4,4,4-nonfluoro-4-methoxy- (TSCA, DSL, SWISS)</td>
<td>Perfluoro ethers (P5)</td>
<td>4</td>
<td>&lt; 0.1</td>
<td>N.R.</td>
</tr>
<tr>
<td>29420-49-3</td>
<td>1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonfluoro-, potassium salt (TSCA, DSL, ENCS, AICS) (PFBS)</td>
<td>PFAS</td>
<td>4</td>
<td>&lt; 0.1</td>
<td>N.R.</td>
</tr>
<tr>
<td>3871-99-6</td>
<td>1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,4,5,5,6,6,6-tridecafluoro-, potassium salt (TSCA, DSL, ENCS, AICS) (PFHxS)</td>
<td>PFAS</td>
<td>6</td>
<td>&lt; 0.1</td>
<td>N.R.</td>
</tr>
<tr>
<td>60270-55-5</td>
<td>1-Heptanesulfonic acid, 1,1,2,2,3,3,4,4,4,5,5,6,6,6,7,7,7-pentadecafluoro-, potassium salt (TSCA, DSL, ENCS, AICS) (PFHxS)</td>
<td>PFAS</td>
<td>7</td>
<td>&lt; 0.1</td>
<td>N.R.</td>
</tr>
<tr>
<td>68156-07-0</td>
<td>Cyclohexanesulfonic acid, decafluoro(trifluoromethyl)-, potassium salt (TSCA, DSL, AICS)</td>
<td>PFAS</td>
<td>7</td>
<td>&lt; 0.1</td>
<td>N.R.</td>
</tr>
<tr>
<td>CAS No.</td>
<td>Substance name</td>
<td>OECD class</td>
<td>Chain length</td>
<td>Total amount in tonnes</td>
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<tr>
<td>67584-61-6</td>
<td>2-Propenoic acid, 2-methyl-, 2- [methyl((tridecafluorohexyl)sulfonyl)amino] ethyl ester (TSCA, NDSL)</td>
<td>PFAS</td>
<td>6</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>90622-43-8</td>
<td>Alcohols, C7–22, ε-ω-perfluoro-, β-δ-fluoro (EINECS)</td>
<td>Fluoro alcohols (F1)</td>
<td>3-18</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>150135-57-2</td>
<td>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)</td>
<td>Fluoro ester (F5)</td>
<td>6-12</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>34362-49-7</td>
<td>2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodo- (TSCA, NDSL)</td>
<td>Fluoro ester (F5)</td>
<td>14</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>65605-70-1</td>
<td>Poly(difluoromethylene), α-fluoro-ω-[2-(1-oxo-2-propenyl)oxy]ethyl] (DSL)</td>
<td>Fluoro ester (F5)</td>
<td>n</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>2043-53-0</td>
<td>Decane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodo- (TSCA, NDSL)</td>
<td>Fluoro iodide (F7)</td>
<td>8</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>2043-54-1</td>
<td>Dodecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heneicosafluoro-12-iodo- (TSCA, NDSL)</td>
<td>Fluoro iodide (F7)</td>
<td>10</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>78560-44-8</td>
<td>Silane, trichloro (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoredecyl) (TSCA, NDSL)</td>
<td>Fluoro siloxane/silicone/silanes (F12)</td>
<td>8</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>68140-18-1</td>
<td>Thiols, C4-10, γ-ω-perfluoro (TSCA, NDSL, EINECS)</td>
<td>Fluoro thiols (F13)</td>
<td>2-8</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>68140-19-2</td>
<td>Thiols, C4-10, γ-ω-perfluoro (TSCA, NDSL, EINECS)</td>
<td>Fluoro thiols (F13)</td>
<td>2-18</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>68140-20-5</td>
<td>Thiols, C6-12, γ-ω-perfluoro (TSCA, NDSL, EINECS)</td>
<td>Fluoro thiols (F13)</td>
<td>4-10</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>68140-21-6</td>
