UNITED NATIONS

SC

UNEP/POPS/POPRC.8/INF/17

Distr.: General
15 August 2012

English only

Stockholm Convention on Persistent Organic Pollutants

Persistent Organic Pollutants Review Committee
Eighth meeting
Geneva, 15–19 October 2012
Item 5 (g) of the provisional agenda*

Technical work: assessment of alternatives to perfluorooctane sulfonic acid in open applications

Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid in open applications

Note by the Secretariat

1. In paragraph 6 of decision SC-5/5, the Conference of the Parties to the Stockholm Convention requested the Secretariat, subject to the availability of resources, to commission a technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid in open applications for consideration by the Persistent Organic Pollutants Review Committee at its eighth meeting.

2. That technical paper has been prepared, with financial support provided by the Government of Norway, on the basis of the terms of reference and an outline developed by the Committee at its seventh meeting. It is set out in the annex to the present note, where it is presented without formal editing.

* UNEP/POPS/POPRC.8/1.

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Annex

Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid in open applications

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Executive summary

Production and use of perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) is restricted by the Stockholm Convention on Persistent Organic Pollutants, but some use and production are still allowed as provided in Annex B to the Convention. The objectives under the Convention are to reduce and ultimately eliminate production and use of these chemicals. Parties are encouraged to phase out uses when suitable alternatives or methods are available.

This technical paper was commissioned by the Persistent Organic Pollutants Review Committee to support and facilitate the evaluation of global use and production of PFOS and its related compounds and the substitution to safer alternatives, in accordance with decision SC-5/5. The Conference of the Parties requested the Committee to develop recommendations on the basis of the technical paper for consideration at its sixth meeting.

There were major data gaps for most perfluorinated and polyfluorinated chemicals and their quantities produced and used on the market. Concerning several non fluorinated insecticides, a number of toxicological and ecotoxicological data was available; however information on actual handling on site and exposure to humans and the environment was limited.

There was little or no independent and reliable information publicly available on the toxicological and ecotoxicological characteristics of alternatives to PFOS and its related substances, with the exception of perfluorohexanoic acid (PFHxA) and perfluorobutanesulfonic acid (PFBS) and their related substances. It was concluded that perfluorohexane sulfonyl fluoride (PFHxSF) and its derivatives were not feasible alternatives to PFOS and related substances since industry and public bodies considered these group of C6 sulfonates as long chain polyfluorinated and perfluorinated substances with similar environmental impact as PFOS. Perfluorohexane sulfonic acid (PFHxS) is recommended to be further assessed as potential persistent organic pollutants considering the characteristics identified in this technical paper.

There were considerable information gaps concerning alternative chemical composition of aviation hydraulic fluids, though there were several products established on the market for years. It was hard to obtain information on the exact chemical composition of these products since it was considered confidential by manufacturers. There was however a need to release this information to properly evaluate the health and environmental impacts of these alternatives.

There was plenty of chemical data for the specific fluorinated and non–fluorinated alternatives for fire-fighting foams that enabled sufficient health and environmental assessment of these components. However, there were information gaps concerning the exact chemical composition of commercial fire-fighting foams due to manufacturers’ trade secrets. This may have resulted in weak points in case assessments, as to when these fire-fighting foams are used in real situations.

The chemical alternatives for pesticide uses of PFOS were mostly systemic insecticides of which the toxicity ranged from high toxicity to both humans and the environment, to low toxicity for humans and moderately to high toxicity to the environment. Some of the alternatives were considered as less effective than PFOS. Biological control methods are important non-chemical alternatives because pests are prone to evolve multiple resistances to chemical pesticides. As the suggested alternative pesticides have been on the market for decades and have been observed closely because of their hazardous properties, there was a lot of data available for these substances. Some of the biological controls have also been on the market for some years and been shown to be efficacious against a number of pests.

There were a lot of information and application scenarios available for alternatives to PFOS for metal plating such as 6:2 fluorotelomer sulfonic acid (FTS). However, it was not considered as equivalent to the performance of PFOS which is still used in large quantities worldwide for this purpose. More research is needed to develop equal or better alternatives to PFOS for metal plating to permit the phase out of PFOS for these applications.

There were considerable information gaps on alternatives to PFOS for electrical and electronic parts. More information needs to be collected from the market concerning the chemistry, market volumes etc of alternatives in order to assess them at all.

Alternatives to PFOS for impregnation or coating of textiles, leather and carpets as well as coating agents were well known and there was a good access of data available for further evaluations on health and environment. There were manufacturer trade secrets concerning detailed chemical product compositions that may be a weak point for detailed assessments when these alternatives are applied in production.

Dendrimers has been used as non-fluorine alternatives to PFOS as water proofing agents on textiles and as coating agents. There were considerations of their impact on human health since cytotoxicity studies have shown dendrimers is able to cross cell membranes, disrupt platelet function, and cause hemolysis. Due to lack of scientific knowledge on their potential impact to health, it was hard to evaluate potential risks to human health.

There were considerable information gaps concerning alternatives to PFOS for water proofing agents on paper especially concerning esters and diesters of polyfluoroalkyl phosphonic acids (diPAPs) and phosphoric acids (PAPs). Recent research indicated that these agents may transform into persistent perfluorinated carboxylic acids (PFCA). Still further research is needed to better understand all available alternatives to PFOS for paper proofing agents.

Consequently, for several reasons, it is currently not possible to perform comprehensive risk assessment on the alternative chemicals to PFOS and related substances, since either little or no information was available concerning how these chemicals were actually used in the specific applications and on their pathways and the environmental fate which are key elements in the assessment of persistent organic pollutants.

1 Background and introduction

Having amended the Stockholm Convention on Persistent Organic Pollutants by decisions SC 4/10–SC-4/18 to list nine additional chemicals in Annexes A, B and C to the Convention, by its decision SC-4/19 the Conference of the Parties decided to undertake a work programme to provide guidance to parties on how best to restrict and eliminate brominated diphenyl ethers, perfluorooctane sulfonic acid (PFOS) and its salts, perfluorooctane sulfonyl fluoride (PFOSF) and the other newly listed chemicals.

At its fifth meeting, the Conference of the Parties considered and endorsed the recommendations of the Persistent Organic Pollutants Review Committee developed pursuant to the work programmes for newly listed persistent organic pollutants, including on the elimination of brominated diphenyl ethers from the waste stream and on risk reduction for PFOS, its salts and PFOSF.

By its decision SC-5/5, the Conference of the Parties, among other things, requested the Committee at its seventh meeting to develop terms of reference for a technical paper on the identification and assessment of alternatives to the use of PFOS in open applications, taking into account the general guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals.

The Conference of the Parties also requested the Secretariat, subject to the availability of resources, to commission a technical paper, based on the terms of reference prepared by the Committee pursuant to paragraph 5 of the decision, to be completed in time for consideration by the Committee at its eighth meeting. The Committee was requested to develop recommendations on the basis of the technical paper for consideration by the Conference of the Parties at its sixth meeting.

Thus, this technical paper was developed based on the terms of reference and the outline of the technical paper agreed by the Committee as contained in its decision POPRC-7/5 and in document UNEP/POPS/POPRC.7/INF/22/Rev.1.

2 Objectives

This is a technical paper on the identification and assessment of alternatives to the use of PFOS in open applications[1], including consideration of the following aspects of the substitution of PFOS[2], taking into account the general guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals: technical feasibility; health and environmental effects; cost-effectiveness; efficacy; availability; accessibility.

The objective of this paper is to be used by the POPs Review Committee to develop recommendations on the alternatives to the use of PFOS in open applications for consideration by the Conference of the Parties at its sixth meeting.

3 Methodology

Parties and observers were invited to submit information on alternatives to the use of PFOS in open application, using a form with explanatory notes developed by the Committee[3] by the letter dated 21 October 2011. PFOS in open application included the following: aviation hydraulic fluids; fire fighting foams; insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp*; insecticides for control of red imported fire ants and termites; metal plating (hard metal plating); metal plating (decorative plating); electric and electronic parts for some color printers and color copy machines; chemically driven oil production; carpets; leather and apparel; textiles and upholstery; paper and packaging; coating and coating additives; rubber and plastics.

The technical paper takes due account of the general guidance on considerations related to alternatives to and substitutes for listed chemicals and candidates chemicals[4], the guidance on alternatives to PFOS and its derivatives[5], the recommendations on risk reduction for perfluorooctane sulfonic acid and its salts and perfluorooctane sulfonyl

1 An open application has no recovery of PFOS and related substances in process and consequently need a stringent waste management facility.

2 The term "perflurorooctane sulfonic acid" or "PFOS" is understood to include perflurorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride, as listed in part I of Annex B to the Stockholm Convention and PFOS related chemicals. PFOS related chemicals are chemicals that contain the structural element PFOS in their molecular structure as they are and were produced with one of the above mentioned chemicals as an intermediate or starting material. Examples of these chemicals can be found in the Guidance on alternatives to perfluorooctane sulfonate and its derivatives (http://www.pops.int) and at OECD website (http://www oecd.org).

3 UNEP/POPS/POPRC.7/INF/22/Rev.1

4 UNEP/POPS/POPRC.5/10/Add.1

5 UNEP/POPS/POPRC.6/13/Add.3

fluoride[6], and any other relevant documents such as the OECD overview and list of PFOS, PFAS, PFOA, PFCA, Related Compounds and Chemicals issued in 2007[7].

Furthermore, in relation to the alternatives to PFOS, its salts and PFOSF, the POPs Review Committee has developed and revised a guidance document on alternatives to PFOS and its derivatives[8].The information from the guidance document was also used in elaborating the current technical paper.

Please note that the main difference between the previous guidance and the current technical paper is that the previous guidance was a compilation of all available information on alternatives to PFOS and its derivatives without any evaluation, where as the current technical paper considers the POPs characteristics of the alternatives and conduct assessment taking into account the general guidance on alternatives[9] . Also the current technical paper focuses only on "open applications", as requested by the COP in decision SC-5/5. It is likely that significant quantities of the chemical reach human and the environment during the use of PFOS in open applications, as opposed to closed-system applications.

The Committee may consider updating the guidance document on alternatives to PFOS and its derivatives[10] in the future, to include the new information obtained during the development of the current technical paper.

4 Identification and description of alternatives

Fluorinated chemicals are extremely versatile and have a very complex chemistry. In order to clarify this complex chemistry, every characterized alternative to PFOS and related substances are addressed by category. e.g intermediate, precursor etc where applicable, see terminology glossary appendix 4. Where no category is mentioned then the characterized fluorinated substance is actually used in the open application in question.

There is a complementary collection of measured and modeling data to the characteristics tables in this report, see appendix 1 (excel format). These data are based on available physical/chemical, toxicological and environmental data of alternatives and their principal degradation products.

4.1 Aviation hydraulic fluids

Alternative hydraulic fluid additives must undergo extensive testing to qualify for use in the aviation industry so sustain severe conditions during use.

In the manufacturing process for aviation hydraulic fluids, a PFOS-related substance or precursor, such as potassium perfluorooctane sulphonate, was used as an additive to the aviation hydraulic fluids with a content of about or less than 0.1%[11]. According to the manufacturers, this formulation helps prevent evaporation, fires, and corrosion [3] [38].

Aviation hydraulic fluids without fluorinated chemicals but based on, for example, phosphate esters are used. These substances can absorb water and the subsequent formation of phosphoric acid can damage metallic parts of the hydraulic system. [37] For this reason, phosphate ester-based hydraulic fluids are routinely examined for acidity as this determines its useful lifetime. Additionally fluorinated chemicals other than PFOS can be used. The potassium salt of perfluoroethylcyclohexyl sulphonate (CAS no. 67584-42-3)[12] is not PFOS precursor, and it has been used in hydraulic oils instead of PFOS in the past. However, like other C_6 compounds it is likely to be persistent and 3M which formerly produced this chemical, has ceased to do so [2]. A search for other alternatives is said to have been going on for 30 years, starting before PFOS was considered a problematic substance. However it is not possible to get any specific chemical composition of alternatives due to trade secrets. Consequently there is no way to describe their potential feasibility and impact to health and environment in a comprehensive way.

6 UNEP/POPS/COP.5/15, annex

7 Lists of PFOS, PFAS, PFOA, PFCA, Related Compounds and Chemicals that may degrade to PFCA (as revised in 2007). Organization for Economic Co-operation and Development, 21-Aug-2007. ENV/JM/MONO(2006)15

8 UNEP/POPS/POPRC.6/13/Add.2/Rev.1

9 UNEP/POPS/POPRC.5/10/Add.1

10 UNEP/POPS/POPRC.6/13/Add.2/Rev.1

11 The potassium salt of PFOS was used in such a small quantity that it was not listed on the MSDS at Boeing (Boeing 2001). http://www.boeingsuppliers.com/environmental/TechNotes/TechNotes2001-02.pdf

12 In the U.S. this chemical is considered a C8 PFOS equivalente and its use in hydraulic fluids is regulated under a Significant New Use Rule:https://www.federalregister.gov/articles/2002/12/09/02-31011/perfluoroalkyl-sulfonates-significant-new-use-rule

4.1.1 Identity and properties of the alternatives

Information gaps

4.1.2 Type of uses, quantities, producers, and traders

There are several trade names and traders on the market. Some are as follows: Arnica, Tellus, Durad, Fyrquel, Houghto-Safe, Hydraunycoil, Lubritherm Enviro-Safe, Pydraul, Quintolubric, Reofos, Reolube,Valvoline Ultramax, Exxon HyJet, and Skydrol[13]

The fire-resistant aviation hydraulic fluids principally contain tri-alkyl phosphates, tri-aryl phosphates, and mixtures of alkyl-aryl-phosphates. [37] However, the products only provide rough descriptions of their chemical composition such as “contain phosphate esters”. Conclusively there are several information gaps concerning the specific chemical composition of each aviation hydraulic fluid but similarly the traders need to know in detail of these oil characteristics since these characteristics are important to aviation security. [37][38].

Since very little is published concerning the chemical composition of these aviation hydraulic oils there is no current possibility to assess their environmental and health impact.

There is currently no, scarce or uncertain data available concerning quantities used on the market[14].

4.1.3 Risks, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention

4.1.3.1 Environmental risk assessment

Since there are considerable information gaps concerning CAS RN of chemicals that are used it is not possible to assess risk and hazard characteristics of alternatives to PFOS and its related substances in aviation hydraulic fluids.

Table 1: Characteristics of alternatives to PFOS and related substances for aviation hydraulic fluids

Alternatives	CAS RN	References
Literature describes phosphate compounds e.g. tri-alkyl phosphates, tri-aryl phosphates, and mixtures of alkyl-aryl-phosphates	Information gaps	[37]
Health and environmental hazards		
Information gaps since due to lack of the real composition of commercial surfactants for aviation hydraulic fluids. Since very little is published concerning the chemical composition of these aviation hydraulic oils there is no current possibility to assess their environmental and health impact. Phosphate compounds are hygroscopic and very sensitive to contaminants that may have a direct impact on flight safety. When these aromatic phosphate esters are consumed they transform into strong acids and may have a local impact if not taken care of in a safe and correct way.		

4.2 Fire fighting foams

Fluorosurfactants that are a key ingredient in aqueous film forming foams (AFFF) have been manufactured by different processes and have many different chemical structures [71]

Aqueous film forming foam (AFFF), sometimes referred to a aqueous fire-fighting foam, is a generic term for fire-fighting and/or vapor suppression products used globally to protect both lives and property. AFFFs are unique amongst other fire-fighting foams in that they contain a small percentage of fluorinated surfactant (fluorosurfactant). This key ingredient brings unique performance attributes to the product that enables it to be extremely effective in preventing and extinguishing fires, especially Class B flammable liquid fires. AFFF products can be used in fixed and portable systems (i.e. sprinkler systems, handheld fire extinguishers, portable cylinders, fire-fighting vehicles (fire trucks), etc). In most situations, AFFF is purchased as a concentrate, typically referred to as “3%” or “6%” depending on its mixture ratio (during use) with water. Not every situation will necessarily require the use of fire-fighting foams. Only a careful consideration of the specific situation at hand (emergency incident or design of fire/property protection system) and review of local building codes and other regulations can determine the proper product selection. It is important to remember that foams have proven to be highly effective for their intended purpose to protect lives and property.

13 http://www.atsdr.cdc.gov/toxprofiles/tp99-c3.pdf

14 As aviation hydraulic fluids are essential to the military in Convention member countries they may be a source of information regarding the alternative substances and their quantities used.

Prior to 2000, the majority of the fluorosurfactants used in the AFFF were PFOS-based which resulted in AFFF that contained PFOS and PFOS precursors. During this same time, AFFFs based on long-chain fluorotelomers were also available for the same fire-fighting uses. Shortly after the manufacturing phase out announcement by 3M of PFOS-based products in 2000, PFOS-based AFFFs were generally became more difficult to purchase.

The primary supply of AFFF then became fluorotelomer-based. Over the last several years, manufacturers of fluorotelomer AFFF have been replacing PFOS based products with fluorotelomer-based fluorosurfactants. that will during use or presence in the environment degrade to the basic PFCAs such as PFOA and its homologues. There was a concern that these products would lead to higher exposures to perfluorooctanoic acid (PFOA which has similar toxicities to PFOS). The current effort is to replace these PFOA based long-chain fluorosurfactants with shorter-chain fluorosurfactants such as perfluorohexylethanol [6-2 FTOH] derivatives[15] [64] In addition, alternative fluorosurfactants based on perfluorobutane sulfonate (PFBS) and related substances have also been considered along with various non-fluorinated alternatives[1]. The short chain perfluoroalkyl sulphonates perfluorobutane sulphonate (PFBS) has never been applied or successfully used in fire fighting foams due to its non dispersive properties[16]. This is also the case for perfluorohexane sulphonate (PFHxS) that currently is considered as a long chain PFC according to the OECD definition[17].

4.2.1 Identity and properties of the alternatives

See appendix 1

4.2.2 Type of uses, quantities, producers, and traders

There is currently no publicity avialible data concerning quantities used on the market and consequently these data are not presented in table 2[18]. For detailed information on composition, trade names and manufacturers, see appendix 2.

4.2.3 Risks, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention

4.2.3.1 Environmental risk assessment

It is hard to assess risks for the substances in table 2 below since there is little known from open sources about their path ways into the environment and to humans.

Table 2: Characteristics of alternatives to PFOS and related substances for fire fighting foams.

Alternatives	CAS RN	References
Perfluorohexanoic acid (PFHxA)	307-24-4	[9][31][32] [75][76][77][78][79][80] Appendix 1
Category: Potential degradation product from short chain (C_6) fluorotelomer-based surfactants.		
Toxicology: Toxicological data for PFHxA is extensive However earlier studies show that PFHxA induces hepato-megaly, peroxisomal beta-oxidation and microsomal 1-acyl-GPC acyltransferase (potential endocrine toxicity)Two studies by DuPont in rats and mice indicate that PFHxA is rapidly eliminated. These include acute, sub-chronic and chronic as well as pharmaco- and toxicokinetics in multiple mammalian species. Moreover, the acute and repeated exposure aquatic toxicity (e.g., early life-stage fish) has been studied. PFHxA does not bioconcentrate, bioaccumulate or biomagnify. **Degradation in the environment:** Persistent. Perfluorohexanoate (PFHxA) is the potential degradation product from short chain (C_6) fluorotelomer-based surfactants **Emissions:** Possible from use and manufacturing of fire fighting foams. **Monitoring data:** High concentrations were detected in several European rivers. Moreover, there are also subchronic and bioaccumulation studies in aquatic species. Early Life-Stage Fish Study (NH4PFHx, ammonium perfluorohexanoate) have been presented at scientific meetings in the past year. *Note: Some additional indicative data is available in appendix 1*		
Dodecafluoro-2-methylpentan-3-one. IUPAC name: 1,1,1,2,2,4,5,5,5- nonafluoro – 4 – (trifluoromethyl) – 3 - pentanone	756-13-8	Appendix 1

15 http://www.fffc.org/images/APFarticle08.pdf

16 Communication with Dr. Roger Klein.

17 http://www.oecd.org/site/0,3407,en_21571361_44787844_1_1_1_1_1,00.html

18 Information on the quantities produced and used in the various markets of these alternatives are generally proprietary information. Some data is available in market-specific third-party assessment reports.

Toxicology: Information gaps though the MSDS lists a variety of liver effects and hydrogen fluoride and carbon monoxide as decomposition products[19]. **Degradation in the environment**: Probably persistent **Emissions**: Modeling data indicate volatility **Monitoring data**: Information gaps *Note: Some additional indicative data is available in appendix 1*		
Fluorine free surfactants	Information gaps	--
Information gaps due to lack of the real composition of commercial fire fighting foams[20]		

4.3 Pesticides (insect baits for control of leaf-cutting ants from *Atta spp*. and *Acromyrmex spp.* and insecticides for control of red imported fire ants and termites)

N-Ethyl perfluorooctane sulfonamide (known as sulfluramid or sulfuramid), a PFOS related substance, has been used as an active ingredient in ant baits to control leaf-cutting ants, as well as for control of red imported fire ants, and termites. PFOS and other fluorinated substances have also been used as inert ingredients in pesticides[2].

Several mechanical, cultural, biological and chemical methods have been studied as early as the 1950s for controlling leaf-cutting ants. Cultural management using resistant plants, plants toxic to ants, and applied biological management by manipulating predators, parasitoids and micro-organisms, have so far rendered unsatisfactory and inconsistent results, and have not provided technical, economic, or operational viability. However research is continuing.

With the development of synthetic insecticides, chemical methods have been effectively used to control Atta and Acromyrmex ants[21].

There are a number of chemical alternatives to *N*-Ethyl perfluorooctane sulfonamide (known as sulfluramid or sulfuramid), with a multitude of uses[22]: Chlorpyrifos, Cypermethrin, mixture of Chlorpyrifos and Cypermethrin, Fipronil, Imidacloprid[23], Abamectin, Deltamethrin, Fenitrothion, mixture of Fenitrothion and Deltamethrin.

4.3.1 Identity and properties of the alternatives

See appendix 1

4.3.1.1 Non-chemical control methods for leaf-cutter ants

Leaf-cutter ants cause significant harm in agricultural, forest, and livestock agronomic ecosystems. Colonies persist and grow despite the innumerable control strategies to which they are subject. There are a number of alternative means to control leaf cutter ants that are not based on chemical pest control. These methods are biological, physical or natural control. However leafcutter ants have developed defensive mechanisms against some of these control measures:

<u>Defense against biological control</u>:

- Leaf-cutter ants are provided with spines that serve as means of protection against their natural enemies.
- When infected with a symbiotic fungus, the contaminated parts of the ant colony are disinfected, pruned, and isolated, reducing the impact of the fungus.

Leaf-cutter ants have mechanical and chemical defenses that help them to counterbalance the effect of some control measures. Exocrine glands and symbiotic bacteria are the main sources of antimicrobials in leaf-cutter ants, and are used to counter biological control agents. Studying the adaptation mechanisms of leaf-cutter ants is recommended to improve effectiveness of strategies for their ecological management [8].

However biological control can be effective. The entomopathogenic *Metarrhizium anisopliae* can cause the decline and ultimate death of small colonies [50] and recent research indicates that the entomopathogenic fungi *Beauveria bassiana* and *Aspergillus ochraceus* both show a high degree of control, causing 50% mortality within 4-5 days [43]. Effective natural products include limonoids extracted from the roots of the South Brazilian endemic plant *Raulinoa echinata* [44].

19 http://www.chemcas.org/msds_archive/msds_01/cas/gb_msds/756-13-8.asp
20 Some information might be presented here from MSDS sheets, even though it is unfortunately quite minimal.
21 Contribution from Brazil
22 Contribution from Argentina and China
23 Contribution from China

Defense against physical control:

Leaf-cutter ants display specialization in tasks within the ant colony; however when nests are destroyed, any remaining worker ants are able to focus their work on re-structuring the tunnels and chambers. Full destruction of the ant colony overcomes this problem.

4.3.1.2 Non-chemical control methods for red imported fire ants and termites

The general consensus of entomologists and myrmecologists is that permanent, sustainable control of these ants in the USA will likely depend on self-sustaining biological control agents. At least 30 natural enemies have been identified in South America [45].