<td>Thiols, C10-20, γ-ω-perfluoro (TSCA, NDSL, EINECS)</td>
<td>Fluoro thiols (F13)</td>
<td>8-18</td>
<td>0.00</td>
<td>n.r.</td>
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<tr>
<td>376-14-7</td>
<td>2-Propenoic acid, 2-methyl-, 2- (ethyl(heptadecafluorooctyl)sulfonyl)amino)ethyl ester</td>
<td>None (PFAS precursors)</td>
<td>16</td>
<td>0.00</td>
<td>n.r.</td>
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<tr>
<td>9011-17-0</td>
<td>1,1-Difluorethen/hexafluoropropen polymer</td>
<td>None (miscellaneous perfluoroalkyl)</td>
<td>n</td>
<td>0.00</td>
<td>n.r.</td>
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<tr>
<td>376-18-1</td>
<td>1-Nonanol, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro- (TSCA, NDSL)</td>
<td>Partial fluoro &amp; miscellaneous fluoro (F17)</td>
<td>8</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
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<td>CAS No.</td>
<td>Substance name</td>
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<td>Total amount in tonnes 2006</td>
<td>Total amount in tonnes 2012</td>
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<tr>
<td>86508-42-1</td>
<td>Perfluoro compounds, C5-18 (TSCA, DSL, AICS)</td>
<td>Partial perfluoro &amp; miscellaneous perfluoro (P8)</td>
<td>5-18</td>
<td>0.00</td>
<td>n.r.</td>
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<tr>
<td>17202-41-4</td>
<td>1-Nonanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,7,7,8,8,9,9,9-nonadecafluoro-, ammonium salt (TSCA, DSL, AICS) (PFNS)</td>
<td>PFAS</td>
<td>9</td>
<td>0.000</td>
<td>n.r.</td>
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<tr>
<td>3872-25-1</td>
<td>1-Pentanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-, potassium salt (TSCA, DSL, ENCS, AICS) (PFPeS)</td>
<td>PFAS</td>
<td>5</td>
<td>0.000</td>
<td>n.r.</td>
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<tr>
<td>56372-23-7</td>
<td>Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(tridecafluorohexyl)sulfonyl]amino]ethyl]-ω-hydroxy- (TSCA, DSL, AICS)</td>
<td>PFAS</td>
<td>6</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>67584-59-2</td>
<td>2-Propanoic acid, 2-methyl-, 2-[methyl[(nonafluorobutyl)sulfonyl]amino]ethyl ester (TSCA, NDSL)</td>
<td>PFAS</td>
<td>4</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>67584-60-5</td>
<td>2-Propanoic acid, 2-methyl-, 2-[methyl[(undecafluoropentyl)sulfonyl]amino]ethyl ester (TSCA, NDSL)</td>
<td>PFAS</td>
<td>5</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>67906-42-7</td>
<td>1-Decanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9,10,10-heneicosfluoro-, ammonium salt (TSCA, DSL, AICS) (PFDS)</td>
<td>PFAS</td>
<td>10</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>67939-96-2</td>
<td>2-Propanoic acid, 2-methyl-, 2-[methyl[(pentadecafluoroheptyl)sulfonyl]amino]ethyl ester (TSCA, NDSL)</td>
<td>PFAS</td>
<td>7</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>68298-79-3</td>
<td>Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(nonafluorobutyl)sulfonyl]amino]ethyl]-ω-hydroxy- (TSCA, DSL, AICS)</td>
<td>PFAS</td>
<td>4</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>68298-80-6</td>