Biological controls for red imported fire ant (RIFA) include a group of decapitating phorid flies (*Pseudacteon* spp) which parasitize the ants [48]. The microsporidian protozoan *Thelohania solenopsae* and the fungus *Beauveria bassiana* are also promising controls for RIFA. *B. bassiana* has been shown to control RIFA under field conditions in Taiwan [46].

Three viruses, SINV-1, SINV-2, SINV-3, have been found infecting fire ants in the field, and two of these, SINV1 and 3 appear to be associated with significant mortality, indicating their potential as biological control agents [47]. Other potential biological controls include the endoparasitic fungi *Myrmecomyces annellisae* and *Myrmicinosporidium durum*, and the parasite *Mattesia* sp [47]

Biological control options [49] for termites include *Beauvaria bassiana* and *Metarhizium anisopliae*

4.3.2 Type of uses, quantities, producers, and traders

Information gaps.

For detailed information on composition, trade names and manufacturers, see appendix 2.

4.3.3 Risks, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention

4.3.3.1 Environmental risk assessment

For the substances in table 3 main hazards are described. Since there is scarce public information on how insecticides really are handled and exposed to the surrounding environment, it is hard to assess real risk to humans and environment.

Table 3: Characteristics of alternatives to PFOS and related substances for pesticides.

Alternatives	CAS RN	References
S-Methoprene Pyriproxyfen Fipronil Imidacloprid Chlorpyrifos Cypermethrin Deltamethrin Fenitrothion Abamectin (commercial mixture) and their mixtures.	65733-16-6 95737-68-1 120068-37-3 138261-41-3, 105827-78-9 2921-88-2 52315-07-8 52918-63-5 122-14-5 71751-41-2	[1][30][39][58] Appendix 1
Toxicology: Imidacloprid is considered as moderate toxic to humans and environment. In addition, a recent study linked imidacloprid to colony collapse disorder in bees. S-Methoprene is considered as low toxic to humans. Pyriproxyfen is not considered as carcinogenic or genotoxic. **Environmental hazards:** Fipronil and chlorpyrifos are considered more acutely toxic to humans and the environment than sulfluramid. *Note: Some additional data is available in appendix 1.*		

4.4 Metal plating (hard metal plating and decorative plating)

PFOS is a surfactant, wetting agent and mist suppressing agent for chrome plating. It was previously used for both decorative chrome plating and hard chrome plating processes, but new technology using chromium-III instead of chromium-VI has made PFOS use in decorative chrome plating obsolete. Chromium-III does not work for hard chrome plating, however. [2]

In Europe common alternative used in hard metal plating is 1H,1H,2H,2H-perfluoroctane sulfonic acid (H-PFOS). Other names are 6:2-Fluorotelomer sulfonate (6:2 FTS) or (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate). It is not fully fluorinated, and can slowly degrade to perfluorocarboxylic acids such as perfluorohexanoic acid (PFHxA). Since it is structurally very similar to PFOS, its common name is THPFOS (Tetra Hydro PFOS). [5]

According to the Guidance on alternatives to perfluorooctane sulfonate and its derivatives [2], currently, no other surfactant can match the low surface tension of PFOS. Therefore, the quantity required for substitution of PFOS by polyfluorinated surfactants increases considerably about three to ten times [2].

Non-fluorinated surfactants are used during the production process for hard chrome plating and decorative chrome plating. Although they are degraded in the chromium electrolyte or etching bath and must be constantly dosed, the costs are not higher than using fluorinated surfactants. Trivalent chromium is formed by chemical degradation in the bath, which has to be oxidized to hexavalent chromium by membrane electrolysis.[1]

4.4.1 Identity and properties of the alternatives

See appendix 1

4.4.2 Type of uses, quantities, producers, and traders

A lot of products have been tried for the application in hard chrome plating, but all alternatives have proven to be less effective under the harsh conditions of this process. For example Capstone® FS10 (6:2 FTS) from DuPont, could only partly be applied in decorative chromium plating due to its slightly higher surface tension when compared to PFOS.

There is currently no publicity available data concerning quantities used on the market and consequently are not presented in table 5.

Shortchain fluorosurfactant products appear to be less effective, less stable in chromium baths and need more product/replenishment. Moreover no antifoam version is available and, therefore, these products can lead to oxyhydrogen explosions in the chrome baths.[24]

For detailed information on composition, trade names and manufacturers, see appendix 2.

4.4.3 Risks, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention

4.4.3.1 Environmental risk assessment

It is hard to assess risks for the substances in table 4 below since there is little known about their path ways into the environment and to humans.

Table 4: Characteristics of alternatives to PFOS and related substances for metal plating.

Alternatives	CAS RN	References
6:2-Fluorotelomer sulfonate (6:2 FTS)	27619-97-2	[5] [9][57][65][66]
Toxicology:. Acute and repeated-dose mammalian and aquatic toxicity has been reported **Degradation in the environment:** Degradation of fluoroalkylthioamido- sulphonates into FTS is suggested and 6:2 FTS is susceptible to biodegradation under sulphur-limiting and aerobic conditions. **Emissions:** Emission to the environment may be expected from use in metal plating and in manufacturing. 6:2 FTS has been detected in metal plating effluent. Emission of FTS from STP effluents is proven. As 6:2 FTS is also used in fire fighting foams as substitute for PFOS, FTS can be expected in the aqueous environment. In the environment a decrease to the stable perfluorohexane acid (PFHxA) is found. **Monitoring data:** 6:2 FTS has been detected in environmental samples including water, soil, air particulates and biota. During the EU-project PERFORCE[25], FTS were detected in several environmental samples. 6:2 FTS was present in the particle phase of UK air samples with unknown origin so it may be possible that non-volatile ionic FTS might directly undergo atmospheric transport on particles from source regions. 6:2 FTS observations has been done in the Arctic . More data is needed to determine its origin and whether it is a LRT substance or not.		

24 Communication with Lanxes

25 http://www.science.uva.nl/perforce/index.htm?http%3A//www.science.uva.nl/perforce/events.htm

Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxo)ethane sulfonate.	Information gaps	Appendix 1
Toxicology: The substance is poorly characterized. **Environmental hazards:** Probably persistent. The substance is poorly characterized.		
Potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetraflouroethane sulfonate	Information gaps	Appendix 1
Toxicology: The substance is poorly characterized. **Environmental hazards:** Probably persistent. The substance is poorly characterized.		
Non-fluorinated surfactants (Mainly alkane sulfonates)	Information gaps	[5]
Toxicity: The substances cannot be assessed since there are considerable data gaps of their chemical composition. **Environmental hazards:** The substances cannot be assessed since there are considerable data gaps of their chemical composition. .		

Note: More specific data is available in appendix 1

4.5 Electric and electronic parts for some color printers and color copy machines

Electrical and electronic equipment often requires hundreds of parts and thousands of processes. PFOS and related chemicals are used in the manufacturing of printers, scanners and similar products. The PFOS-related substances are process chemicals, and the final products are mostly PFOS-free. PFOS have many different uses in the electronic industry and is involved in a large part of the production processes needed for electric and electronic parts that include both open and close loop processes, Open processes are applied for solder, adhesives and paints. Closed loop processes mostly include etching, dispersions, desmear, surface treatments, photolithography and photomicrolitography [88],

PFOS can be used as a surfactant in etching processes in the manufacture of compound semiconductors and ceramic filters. PFOS are then added as part of an etching agent, and rinsed out during the subsequent washing treatment. Desmear process smoothes the surface of a through-hole in printed circuit boards. PFOS can be used as a surfactant in desmear agent, i.e. etching agent. PFOS is added in a desmear agent, and rinsed out during washing treatment [1].

According to information from OECD survey (2006) less than 1 tonne of *N*-ethyl-*N*-[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide (CAS no. 61660-12-6), a PFOS related substance, had been used as an additive in toner and printing inks. Low volumes of PFOS-related substances were also used in sealants and adhesive products. [2].

4.5.1 Identity and properties of the alternatives

Information gaps

4.5.2 Type of uses, quantities, producers, and traders

Information gaps

4.5.3 Risks, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention

Information gaps.

4.6 Chemically driven oil production

It is reported that PFOS is used in some parts of the world as surfactants in oil well stimulation to recover oil trapped in small pores between rock particles. Oil well stimulation is in general a variety of operations performed on a well to improve the wells productivity. The main two types of operations are acidization matrix and hydraulic fracturing. [2]

Alternatives to PFOS are PFBS,fluorotelomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids, and thioether acids. In most parts of the world where oil exploration and production is taking place, oil service companies engaged in provision of well stimulation services predominantly use a formulation of alcohols, alkyl phenols, ethers, aromatic hydrocarbons, inorganic salts, methylated alcohols, alipathic fluorocarbons for oil well stimulation. Oil well stimulation services also involve corrosion control, water blocks/blockage control, iron control, clay control, paraffin wax and asphaltene removal and prevention of fluid loss and diverting [2].

4.6.1 Identity and properties of the alternatives

See appendix 1

4.6.2 Risks, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention

4.6.2.1 Environmental risk assessment

It is hard to assess risks for the substances in table 5 below since there is little known about their path ways into the environment and to humans. However both PFBS and 6:2 FTS have been found in several parts of the Arcticregion. PFBS may then a potential LRT substance. . For 6:2 FTS more data is needed to determine its origin and whether it is a LRT substance or not.

Table 5: Characteristics of alternatives to PFOS and related substances for chemically driven oil production

<table>
<tr><th>Alternatives</th><th>CAS RN</th><th>References</th></tr>
<tr><td>Perfluorobutane sulfonate (PFBS)</td><td>29420-49-3</td><td>[3][4][9][13][51][52][53][55][57] [59][67][68][69][70]</td></tr>
<tr><td colspan="3">Category: The principal terminal degradation product of N-methyl perfluorobutane sulphonamidoethanol and PFBS-based products.</td></tr>
<tr><td colspan="3">Toxicology: The substance is well characterized. PFBS suppressed differentiation of a neuronotypic cell line used to characterize neurotoxicity.
Degradation in the environment: PFBS is considered as stable in the environment; PFBS is the principal terminal degradation product of N-methyl perfluorobutane sulphonamidoethanol and PFBS-based products.
Emissions: Emission to the environment may be expected from chemically driven oil production and PFBS manufacturing
Monitoring data: PFBS has been widely detected in water and has very low sorption. PFBS is also found in municipal landfill leachates. PFBS has been found in indoor dust from homes and offices. Monitoring near a manufacturing facility found PFBS in groundwater, river water, and in human serum in 93% of the sampled residents located near the plant. Observations in the Arctic may qualify PFBS as a LRT substance. A study of drinking water in Germany detected PFBS in 33% of the children, 4% of the women, and 13% of the men in city where the samples were taken. Overall, the study found that PFC concentrations in blood plasma of children and adults exposed to PFC-contaminated drinking water were increased 4- to 8-fold compared with controls

Note: Some additional indicative data is available in appendix 1</td></tr>
<tr><th>Alternatives</th><th>CAS RN</th><th>References</th></tr>
<tr><td>6:2-Fluorotelomer sulfonate (6:2 FTS)</td><td>27619-97-2</td><td>[5] [9][57][65][66]</td></tr>
<tr><td colspan="3">Toxicology: Acute and repeated-dose mammalian and aquatic toxicity has been reported
Degradation in the environment: Degradation of fluoroalkylthioamido- sulphonates into FTS is suggested and 6:2 FTS is susceptible to biodegradation under sulphur-limiting and aerobic conditions.
Emissions : Emission to the environment may be expected from chemically driven oil production and in manufacturing.
Emission of 6:2 FTS from STP effluents is found. FTS can be expected in the aqueous environment. In the environment a decrease to the stable perfluorohexane acid (PFHxA) is found.
Monitoring data: 6:2 FTS has been detected in environmental samples including water, soil, air particulates and biota.
During the EU-project PERFORCE, FTS were detected in several environmental samples. 6:2 FTS was present in the particle phase of UK air samples with unknown origin and may be that non-volatile ionic FTS might directly undergo atmospheric transport on particles from source regions.</td></tr>
<tr><th>Alternatives</th><th>CAS RN</th><th>References</th></tr>
<tr><td>Fluorotelomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids, and thioether acids</td><td>Information gaps</td><td>[2]</td></tr>
<tr><td colspan="3">Toxicology: Information gaps since there are no specific surfactant substances identified
Environmental hazards: Information gaps since there are no specific surfactant substances identified</td></tr>
</table>

4.7 Carpets, leather, apparel, textiles and upholstery

Fluorinated finishes are a technology known to deliver durable and effective oil and water repellence and stain and oil release properties. Historically, fluorinated polymers based on perfluorooctane sulfonyl (PFOS) electrochemical fluorination chemistry have been used. PFOS was not directly used to treat textiles but used to be present at up to 2 wt% in products. In addition, fluorotelomer-based polymers have also been used.

Major manufacturers in conjunction with global regulators have agreed to discontinue the manufacture of "long-chain" fluorinated products and move to "short-chain" fluorinated products. Novel short-chain fluorinated products, both short-chain fluorotelomer-based and perfluorobutane sulfonyl-based, have been applied for manufacture, sale and use in carpets, textiles, leather, upholstery, apparel, and paper applications. Non-fluorinated alternative technologies such as hydrocarbon waxes and silicones can provide durable water repellence (DWR; aka hydrophobic properties) but do not provide oil repellence or soil and stain release.

Hyperbranched hydrophobic polymers (dendritic i, e. highly branched polymers) and specifically adjusted comb polymers as active components is one example of nonfluorinated alternative technologies that can provide superhydrophobic surfaces (but not provide oil repellency, soil and stain release), meaning contact angles larger than 150° that can be applied in coatings, textile, leather etc[26]. Dendrimers may be in the region of nano sized materials meaning features with an average diameter between 1 to 100 nm[27].

4.7.1 Identity and properties of the alternatives

See appendix 1

4.7.2 Type of uses, quantities, producers, and traders

There is currently no publicity available data concerning quantities used on the market. For detailed information on composition, trade names and manufacturers, see appendix 2.

4.7.3 Risks, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention

4.7.3.1 Environmental risk assessment

It is hard to assess risks for the substances in table 6 below since there is little known about their path ways into the environment and to humans with the execption of PFBS. . PFHxS and related substances are considered as long-chain perfluorinated chemicals (LCPFCs) by OECD, which are not feasible as alternatives to PFOS and related substances due to their similar environmental hazards.

Table 6: Characteristics of alternatives to PFOS and related substances for carpets, leather and apparel, textiles and upholstery.

Alternatives	CAS RN	References
Dendrimers : Hyperbranched hydrophobic polymers (dendritic i, e. highly branched polymers)	Information gaps (*possibly not relevant*)	[1][60][61][62]
Toxicology: Dendrimers are poorly characterized. Cytotoxicity studies have shown dendrimers able to cross cell membranes. Most nano dendrimers display toxic and hemolytic activity, thought to be due to their positively-charged surface. Nano-dendrimers activate platelets and alter their morphology and function including attenuating platelet-dependent thrombin generation. Nano-dendrimer cytotoxicity has also been observed in human keratinocytes in vitro. **Environmental hazards:** Information gaps		
Alternatives	**CAS RN**	**References**
Siloxanes (cyclic : D3, D4, D5 and D6 (linear: MM, MDM, MD2M and MD3M) and silicone polymers (polysiloxanes). For more detailed information of these substances see footnote[28]	556-67-2 (D4) 541-02-6 (D5) 540-97-6 (D6) 107-46-0 (MM) 107-51-7 (MDM) 141-62-8 (M2DM) 141-63-9 (M3DM)	[1][10][63]

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27 http://ec.europa.eu/environment/chemicals/nanotech/
http://www.oecd.org/department/0,3355,en_2649_37015404_1_1_1_1_1,00.html

28 http://extra.ivf.se/kemi/common/downloads/Kunskapsarkiv/Polysiloxaner/presentation_polysiloxanes.pdf

Toxicology: Some siloxanes will be metabolized and the metabolites (hydroxylation metabolites) are expected to be found in blood and urine California State EPA[29] notes the weak estrogenic activity of D4 combined with long half life and uterine tumors resulting from D5 exposure. The government of Canada[30] concluded that D4 is inherently toxic to aquatic biota.

Degradation in the environment: Persistent. Siloxane polymers are considered as inert. The California State EPA notes that cyclosiloxanes appear to have long half lives in people.

Emissions: Siloxanes are volatile.

Monitoring data: Siloxanes are persistent and occur in environmental media, especially in sewage sludge. In studies conducted by the Nordic countries, D5 was the dominant siloxane in all environmental matrices sampled except for air, where D4 dominated. A recent study of the food web in Norway from zooplankton and Mysis to planktivorous and piscivorous fish found food biomagnification of D5. The authors noted that the biomagnification was sensitive to the species included at the higher trophic level. The Government of Canada preliminary assessment finds that MDM meets the criteria for persistence and bioaccumulation potential but does not meet the criteria for water and soil as set out in the Persistence and Bioaccumulation Regulations. Empirical and modelled bioconcentration factors in excess of 5000 indicate that MDM also meets the criterion for bioaccumulation potential as set out in the Persistence and Bioaccumulation Regulations[31]...Certain siloxanes are persistent in the environment, resisting oxidation, reduction, and photodegradation. Varying information exists on the susceptibility of siloxanes to hydrolysis.

Note: Some additional indicative data is available in appendix 1

Alternatives	CAS RN	References
Fluorotelomer alcohols (FTOH)	2043-47-2 (4:2 FTOH) 647-42-7 (6:2 FTOH)	[9][15][33][34] [35][56][72][73][74]

Category: precursors for fluorotelomer-based polymers.

Toxicology: 4:2 FTOH is poorly characterized. 6:2 FTOH is well characterized Acute and repeated-dose mammalian toxicity, pharma- and toxicokinetics studies have been conducted. Recent research show that 4:2 FTOH is more potent than 6:2 and 8:2 for cytotoxicity.

Degradation in the environment: The oxidation of fluorotelomer alcohols in the atmosphere by OH-radicals leads quantitatively to the production of the corresponding polyfluorinated aldehyde, being further degraded to perfluorinated carboxylic acids (PFCA).

Emissions: On the basis of their volatility, polyfluorinated telomer alcohols are expected to occur predominantly in the atmospheric gas phase. However, given their low solubility in water and high sorptivity to organic solvent or sorbent, the fluorotelomer alcohol is expected to partition to the air compartment only under conditions where no sorptive medium is present.

Monitoring data: FTOHs were found in the North American atmosphere. However, present modelling results show that with current estimates of chemistry and fluxes the atmospheric oxidation of FTOH can provide a quantitative explanation for the presence of PFCAs in remote regions. FTOHs were present in the highest concentrations in a study of office air monitoring which also correlated PFOA levels in the serum of office workers with air levels of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH.

Note: Some additional indicative data is available in appendix 1

Alternatives	CAS RN	References
Perfluorobutane sulfonate (PFBS) as processing agent for perfluorobutane sulfonyl (PFBS)-based polymers	29420-49-3	[3][4][9][13][51][52][53][55][57] [59][67][68][69][70]

Category: precursor for perfluorobutane sulfonyl (PFBS)-based polymers and terminal degradation product.

Toxicology: The substance is well characterized. PFBS suppressed differentiation of a neuronotypic cell line used to characterize neurotoxicity.

Degradation in the environment: PFBS is considered as persistant in the environment. PFBS is considered the terminal degradation product**.**

29 http://oehha.ca.gov/multimedia/biomon/pdf/1208cyclosiloxanes.pdf

30 http://www.chemicalsubstanceschimiques.gc.ca/challenge-defi/batch-lot-2/index-eng.php http://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=2481B508-1

31 http://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=19584F14-1#a1

Emissions: Poorly characterized though emissions are expected from PFBS manufacturing.

Monitoring data: PFBS has been widely detected in water and has very low sorption. PFBS is also found in municipal landfill leachates. PFBS has been found in indoor dust from homes and offices. Monitoring near a manufacturing facility found PFBS in groundwater, river water, and in human serum in 93% of the sampled residents located near the plant. A study of drinking water in Germany detected PFBS in 33% of the children, 4% of the women, and 13% of the men in city where the samples were taken. Overall, the study found that PFC concentrations in blood plasma of children and adults exposed to PFC-contaminated drinking water were increased 4- to 8-fold compared with controlsObservations in the Arctic may qualify PFBS as a LRT substance.

Note: Some additional indicative data is available in appendix 1

Alternatives	CAS RN	References
Perfluorohexane sulfonic acid (PFHxS)	3871-99-6	[9][14][40][41][42][57] Appendix 1

Category: precursor for perfluorohexylsulfonyl (PFHxS)-based polymers and terminal degradation product

Toxicology: PFHxS affected the thyroid hormone (TH) pathway at multiple levels of biological organization – somatic growth, mRNA expression and circulating free T4 concentrations. The lowest PFHxS concentration for which an effect in mRNA expression and circulating free and circulating free T4 levels was observed was 890 ng/g (injected concentration) or 5100 ng/g ww (liver concentration). PFHxS was also found to inhibit gap junction intercellular communication in a dose-dependent fashion. In a recent study of attention deficit / hyperactivity disorder (ADHD) in children, increasing PFHxS levels were associated with increasing prevalence of ADHD (adjusted odds ratio of 1.59).

Degradation in the environment : PFHxS is considered as persistent and stable in the environment and is regarded as degradation product of other perfluorinated compounds.

Emissions : Possible from treated textiles and manufacturing.

Monitoring data: There is a high potential for contamination of surface and ground water[32]. PFHxS was detected with a range of 2-4300 ng/g in dust samples from Canada as well as a median of 2 ng/mL and 6 ng/mL in human plasma. No substantial difference was found in levels of perfluorinated sulphonates (PFASs) between the urban and rural regions. A study of 300 children in the US from birth to 12 years of age showed that PFHxS was present in >92% of them with significantly increasing concentrations by age. In the marine ecosystem PFHxS was found in fish from Japan and sediments collected from shallow water. Verreault et al (2005) detected up to 2.7 ng/g ww PFHxS in plasma of glaucous gull from the Norwegian Arctic. This observation may qualify PFHxS as a LRT substance.

Note: Some additional indicative data is available in appendix 1

4.8 Paper and packaging

Fluorinated surfactants have been evaluated for paper uses since the early 1960s . Perfluorooctyl sulfonamido ethanol-based phosphates were the first substances used to provide grease repellence to food contact papers. Fluorotelomer thiol-based phosphates and polymers followed. currently polyflouroalkyl phosphonic acids (PAPs) are used in food-contact paper products and as eveling and wetting agents. Since paper fibers and phosphate-based fluorinated surfactants are both anionic, cationic bridge molecules need to be used in order to ensure the electrostatic adsorption of the surfactant onto the paper fiber. These surfactants are added to paper through the wet end press where cellulosic fibers are mixed with paper additives before entering the paper forming table of a paper machine. This treatment provides excellent coverage of the fiber with the surfactant and results in good folding resistance. An alternative treatment method involves application of a grease repellent at the size press and film press stage which consists of impregnating the formed paper sheet with a surface treatment. Fluorinated phosphate surfactants are not preferred for this mode of paper treatment. In this latter case, fluorinated polymers are used instead of surfactants. In terms of oil and water repellency, it is well recognized in the paper industry that phosphate-based fluorinated surfactants provide good oil repellency but have limited water repellency. Acrylate polymers with fluorinated side chains derived from sulfonamido alcohols and fluorotelomer alcohols are the most widely used polymers because they deliver oil, grease, and water repellence. Most recently, perfluoropolyether-based phosphates and polymers have become widely used treatments for food contact paper and paper packaging [6].

32 Presentation by Germany at OECD/UNEP Workshop on perfluorinated chemicals and the transition to safer alternatives, Beijing China, September 2011, http://www.oecd.org/dataoecd/50/29/48725491.pdf

At least one manufacturer has developed a non-chemical alternative for this use. The Norwegian paper producer Nordic Paper is using mechanical processes to produce, without using any persistent chemical, extra-dense paper that inhibits leakage of grease through the paper. [2]

4.8.1 Identity and properties of the alternatives

See appendix 1

4.8.2 Risks, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention

4.8.2.1 Environmental risk assessment

It is hard to assess risks for the substances in table 7 and 8 below since there is little known about their path ways into the environment and to humans. However PFBS has been found in the arctic that may qualify it as a potential LRT substance.