<td>Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(undecafluoropentyl)sulfonyl]amino]ethyl]-ω-hydroxy- (TSCA, DSL, AICS)</td>
<td>PFAS</td>
<td>5</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>68298-81-7</td>
<td>Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(pentadecafluoroheptyl)sulfonyl]amino]ethyl]-ω-hydroxy- (TSCA, DSL, AICS)</td>
<td>PFAS</td>
<td>7</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>68957-62-0</td>
<td>1-Heptanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro- (TSCA, DSL) (EtPHpSA)</td>
<td>PFAS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>68958-60-1</td>
<td>Poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(pentadecafluoroheptyl)sulfonyl]amino]ethyl]-ω-methoxy- (TSCA, DSL, AICS)</td>
<td>PFAS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70225-15-9</td>
<td>1-Heptanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1) (TSCA, DSL)</td>
<td>PFAS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAS No.</td>
<td>Substance name</td>
<td>OECD class</td>
<td>Chain length</td>
<td>Total amount in tonnes</td>
<td>Number of preparations</td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------------------------------------------------------------</td>
<td>------------</td>
<td>--------------</td>
<td>------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>70225-16-0</td>
<td>1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1) (TSCA, DSL)</td>
<td>PFAS</td>
<td>6</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>70225-17-1</td>
<td>1-Pentanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1) (TSCA, DSL)</td>
<td>PFAS</td>
<td>5</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>70225-18-2</td>
<td>1-Butanesulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, compd. with 2,2'-iminobis[ethanol] (1:1) (TSCA, DSL)</td>
<td>PFAS</td>
<td>4</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>29117-08-6</td>
<td>Poly(oxy-1,2-ethanediyl), α-[2-ethyl[(heptadecafluorooctyl)sulfonyl]amino]ethyl]-ω-hydroxy- (TSCA, DSL, ENCS, AICS)</td>
<td>PFOS</td>
<td>8</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>4151-50-2</td>
<td>1-Octanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- (TSCA, DSL) (EtFOSA)</td>
<td>PFOS</td>
<td>8</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>76752-82-4</td>
<td>Heptadecafluoroctane-1-sulfonamide, compound with triethylamine (1:1) (EINECS)</td>
<td>PFOS</td>
<td>8</td>
<td>0.00</td>
<td>n.r.</td>
</tr>
<tr>
<td>68958-61-2</td>
<td>Poly(oxy-1,2-ethanediyl), α-[2-ethyl[(heptadecafluorooctyl)sulfonyl]amino]ethyl]-ω-methoxy- (TSCA, DSL, AICS)</td>
<td>PFOS</td>
<td>8</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>70225-14-8</td>
<td>1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compd. With 2,2'-iminobis[ethanol] (1:1) (TSCA, DSL)</td>
<td>PFOS</td>
<td>8</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
<tr>
<td>68081-83-4</td>
<td>Carbamic acid, (4-methyl-1,3-phenylene)bis-, bis[2-ethyl[(perfluoro-C4-8-alkyl)sulfonyl]amino]ethyl]ester (TSCA, DSL, EINECS, AICS)</td>
<td>PFOS, PFAS</td>
<td>4-8</td>
<td>0.000</td>
<td>n.r.</td>
</tr>
</tbody>
</table>
Annex 4: Background information to chapter 3 on legal framework