Table 7: Characteristics of alternatives to PFOS and related substances for paper and packaging.

<table>
<tr><th>Alternatives</th><th>CAS RN</th><th>References</th></tr>
<tr><td>Fluorotelomer based phosphate esters such as diesters of polyfluoroalkyl phosphonic acids and phosphoric acids (diPAPs)
and
polyfluoroalkyl phosphonic acids and phosphoric acids (PAPs)</td><td>Some examples of PAPs and diPAPs are listed in appendix 1</td><td>[1][36][81][82][83][84][85][86][87]
Appendix 1.</td></tr>
<tr><td colspan="3">Toxicology: diPAPs facilitates human exposure to perfluorocarboxylates (PFCAs) since PAPs have been proved to be metabolized to PFCAs in an in vivo metabolism experiment.
Degradation into the environment: PAPs and diPAPs transform into the corresponding PFCAs
Emissions: The PAPs and diPAPs have been detected in waste water treatment plants (WWTP) sludge in concentrations ranging from 47 to 200 ng/g and therefore diPAPs could be discharged into drinking water sources and as residuals in drinking water as exemplified by the increased PFC concentrations at downstream drinking water facilities due to discharge from WWTP.
Monitoring data: The diester of polyfluoroalkyl phosphonic acids (diPAPs) have been detected in human serum in a concentration from 1,9 to 4,5 ug/L.

Note: Some additional indicative data is available in appendix 1</td></tr>
<tr><th>Alternatives</th><th>CAS RN</th><th>References</th></tr>
<tr><td>Fluorotelomer alcohols (FTOH) that are processing agents for short-chain fluorotelomer-based polymers.</td><td>2043-47-2 (4:2 FTOH)
647-42-7 (6:2 FTOH)</td><td>[9][15][33][34]
[35][56][72][73][74]</td></tr>
<tr><td colspan="3">Category: precursors for fluorotelomer-based polymers.</td></tr>
<tr><td colspan="3">Toxicology: 4:2 FTOH is poorly characterized. 6:2 FTOH is well characterized Acute and repeated-dose mammalian toxicity, pharma- and toxicokinetics studies have been conducted. Recent research show that 4:2 FTOH is more potent than 6:2 and 8:2 for cytotoxicity.
Degradation in the environment : The oxidation of fluorotelomer alcohols in the atmosphere by OH-radicals leads quantitatively to the production of the corresponding polyfluorinated aldehyde, being further degraded to perfluorinated carboxylic acids (PFCA).
Emissions : On the basis of their volatility, polyfluorinated telomer alcohols are expected to occur predominantly in the atmospheric gas phase. However, given their low solubility in water and high sorptivity to organic solvent or sorbent, fluorotelomer alcohols are expected to partition to the air compartment only under conditions where no sorptive medium is present.
Monitoring data: FTOHs were found in the North American atmosphere. However, present modelling results show that with current estimates of chemistry and fluxes the atmospheric oxidation of FTOH can provide a quantitative explanation for the presence of PFCAs in remote regions. FTOHs were present in the highest concentrations in a study of office air monitoring which also correlated PFOA levels in the serum of office workers with air levels of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH.

Note: Some additional indicative data is available in appendix 1</td></tr>
</table>

4.9 Rubber and plastics

Perfluorobutane sulphonate (PFBS) derivatives or various C_4-perfluoro compounds are used as alternatives to PFOS in rubber moulding defoamers in electroplating and as additives in plastics [2].

4.9.1 Identity and properties of the alternatives

See appendix 1.

4.9.2 Risks, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention

It is hard to assess risks for the substances in table 8 below since there is little known about their path ways into the environment and to humans.

Table 8: Characteristics of alternatives to PFOS and related substances for rubber and plastics.

Alternatives	CAS RN	References
Perfluorobutane sulfonate (PFBS)	29420-49-3	[3][4][9][13][51][52][53][55][57] [59][67][68][69][70]
Category: precursor for perfluorobutane sulfonyl (PFBS)-based polymers and terminal degradation product.		
Toxicology: The substance is well characterized **Degradation in the environment** : PFBS is considered as persistent in the environment; PFBS is the principal terminal degradation product of N-methyl perfluorobutane sulphonamidoethanol and PFBS-based products**.** **Emissions:** Emission to the environment may be expected from rubber and plastic products and from PFBS manufacturing. **Monitoring data:** PFBS has been widely detected in water and has very low sorption. PFBS is also found in municipal landfill leachates. PFBS has been found in indoor dust from homes and offices. Monitoring near a manufacturing facility found PFBS in groundwater, river water, and in human serum in 93% of the sampled residents located near the plant. A study of drinking water in Germany detected PFBS in 33% of the children, 4% of the women, and 13% of the men in city where the samples were taken. Overall, the study found that PFC concentrations in blood plasma of children and adults exposed to PFC-contaminated drinking water were increased 4- to 8-fold compared with controls. Observations in the Arctic may qualify PFBS as a LRT substance. *Note: Some additional indicative data is available in appendix 1*		

4.10 Coating and coating additives

Fluorinated surfactants provide exceptional wetting, leveling and flow control for water-based, solvent-based and high-solids organic polymer coating systems when added in amounts of just 100–500 ppm. Fluorinated surfactants impart various properties to paints and coatings including anti-crater and improved surface appearance, better flow and leveling, reduced foaming, decreased block, open-time extension, oil repellency, and dirt pickup resistance. They have also been widely used in inks.

The inclusion of fluorinated surfactants in ink jet compositions has led to better processing through modern printers and excellent image quality on porous or non-porous media. Fluorinated surfactants improved surface wetting during the screen printing of carbon black inks onto Polymer Electrolyte Membrane (PEM) fuel cell electrodes. In addition, fluorinated surfactants improved the cold-water swelling and internal bond strength of wood particleboard bonded with urea–formaldehyde (UF) adhesive resins due to reduced interfacial tension of the resins and improved substrate wetting [6].

Hyperbranched hydrophobic polymers (dendritic i, e. highly branched polymers) and specifically adjusted comb polymers as active components is one example of nonfluorinated alternative technologies that can provide superhydrophobic surfaces (but not provide oil repellency, soil and stain release), meaning contact angles larger than 150° that can be applied in coatings, textile, leather etc[33]. Dendrimers may be in the region of nano sized materials meaning features with an average diameter between 1 to 100 nm[34].

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34 http://ec.europa.eu/environment/chemicals/nanotech/
http://www.oecd.org/department/0,3355,en_2649_37015404_1_1_1_1_1,00.html

Propylated naphthalenes and biphenyls, a group of di-aromatic hydrocarbons, can be used as water-repelling agents for different applications such as corrosion protection systems, marine paints, resins, printing inks, coatings and electrical, electronic and mechanical applications. [2]

4.10.1 Identity and properties of the alternatives

See appendix 1

4.10.2 Type of uses, quantities, producers, and traders

There is currently no, scarce or uncertain data available concerning quantities used on the market and consecuently are these data not presented in table 12.

For detailed information on composition, trade names and manufacturers, see appendix 2.

4.10.3 Risks, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention

4.10.3.1 Environmental risk assessment

It is hard to assess risks for the substances in table 9 below since there is little known about their path ways into the environment and to humans.

Table 9: Characteristics of alternatives to PFOS and related substances for coating and coating additives.

Alternatives	CAS RN	References
Dendrimers : Hyperbranched hydrophobic polymers (dendritic i, e. highly branched polymers)	Information gaps (if relevant)	[1][60][61][62]
Toxicology: Low toxicity. Cytotoxicity studies have shown that dendrimers able to cross cell membranes. Most nano dendrimers display toxic and hemolytic activity, thought to be due to their positively-charged surface. Nano-dendrimers activate platelets and alter their morphology and function including attenuating platelet-dependent thrombin generation. Nano-dendrimer cytotoxicity has also been observed in human keratinocytes in vitro. **Environmental hazards:** Information gaps		
Alternatives	**CAS RN**	**References**
Siloxanes (cyclic : D3, D4, D5 and D6 linear: MM, MDM, MD2M and MD3M) and silicone polymers	556-67-2 (D4) 541-02-6 (D5) 540-97-6 (D6) 107-46-0 (MM) 107-51-7 (MDM) 141-62-8 (M2DM) 141-63-9 (M3DM)	[1][10][63]
Toxicology: Some siloxanes will be metabolized and the metabolites (hydroxylation metabolites) are expected to be found in blood and urine. California State EPA notes the weak estrogenic activity of D4 combined with long half life and uterine tumors resulting from D5 exposure. The government of Canada concluded that D4 is inherently toxic to aquatic biota. **Degradation in the environment:** Persistent. Siloxane polymers are considered as inert. The California State EPA notes that cyclosiloxanes appear to have long half lives in people. **Emissions:** Siloxanes are volatile. **Monitoring data:** Siloxanes are persistent and occur in environmental media, especially in sewage sludge. In studies conducted by the Nordic countries, D5 was the dominant siloxane in all environmental matrices sampled except for air, where D4 dominated. A recent study of the food web in Norway from zooplankton and Mysis to planktivorous and piscivorous fish found food biomagnification of D5. The authors noted that the biomagnification was sensitive to the species included at the higher trophic level. The Government of Canada preliminary assessment finds that MDM meets the criteria for persistence and bioaccumulation potential but does not meet the criteria for water and soil as set out in the Persistence and Bioaccumulation Regulations. Empirical and modelled bioconcentration factors in excess of 5000 indicate that MDM also meets the criterion for bioaccumulation potential as set out in the Persistence and Bioaccumulation Regulations. Certain siloxanes are persistent in the environment, resisting oxidation, reduction, and photodegradation. Varying information exists on the susceptibility of siloxanes to hydrolysis.		

Alternatives	CAS RN	References
Fluorotelomer alcohols (FTOH) that are processing agents for short-chain fluorotelomer-based polymers	2043-47-2 (4:2 FTOH) 647-42-7 (6:2 FTOH)	[9][15][33][34][35][56][72][73][74]
Category: precursors for fluorotelomer based polymers		
Toxicology: 4:2 FTOH is poorly characterized. 6:2 FTOH is well characterized Acute and repeated-dose mammalian toxicity, pharma- and toxicokinetics studies have been conducted. Recent research show that 4:2 FTOH is more potent than 6:2 and 8:2 for cytotoxicity. **Degradation in the environment** :The oxidation of fluorotelomer alcohols in the atmosphere by OH-radicals leads quantitatively to the production of the corresponding polyfluorinated aldehyde, being further degraded to perfluorinated carboxylic acids (PFCA) **Emissions:** On the basis of their volatility, polyfluorinated telomer alcohols are expected to occur predominantly in the atmospheric gas phase. However, given their low solubility in water and high sorptivity to organic solvent or sorbent, the fluorotelomer alcohol is expected to partition to the air compartment only under conditions where no sorptive medium is present. **Monitoring data:** FTOHs were found in the North American atmosphere. However, present modeling results show that with current estimates of chemistry and fluxes the atmospheric oxidation of FTOH can provide a quantitative explanation for the presence of PFCAs in remote regions. FTOHs were present in the highest concentrations in a study of office air monitoring which also correlated PFOA levels in the serum of office workers with air levels of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH. *Note: Some additional indicative data is available in appendix 1*		
Alternatives	**CAS RN**	**References**
Propylated naphthalenes and propylated biphenyls	Information gaps	Appendix 1
Toxicology: The substances are poorly characterized **Environmental hazards:** Information gaps, (1-methylethyl)-1,1'-biphenyl is bioaccumulative and toxic to aquatic organisms. *Note: Some additional indicative data is available in appendix 1*		

4.11 Others

4.11.1 Information from Estonia

A more detailed study of the possible use of PFOS was in Estonia in 2010 by the project "Control of hazardous substances in the Baltic Sea Region" under the COHIBA (http://www.klab.ee/infomaterjalid/projektid/cohiba/). In the project examined the potential PFOS uses in Estonia. One of the main sources of industry inspection was based on the statistical data Prodcom Database (2008). Based on these data it was found that there is potential PFOS manufacture and use in two areas: metal (chrome cover) and semiconductor and other electronic products.