The following annex provides some background information on subjects addressed in Chapter 3. The intention is that the reader less familiar with the legal context may read this concurrently with chapter 3.

EU and Danish legislation
Chemicals are regulated via EU and national legislations, the latter often being a national transposition of EU directives.

There are four main EU legal instruments:

- **Regulations** (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.
- **Directives** (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave margin for manoeuvre as to the form and means of implementation. However, there are great differences in the room for manoeuvre between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).

The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set-out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include still valid Danish legislation, e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

- **Decisions** are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a so-called comitology procedure involving member state representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabel criteria for specific product groups.

- **Recommendations and opinions** are non-binding, declaratory instruments.

In conformity with the transposed EU directives, Danish legislation regulate to some extent chemicals via various general or sector specific legislation, most frequently via statutory orders (DK: bekendtgørelser).
Chemicals legislation
REACH and CLP
The REACH Regulation\textsuperscript{13} and the CLP Regulation\textsuperscript{14} are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP provisions and give an overview of ‘pipeline’ procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

(Pre-)Registration
All manufacturers and importers of chemical substance $> 1$ tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered dead-lines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and substances dangerous to aquatic organisms or the environment above 100 tonnes per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

Evaluation
A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

Authorisation
Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substance within a given dead-line (sunset date) or apply for authorisation for certain specified uses within an application date.

Restriction
The ‘safety net’. If the authorities assess that that risks to be addressed at the EU level are still in place despite the above mechanisms, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

Classification and Labelling
The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two classification and labelling provisions are:

1. Harmonised classification and labelling for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised classifications in Annex I of

\textsuperscript{13} Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)
\textsuperscript{14} Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures
the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.

2. Classification and labelling inventory. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publish the classification and labelling inventory based on all notifications received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 2 to the main report.

Ongoing activities - pipeline
In addition to listing substance already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA web-site also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

Community Rolling Action Plan (CoRAP)
The EU member states have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) is developed and published, indicating by who and when a given substance is expected to be evaluated.

Authorisation process; candidate list, Authorisation list, Annex XIV
Before a substance is included in REACH Annex XIV and thus being subject to Authorisation, it has to go through the following steps:

1. It has to be identified as a SVHC leading to inclusion in the candidate list15
2. It has to be prioritised and recommended for inclusion in ANNEX XIV (These can be found as Annex XIV recommendation lists on the ECHA web-site)
3. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA web-site.

Registry of intentions
When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- a harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction

this is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intentions in relation to Annex XV dossiers divided into:

- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and
- withdrawn intentions and withdrawn submissions

15 It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).
for the three types of Annex XV dossiers.

International agreements

OSPAR Convention
OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions, which are legally binding on the Contracting Parties, recommendations and other agreements. Decisions and recommendations set out actions to be taken by the Contracting Parties. These measures are complemented by other agreements setting out:

- issues of importance
- agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out.
- guidelines or guidance setting out the way that any programme or measure should be implemented
- actions to be taken by the OSPAR Commission on behalf of the Contracting Parties

HELCOM - Helsinki Convention
The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the Helsinki Convention.

In pursuing this objective and vision the countries have jointly pooled their efforts in HELCOM, which is works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

Stockholm Convention on Persistent Organic Pollutants (POPs)
The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

Rotterdam Convention
The objectives of the Rotterdam Convention are:
to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;

to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.

The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

**Basel Convention**

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as “hazardous wastes” based on their origin and/or composition and their characteristics, as well as two types of wastes defined as “other wastes” - household waste and incinerator ash.

The provisions of the Convention center around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management; and
- a regulatory system applying to cases where transboundary movements are permissible.

**Eco-labels**

Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the ecolabelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products.

**EU flower**

The EU ecolabelling Regulation lays out the general rules and conditions for the EU ecolabel; the flower. Criteria for new product groups are gradually added to the scheme via ‘decisions’; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

**Nordic Swan**

The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Ecolabelling Board consists of members from each national Ecolabelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval process related to the EU flower and Nordic Swan is
Blue Angel (Blauer Engel)
The Blue Angel is a national German eco-label. More information can be found on:
Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances
This survey is part of the Danish EPA’s review of the substances on the List of Undesirable Substances (LOUS). The report defines the substances groups and present information on the use and occurrence of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure, waste management and information regarding ongoing activities under REACH, among others.

Kortlægning af PFOS, PFOA og andre perfluoralkyl- og polyfluoralkylforbindelser
Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Rapporten definerer stofgrupperne og indeholder blandt andet en beskrivelse af brugen og forekomsten af PFOS, PFOA og andre perfluoralkyl- og polyfluoralkylforbindelser, internationalt og i Danmark, en beskrivelse af miljø- og sundhedseffekter af stofferne, og viden om alternativer, eksisterende regulering, moniteringsdata, eksponering, affaldsbehandling og igangværende aktiviteter under REACH.