During the preparation of this report, the questionnaire was sent to 53 companies listed in open operation, also to four industry-federations (Estonian Furniture Manufacturers Association, the Estonian Plastic Industry Association, Estonian Clothing and Textile Association, the Estonian Association of Structural Steel). In total, 12 companies, which make 22.6% of companies, received the questionnaire. Respondents included the 5 companies engaged in business metalworking, 3 furniture manufacturers and 2 plastic manufacturers one packaging manufacturer and one plywood manufacturer (building materials and furniture components). Coating materials for production piles are too spread out the concept that even in so short a time to identify potential businesses.

All companies which replied to the questionnaire do not and did not use PFOS, and its salts and did not respond if they used any alternatives. Such information is not surprising, because the industry uses lot of intermediate products and to find information on substances is complex and would require a request for information for companies supplying the raw material. A more detailed inventory of the use and presence of PFOS was started in 2012.

As the use of alternatives was not identified, the information required by section 2 of the tasks cannot be presented as well as it is not possible to provide additional information on the items specified in section 3 of the tasks.

4.11.2 Information from Norway

In 2007 Norway did a survey asking users of fire fighting foams what product they have been using after “PFOS” was banned in fire fighting foams in Norway. Before the ban, fire fighting foam was the application which had the highest use of “PFOS”. According to the survey, at least 20 different products are used in Norway today. Norway did not find any of the banned “PFOS” substances in these fire fighting foams. However a number of foams were identified as containing “unknown” substances (trade secrets) listed as “compound containing fluor or surface active substance, and so on”.

Norway has data sheets for about 17 fire fighting foams that can be provided upon request.

4.11.3 Information from USA

In general, the use of PFOS-related substances in open uses for aviation hydraulic fluids, insecticides for control of red imported fired ants and termites, chemically driven oil production, carpets, textiles and upholstery, leather and apparel, electric and electronic parts for some color printers and color copy machines, paper and packaging, fire fighting foams insect baits for control of leaf-cutting ants from Atta spp. and Acromyrmex spp, coating and coating additives rubber and plastics metal plating (hard metal plating) etal plating (decorative plating) are no longer ongoing in the United States, except for any existing stocks or imports of articles. Note that some or all of the ongoing uses may cease in the future when U.S. takes additional regulatory actions on these chemicals.

5 Assessment of alternatives

5.1 Aviation hydraulic fluids[35]

There is no available information on: health and environmental effects including toxicological and ecotoxicological information, cost-effectiveness, efficacy, vailability, accessibility and socio-economic considerations.

5.2 Fire fighting foams[36]

5.2.1 Technical feasibility

Most users in Norway and Canada said in surveys that there has been no change in technical feasibility for the “new” fire fighting foams. Some of the new foams have high viscosity that makes it hard to use with the same equipment as for “PFOS”-foam. The non-PFOS based AFFFs are widely commercially available.

Fire fighting foams with PFOS-related substances are no longer used, except for existing stocks in USA. The specific identities of replacements or substitutes for PFOS and PFOS-related substances and mixtures have been claimed as CBI[37] to the extent they have been disclosed to the U.S. government. Generally speaking, however, these substances and mixtures have included short-chain PFAS and various fluorinated telomers[38].

Dodecafluoro-2-methylpentan-3-one (CAS # 756-13-8) is mentioned as an alternative to PFOS in aqueous fire fighting foams (AFFF). This material is manufactured and sold by 3M as an alternative to halon and other ozone depleting / high global warming substances. Applications for this fluorinated ketone include clean fire extinguishing agents (CEA). Although CAS# 756-13-8 has been used as a clean extinguishing agent to replace a small number of PFOS, it would generally not be considered a viable alternative to PFOS AFFF.

The preliminary results of experiments in China indicate the effects of their technology[39] is close to or can equal with that of fire extinguishing foam containing PFOS. This alternative technology can be developed in the foreseeable future.

5.2.2 Health and environmental effects including toxicological and ecotoxicological information

The primary supply of AFFF has became fluorotelomer-based. Over the last several years, manufacturers of fluorotelomer AFFF have been replacing long-chain fluorosurfactants with shorter-chain fluorosurfactants. The PFCs in current fluorotelomer-based AFFF are shorter chain molecules, generally 6:2 telomer-based, and tend to be less bioaccumulative and less toxic. [1]

Six-carbon telomere-based fluorosurfactants have not been assessed in Canada under the Canadian Environmental Protection Act 1999.

The main contents of compressed air foam fire extinguishing technology in China are Class A foam extinguishing agents. In many countries, manufacturers usually provide Material Safety Data Sheet for commercially available Class A foam fire extinguishing agent products, which includes test data of health and environmental effects. However, the third party assessment of health and environmental impacts for Class A foam extinguishing agents is scarcely done.

35 Contribution from USA.

36 Contributions from Norway, USA, China and Canada.

37 There is no explanation from US to CBI in their contribution. US need to expain CBI.

38 More information is available at http://www.fffc.org

39 China needs to specify their technology.

5.2.3 Cost-effectiveness

Most users say that there has been no change in the cost while others say that the new foam is more expensive. Some users say that the highest cost associated with the ban on "PFOS"-containing foams has been clean-up/destruction of the PFOS-containing foams and not the purchase of the new foams.

5.2.4 Efficacy

Variable efficacy is stated. The non-PFOS based AFFFs retain the same fire suppression capabilities as PFOS containing agents.

5.2.5 Availability

The alternative products are readily available commercially from all major suppliers of fire-fighting equipment. Suppliers in North America include but are not limited to suppliers such as Ansul, Chemguard, DuPont, Dynax, Kidde, and Solberg. There is a similar situation in Norway but with slightly different suppliers. Compressed air foam fire engines and Class A foam fire extinguishing agent are commercially available in China, but a combination of both remains to be resolved. Currently there are no mature products in China for fixed compressed air foam fire extinguishing system.

5.2.6 Accessibility

There are no factors limiting the accessibility of these products in North America.

Class A fire extinguishing agent has been around for over 30 years. In the last decade, Class A foam fire extinguishing agent and compressed air foam system engines have gradually become more and more popular in China.

5.2.7 Socio-economic consideration

There is an initial replacement cost to resupply with non-PFOS based AFFFs. There are no additional operations and maintenance costs associated with using the non-PFOS agents as compared to PFOS-based ones.

5.3 Pesticides (insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.* and insecticides for control of red imported fired ants and termites)[40]

5.3.1 Technical feasibility

The reported alternatives to sulfuramid are:chlorpirifos, cypermethrin, mixture of chlorpirifos and cypermethrin,

fipronil, imidacloprid, abamectin, deltamethrin, fenitrothion mixture of fenitrothion and deltamethrin.

The pesticides listed above are all available as commercial products on the Argentinean market. Argentina has prohibited the import, production, trading and use of chlorpirifos in formulations of household sanitary products but not for the pesticide uses on leaf cutting ants. There is an ongoing legislative prohibition process for fenitrothion for house hold uses and additionally for agriculture purposes of grain. The alternatives to sulfluramide in Argentina can be divided in two main groups namely conventional alternatives (synthetic insecticides) and non-conventional alternatives (non-chemical products). The conventional are Fipronil, applied on the total surface or as an component of a bait and Chlorpyrifos, applied using fogging machines in all main principal entries of the nest.

The non-conventional are Entomopathogenic fungi are a) organic bait consisting of rice grains with *Beauveria sp.* (De Soll *et al*., 2010). b)Diatomaceous earth mixed with waste water in the principal entry of each anthill (Ríos de Saluso, 2010). c) Vegetal substances with insecticide effect: extract of eucalyptus, castor-oil plant (Pelicano *et al*., 2002) and "Palo Amargo" ("Bitter stick", *Aeschirium crenata Vell.* Simaroubaceae) (Rodfígue *et al.,* 2006) d) Natural enemies: parasitoids known as "Moscas descapitadotas" ("Decapitating flies", Diptera: Phoridae) (Guilllade y Folgarait, 2010) and e) organic baits based on yeast and rice (Borgetto, 2009). All these alternatives have been tested in Argentina with promising results[41].

According to Brazin there are many differences between leaf-cutting ants and exotic ants (urban ants), including in alimentary behaviour. Such differences explain why certain active ingredients are effective for controlling urban ants and not for controlling leaf-cutting ants.

According to Brazil active ingredients applied in the dried form and emulsifiable concentrates form are not efficient for the leaf-cutting ants control, in view of aspects related to the biology and behavior of said insects and others, such as the size of nests and operating difficulties. In addition, the utilization of dried powders and emulsifiable concentrates presents enormous toxicological and environmental disadvantages (risks to applier and the environment), comparing to the application of insect baits. Granulated baits is a low-cost method, delivering high efficiency with

40 Contributions from Argentina, Brazil, USA, China and Estonia.

41 Comments from Argentina dated 3rd July 2012 publicy available on SC homepage.

reduced health hazards to humans and the environment during application and being specific to the pest target. Its formulation is developed with low concentrations of active ingredients, and its localized application does not require application equipment. Baits are directly distributed from their packaging, with no manual contact, close to active nest entrance holes or anthill trails and carried into the colony by the ants themselves. The utilization of ready-to-use formulations should reduce or impede releases to humans.[2]

Brazil has studied several mechanical, cultural, biological and chemical methods have been studied since the early 50s for controlling leaf-cutting ants. The management of culture by using resistant plants, toxic plants, or even the applied biological management, by manipulating predators, parasitoids and microorganisms, have already rendered unsatisfactory and inconsistent results, and have offered no indication of any technical, economic, or operational viability. PFOS-related substances are no longer used as insect baits or insecticides for the control of red imported fire ants and termites in USA. The specific identities of replacements or substitutes for PFOS and PFOS-related substances and mixtures have been claimed as confidential business information (CBI) to the extent they have been disclosed to the U.S. government. Generally speaking, however, these substances and mixtures have included short-chain PFAS and various fluorinated telomers.

5.3.2 Health and environmental effects including toxicological and ecotoxicological information

Today, some pests that were once major threats to human health and agriculture but were brought under control by pesticides are on the rebound.

Pesticide resistance is a genetically based phenomenon. Resistance can occur when a pest population is exposed to a pesticide and not all insects are killed. Those individuals that survive frequently have done so because they are genetically predisposed to be resistant to the pesticide.

Multiple resistance is resistance to more than one pesticide and to pesticides in more than one chemical class. This phenomenon is increasing rapidly. There are over 1,000 insect/insecticide resistance combinations, and at least 17 species of insects that are resistant to all major classes of insecticides that include the list of pesticides addressed as alternatives to PFOS listed in section 5.3.1 [7]

According to Brazil the active ingredients fipronil and chlorpyrifos present a much higher toxicity to mammals, water organisms, fish and bees than sulfluramid . Additionally Brazil consider that not use sulfluramid as the main active ingredient in insect baits is a dangerous retrocession in the leaf-cutting ant control, with the use of products or methods with less or no efficiency, more toxic to human beings and with animals and higher environmental impact risk.

According to Bulgaria and Romania the pesticides, as proposed alternatives to sulfluramid, are persistent into environment and highly toxic for aquatic organisms.

5.3.3 Cost-effectiveness

Information gaps

5.3.4 Efficacy

The effectiveness of the substances mentioned in chapter 5.3.1 have been questioned thus new alternatives are being studied in Brazil Fenoxycarb, pyriproxyfen, diflubenzuron, teflubenzuron, silaneafone, thidiazuron, tefluron, prodrone, abamectin and methoprene had been tested for leaf-cutting ants, but in Brazil they have experienced that these pesticides were not effective.

In China Fipronil and Imidacloprid are used for effective prevention from the infestation of hygienic, wood termites and cockroaches, and technologies for hygienic pest control that are mature and efficacious.

5.3.5 Availability

These alternatives mentioned in chapter 5.3.1 are available as commercial products on the Argentinian market.

Currently, the active ingredients registered in Brazil for ant baits are sulfluramid, fipronil and chlorpyrifos. According to the Brazilian Annex F information, sulfluramid cannot currently be efficiently replaced in Brazil by any other registered products commercialized since these alternatives have been questioned concerning their efficiency.

Fipronil and Imidacloprid are available in the Chinese market and ready for use.

5.3.6 Accessibility

The alternatives to PFOS mentioned in chapter 5.3.1 are available as commercial products on the Argentinian market.

In China imidacloprid and fipronil are provided as water dispersible granule, suspending agent, gel bait products are registered and commercialized.

enitrothion,CAS 122-14-5- and S Methoprene –CAS 65733-16-6- are banned/not authorized as active substances in plant protection products in the European Union, according to the Annex I of Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market.

5.3.7 Socio-economic consideration

Imidacloprid and Fipronil are considered to have higher production costs but with efficacious control in China these insecticides are suggested as promising for application.

5.4 Metal plating (hard metal plating and decorative plating)[42]

5.4.1 Technical feasibility

Chemical-mechanical polishing (CMP)[43] and Packed Bed Scrubbers (PBS)[44] are alternatives already on the Canadian market and are the most commonly used control devices. As a control device for metal plating applications, Venturi Scrubbers are new to the Canadian market and do not have the use history of the CMP or the PBS. Non-PFOS based fume suppressants are commercially available in Canada for use with metal plating and chromic acid anodizing applications. Canada is phasing out the use of PFOS fume suppressants by May 2013.

In Estonia the use of alternatives are not identified, the information required by the Stockholm Secretariat of the tasks cannot be presented as well as it is not possible to provide additional information on the items specified in section 3 (questionnaire) of the tasks.

There are no currently available alternatives for metal hard plating and decorative plating, and the use is still ongoing in U.S. However, the U.S. Environmental Protection Agency is seeking to phase out the use of PFOS-related substances from these uses[45].

In China an alternative to PFOS exist, namely F53-b (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxo) ethane sulfonate), see appendix 2.

5.4.2 Health and environmental effects including toxicological and ecotoxicological information

There is little independent and reliable information available on the toxicological and ecotoxicological characteristics of these polyfluorinated substitutes or their persistence and degradation products. Nevertheless, these substitutes and in particular their degradation products, are likely persistent in the environment.

It must be taken into account that it is much more difficult to remove alternatives such as THPFOS or PFBS out of the wastewater by adsorption than for PFOS.

In addition, these alternatives tend to adsorb less to the sewage sludge of wastewater treatment plants - e.g. so that in sum remarkably higher emissions to the environment than in case of using PFOS must be the result. Therefore problems might occur again for soil and in particular for groundwater as well as for surface water and related drinking water.

The frequent presence of persistence, higher emissions, unknown toxicity and degradation to persistent substances observed with fluorinated alternatives to PFOS should incline choice of alternatives toward non-fluorinated alternatives. The current information highlights the necessity for a timely detailed assessment of environmental fate and on the toxicity of the fluorinated alternatives to PFOS in order to clarify as soon as possible to what extent the currently used fluorinated alternatives can contribute to a solution of the problem.[1]

Canada reports no adverse health and environmental effects from the CMP and PBS control devices themselves. No information available due to the proprietary nature of the chemical formulations of the alternative fume suppressants.

Currently in China there is no third party assessment of the health and environmental impact for F53-b.

5.4.3 Cost-effectiveness

In Canada, for CMPs, depending on the air flow to be treated, a control device can cost from ~ $ 60,000 for approximately 14,000 cubic feet per minute (cfm) airflow (396 m^3/minute) to ~ $200,000 for 50,000 cfm airflow (1416 m^3/minute).

These costs are only for the control device itself and not the associated hoods or ducting which will add another ~ 15% of the control device's cost.

42 Contribution from Canada, USA, China and Estonia

43 http://www.faculty.ait.ac.th/visu/images/pdf/Romchat%20Dissertation1.pdf

44 http://archive.defra.gov.uk/environment/quality/chemicals/documents/pfos-riskstrategy.pdf

45 More information is available at http://www.epa.gov/opptintr/pfoa/pubs/pfoschromeplaterstudypdf_final.pdf.

There is an operating cost for a control device: a fan to move the collected air. The fan is powered electrically and this is a daily operating cost. The operating cost is similar to the operating cost of PFOS based fume suppressants (FS).

In China F53-B is 10-15% slightly higher than the price of the product containing PFOS.

5.4.4 Efficacy

Control devices such as Composite Mesh Pads (CMP) operate at over 99% efficiency on 1 micron sized particles. Packed Bed Scrubbers (PBS) are over 98% efficient. CMP's are considered to be maximum achievable control technology.

The performance of the non-PFOS fume suppressant is not equal to that of the PFOS based fume suppressants. To achieve the same reduction in surface tension, more products may be necessary and it may have to be replenished more frequently.

5.4.5 Availability

These control devices, CMPs, PBSs and Venturi scrubbers, are all commercially available in Canada. These fume suppressants are commercially available in Canada.

F53-b has been applied in China for nearly 30 years.

5.4.6 Accessibility

There are no factors limiting the accessibility of these control devices.

There are no factors limiting the accessibility of these fume suppressants. The PFOS and non PFOS fume suppressants are completely miscible with each other.

F53-b is independently developed by China with its total domestic production capacity up to 50 tons per year.

5.4.7 Socio-economic consideration

The cost of the non PFOS fume suppressants is expected to be the same as that of the PFOS fume suppressants.

5.5 Electric and electronic parts for some color printers and color copy machines[46]

5.5.1 Technical feasibility

PFOS-related substances are no longer used on color printers and color copy machines, although these parts may still be imported. The specific identities of replacements or substitutes for PFOS and PFOS-related substances and mixtures have been claimed as CBI to the extent they have been disclosed to the U.S. government. Generally speaking, however, these substances and mixtures have included short-chain PFAS and various fluorinated telomers.

5.5.2 Information gaps

There is no available information on: health and environmental effects including toxicological and ecotoxicological information, cost-effectiveness, efficacy, availability, accessibility and socio-economic considerations.

5.6 Chemically driven oil production[47]

5.6.1 Technical feasibility

PFOS-related substances are no longer used for chemically driven oil production. The specific identities of replacements or substitutes for PFOS and PFOS-related substances and mixtures have been claimed as CBI to the extent they have been disclosed to the U.S. government. Generally speaking, however, these substances and mixtures have included short-chain PFAS and various fluorinated telomers.

5.6.2 Information gaps

There is no or scarce available reference and member state information on: health and environmental effects including toxicological and ecotoxicological information, cost-effectiveness, efficacy, availability, accessibility and socio-economic considerations.

46 Contribution from USA.

47 Contribution from USA.

5.7 Carpets, leather and apparel, textiles and upholstery[48]

5.7.1 Technical feasibility

PFOS-related substances are no longer used on carpets. The specific identities of replacements or substitutes for PFOS and PFOS-related substances and mixtures have been claimed as CBI to the extent they have been disclosed to the U.S. government. Generally speaking, however, these substances and mixtures have included short-chain PFAS and various fluorinated telomers.

Perfluorohexane sulfonyl fluoride (PFHxSF) and its derivatives exist on the Chinese market and are commercialized with a production volume of 20 tons per year.

5.7.2 Health and environmental effects including toxicological and ecotoxicological information

Currently in China, which is an important producer of one of the alternatives, there is no third party assessment of the health and environmental impact for perfluorohexane sulfonyl fluoride (PFHxSF) and its derivatives. However PFHxS and related substances are considered by OECD as long-chain perfluorinated chemicals (LCPFCs) which are not feasible as alternatives to PFOS and related substances due to their similar environmental hazards.

The OECD Working Party on Manufactured Nanomaterials is trying to address the gap in safety information about different kinds of nanomaterials produced by man and don't naturally occur in nature. This include dendrimers, since there is a range of interesting applications soon to enter or already in the market or under development with dendrimers that include non-fluorine based coating operations on textile and leather.

Cytotoxicity studies have shown dendrimers able to cross cell membranes (useful for transfection) with toxicities depending on the molecule composition, particularly the type of functional groups and charges at the dendritic surface. It is a mistake to consider dendrimers as simple polymers. Once in the body the effects and translocation to secondary organs are practically unknown for dendrimers.[49]

5.7.3 Cost-effectiveness

Perfluorohexane sulfonyl fluoride (PFHxSF) and its derivatives, which are not feasible alternatives to PFOS and related substances, costs are 10% higher in China than the prices of products containing PFOS.

5.7.4 Efficacy

Perfluorohexane sulfonyl fluoride (PFHxSF) and its derivatives, which are not feasible alternatives to PFOS and related substances, are 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.

5.7.5 Availability

Perfluorohexane sulfonyl fluoride (PFHxSF) , which are not feasible alternatives to PFOS and related substances, and its derivatives are with current knowledge produced and available on the Chinese market. There is no information of availability on other markets.

5.7.6 Accessibility

Domestic production capacity in China is up to 50 tons per year. Another five companies have begun to study if perfluorohexane sulfonyl fluoride and its derivatives can be used for other areas. It is expected that the total capacity can reach the same levels as PFOS.

5.7.7 Socio-economic consideration

Information gaps

5.8 Paper and packaging, rubber and plastics[50]

5.8.1 Technical feasibility

PFOS-related substances may be used on paper (regulated by U.S. Food and Drug Administration) and paper containing PFOS-related substances may still be imported. The specific identities of replacements or substitutes for PFOS and PFOS-related substances and mixtures have been claimed as CBI to the extent they have been disclosed to the U.S. government. Generally speaking, however, these substances and mixtures have included short-chain PFAS and various fluorinated telomers.

48 Contribution from USA.

49 Personnel communication with Professor Juan Carlos Flores (OECD).

50 Contribution from USA.

PFOS-related substances are no longer used on rubber and plastics, although such articles may still be imported. The specific identities of replacements or substitutes for PFOS and PFOS-related substances and mixtures have been claimed as CBI to the extent they have been disclosed to the U.S. government. Generally speaking, however, these substances and mixtures have included short-chain PFAS and various fluorinated telomers.

5.8.2 Information gaps

There is no available information on: health and environmental effects including toxicological and ecotoxicological information, cost-effectiveness, efficacy, availability, accessibility and socio-economic considerations.

5.9 Coating and coating additives[51]

5.9.1 Technical feasibility

PFOS-related substances are no longer used on coatings and coating additives, although such articles may still be imported. The specific identities of replacements or substitutes for PFOS and PFOS-related substances and mixtures have been claimed as CBI to the extent they have been disclosed to the U.S. government. Generally speaking, however, these substances and mixtures have included short-chain PFAS and various fluorinated telomers.

5.9.2 Information gaps

There is no available information on: health and environmental effects including toxicological and ecotoxicological information, cost-effectiveness, efficacy, availability, accessibility and socio-economic considerations.

5.10 Others

No information available

6 Summary of the use of PFOS in open applications and the use of alternatives

Table 14: Summary overview of PFOS use and its alternatives in open applications

Use status	Alternatives used
Aviation hydraulic oils	
PFOS-related compounds may still be used.	Other fluorinated substances and non-fluorinated phosphate compounds other fluorinated substances and non-fluorinaed phosphate compounds could be use after considering hazards/risk characteristics.
Remarks: Considerable information gaps though there are several products established on the market for years.	
Fire-fighting foams	
The use of PFOS-related substances in new products has been phased out in most OECD countries. Stocks are still being used up.	C_6– fluorotelomers are used as substitutes in new products; fluorine-free alternatives are used for training exercises and possibly in other settings than offshore.
Remarks: 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.	
Pesticides	
Sulfluramid 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.	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
Remarks: 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).	

51 Contribution from USA.

Use status	Alternatives used
Metal plating	
PFOS-compounds are still used in hard chrome plating. Cr-III has replaced Cr-VI in decorative chrome plating.	Some non-fluorinated alternatives are marketed but they are not considered equally effective in hard chrome plating. A C_6-fluortelomer is used as a substitute and may be effective. PFBS derivatives may also be used. Non-chemical alternatives such as physical barriers may also be used.
Remarks: 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 is slightly higher than PFOS.	
Electrical and electronic parts	
PFOS-based chemicals are or have been used in the manufacture of digital cameras, mobile phones, printers, scanners, satellite communication, radar systems, etc.	For most of these uses, alternatives are available or are being developed.
Remarks: Considerable information gaps.	
Chemically driven oil production (Oil production and mining)	
PFOS derivatives may occasionally be used as surfactants in the oil and mining industries.	PFBS, telomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids and thioether acids
Remarks : Considerable information gaps.	
Carpets, leather and apparel, textiles and upholstery (Impregnation of textiles, leather and carpets)	
PFOS-related substances have been phased out in most OECD countries.	Other fluorinated compounds, like C_6-fluorotelomers and PFBS, silicone-based products, stearamidomethyl pyridine chloride, perfluorobutane sulfonate for leather[52]. Dendrimers.
Remarks: Both USA and China describe short chain alternatives used on their markets on a regular basis as alternatives to PFOS. Perfluorohexane sulfonyl 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 sulfonyl fluoride (PFhxSF) and its derivatives is up to 50 tons per year that is in line with production of PFOS. Perfluorohexane sulfonyl 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.	
Paper and packaging (Impregnation of paper and cardboard)	
PFOS-related substances have been phased out in most OECD countries.	Fluorotelomer-based substances and phosphates, mechanical processes
Remarks: Considerable information gaps.	
Coatings and coating additives (Surface coatings, paint and varnish)	
PFOS-related substances have been phased out in most OECD countries.	Telomer-based compounds, fluorinated polyethers, PFBS, propylated aromatics, silicone surfactants, sulfosuccinates, polypropylene glycol ethers. Dendrimers.
Remarks: Considerable information gaps. PFOS-related substances are no longer used on coatings and coating additives, although such articles may still be imported.	
Others (Cleaning agents, waxes and polishes for cars and floors)	
PFOS-related substances have been phased out in most OECD countries.	Fluorotelomer-based substances, fluorinated polyethers, C_4-perfluorinated compounds
Remarks: *Note that these applications are banned.*	

52 Information provided by Argentine in 2011.

7 Knowledge gaps and challenges

There are considerable information gaps concerning alternative chemical composition of aviation hydraulic oils though there are several products established on the market for years. It is hard to get information on the exact chemical composition of these products since it is considered confidential by manufacturers. There is a need however to release this information to properly evaluate health and environmental impact from these alternatives.

There is a lot of chemical data for the specific fluorinated and non –fluorinated alternatives for fire fighting foams that enable good health and environmental assessments of these components. However there are information gaps concerning in exact chemical composition of commercial fire fighting foams due to manufacturers' trade secrets, that may result in weak points in case assessments when these fire fighting foams are used in real situations.

The chemical alternatives for pesticide uses of PFOS are mostly systemic insecticides that range from highly toxic to humans and environment to low toxicity for humans and moderately to high toxicity to environment. Some of the alternatives are considered as less effective than PFOS. There are non-chemical alternatives including biological control methods which is important as pests are prone to evolve multiple resistance to chemical pesticides making them useless. As the suggested alternative pesticides have been on the market for decades and have been observed closely because of their hazardous properties, there is a lot of data available for these substances. Some of the biological controls have also been on the market for some years and been shown to be efficacious against a number of pests.

There is a lot of information and application scenarios available for alternatives to PFOS for metal plating where 6:2 FTS is considered as a possible alternative. However 6:2 FTS is not considered as equivalent to the performance of PFOS which is still used in large quantities worldwide for this purpose. More research is needed to develop equal or better alternatives to PFOS for metal plating to permit the phase out of PFOS for these applications.

There are considerable information gaps of alternatives to PFOS for electrical and electronic parts. More information needs to be collected from the market concerning the chemistry, market volumes etc of alternatives in order to assess them at all.

Alternatives to PFOS for impregnation or coating of textiles, leather and carpets as well as coating agents are well known and there is a good access of data available for further evaluations on health and environment. There are manufacturer trade secrets concerning detailed chemical product compositions that may be a weak point for detailed assessments when these alternatives are applied in production.

Dendrimers are used as non-fluorine alternatives to PFOS as water proofing agents on textiles and as coating agents. There are considerations concerning their impact on human health since cytotoxicity studies have shown dendrimers able to cross cell membranes, disrupt platelet function, and cause hemolysis. Due to our current lack of scientific knowledge of their potential impact to health it is currently hard to evaluate potential risks to human health.

There are considerable information gaps concerning alternatives to PFOS for water proofing agents on paper especially concerning esters and diesters of polyfluoroalkyl phosphonic acids and phosphoric acids (PAPs and diPAPs). Recent research indicates that these agents may transform into persistent perfluorinated carboxylic acids (PFCA). Still further research is needed to better understand all available alternatives to PFOS for paper proofing agents.

8 Conclusions and recommendations

There is little or no independent and reliable information publicly available on the toxicological and ecotoxicological characteristics of alternatives to PFOS and its related substances, with the exeption for PFHxA and PFBS and their related substances . There are major data gaps for most per- and polyfluorinated chemicals and their quantities produced and used on the market. Concerning several non fluorinated insecticides there is a lot of toxicological and ecotoxicological data available but very litte described concerning their actual handling at site and exposure to humans and the environment. However, efficacious non-chemical alternatives are available for these uses. Consequently it is for several reasons currently not possible to perform comprehensive risk assessment studies of the alternative substances since either little or no information is available concerning how these chemicals are actually used and their path ways and environmental fate in the environment which are key elements in the POP assessment process.

It is therefore strongly recommended to improve transparency of manufacturers on health and safety information, construct inventories on how these alternatives are actually used, quantities on the market and additionally assess independent scientific toxicological and ecotoxicological data together with monitoring data in order to assess any potential POP characteristics for the alternatives in question.

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Appendix 1

Summary of the types of data collected on the properties of identified alternatives to PFOS

A collection of measured and modelling data on the properties of identified alternatives to PFOS is contained in a complementary document (**in Excel format**). To view the Excel file, please download it from the website of the Stockholm Convention (www.pops.int/poprc) or contact the Secretariat by e-mail (kohno@pops.int).

The collection is based on available physical/chemical, toxicological and environmental data on alternatives and their principal degradation products. The table below provides a summary of the types of data collected and a description of their sources.

Table A1-1: Summary of the types of data collected on of the properties of alternatives and their principal degradation products (where applicable)

Property	References (if nothing else is stated)	Information
Substance:		
CAS RN:		If no CAS is available but the structure known then is the smiles created in MedChem designer added.
CA index name:		
Molecular formula:		
Molecular weight:		
Physical state at 20 C and 101.3 KPa		
Melting Point/range (°C)	Epi Suite v 1.43	Per default is the EPI Suite values given. The versions given in the reference list are the corresponding tools in EPI Suite version 4.1. In Brackets are the experimental values given. If no reference is given it is a experimental value collected in EPI suite. EPI SuitThe EPI (Estimation Programs Interface) Suite™ is a Windows®-based suite of physical/chemical property and environmental fate estimation programs developed by the EPA's Office of
Boiling Point/range (°C)	Epi Suite v 1.43	
Vapour Pressure, Pa (25°C)	Epi Suite v 1.43	
Water Solubility, g/l (25°C)	Epi Suite v 1.42	
Surface tension (optional)		
Partition coefficient n-octanol/water (log Pow)	Epi Suite v 1.68	
Soil adsorption coefficient (log Koc)	Epi Suite v 2.0	
Partition coefficient air/water (log Kaw)	Epi Suite v 1.10	

Property	References (if nothing else is stated)	Information
Partition coefficient octanol/air (log Koa)	Epi Suite v 1.10	Pollution Prevention Toxics and Syracuse Research Corporation (SRC). EPI Suite™ uses a single input to run the following estimation programs: KOWWIN™, AOPWIN™, HENRYWIN™, MPBPWIN™, BIOWIN™, BioHCwin, KOCWIN™, WSKOWWIN™, WATERNT™, BCFBAF™, HYDROWIN™, KOAWIN and AEROWIN™, and the fate models WVOLWIN™, STPWIN™ and LEV3EPI™. ECOSAR™, which estimates ecotoxicity, is also included in EPI Suite™. EPI Suite™ is a screening-level tool and should not be used if acceptable measured values are available. The Log Kow (Pow) is calculated also for compounds where this value is irrelevant (surfactants)
Atmospheric Oxidation, days (25 deg C)	Epi Suite AopWin v1.92	AOPWIN calculates half-lives in air, and if the half-life in air exceeds 2 days, this is an indication of LRTP (according to Annex D of the SC).
Half life (days/hours temp and media)		
Air	Epi Suite, level III fugacity model	LEV3EPI™: This program contains a level III multimedia fugacity model and predicts partitioning of chemicals among air, soil, sediment, and water under steady state conditions for a default model "environment". Some (but not all) system default values can be changed by the user.
Water	Epi Suite, level III fugacity model	
Soil	Epi Suite, level III fugacity model	
Sediment	Epi Suite, level III fugacity model	
Fish		
Human		
Toxicity		
	HSDB (http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB)	HSDB is a toxicology data file on the National Library of Medicine's (NLM) Toxicology Data Network (TOXNET®). It focuses on the toxicology of potentially hazardous chemicals. It is enhanced with information on human exposure, industrial hygiene, emergency handling procedures, environmental fate, regulatory requirements, nanomaterials, and related areas. All data are referenced and derived from a core set of books, government documents, technical reports and selected primary journal literature. HSDB is peer-reviewed by the Scientific Review Panel (SRP), a committee of experts in the major subject areas within the data bank's scope. HSDB is organized into individual chemical records, and contains over 5000 such records.

<table>
<tr><th>Property</th><th>References (if nothing else is stated)</th><th>Information</th></tr>
<tr><td>C&L Inventory database</td><td>http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database</td><td>This database contains classification and labelling information on notified and registered substances within REACH received from manufacturers and importers. It also includes the list of harmonised classifications.</td></tr>
<tr><td>Environment Canadas Substances on the DSL</td><td></td><td rowspan="5">On May 4, 1994, Environment Canada published the Domestic Substances List (DSL) in Part II of the Canada Gazette. The DSL is an inventory of approximately 23 000 substances manufactured in, imported into or used in Canada on a commercial scale. It is based on substances present in Canada, under certain conditions, between January 1, 1984 and December 31, 1986.
Meets CEPA Categorization Criteria (yes/no)
A substance meets the Government of Canada's criteria for categorization if it meets the human health criteria and/or the environmental criteria for categorization as defined in Section 73 of CEPA 1999.
Meets Human Health Categorization Criteria (yes/no)
A substance meets the human health categorization criteria as defined in Section 73 of CEPA 1999 if it has great potential for human exposure or if it is persistent and/or bioaccumulative and inherently toxic to humans.
Human Health Priorities (high/moderate/low/post 2006)
Substances designated as "human health priorities" are substances that did not necessarily meet the strict criteria of the categorization exercise, but do require further attention from a human health perspective because they have potential for human exposure and/or they are inherently toxic to humans. Visit Health Canada's website for more information.
Meets Environmental Criteria for Categorization (yes/no)
A substance meets the environmental criteria for categorization if it is Inherently Toxic to aquatic organisms, and it is Persistentand/orBioaccumulative in the environment.
Persistent (yes/no)
Persistent chemical substances take a very long time to break down in the environment - sometimes many years. Because they last for so long, they can travel long distances and pollute a much wider area than those that break down quickly.</td></tr>
<tr><td>Meets GoC categorization criteria</td><td>http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=5F213FA8-1&wsdoc=D031CB30-B31B-D54C-0E46-37E32D526A1F</td></tr>
<tr><td>Meets Human health Categorization criteria</td><td></td></tr>
<tr><td>Other human health Priorities</td><td></td></tr>
<tr><td>Meets Environmnetal criteria for categorisation</td><td></td></tr>
</table>

Property	References (if nothing else is stated)	Information
Persistent		**Bioaccumulative (yes/no)** Bioaccumulative chemical substances can be stored in the organs, fat cells or blood of living organisms. Concentrations can build up and reach very high levels, and can also be transferred up the food chain. **Inherently toxic to aquatic organisms (yes/no)** Chemical substances that are known, through laboratory or other studies, or models to have a harmful effect on aquatic organisms, were considered, for the purpose of categorization, to represent substances that are inherently toxic to the environment.
Bioaccumulative		
Inherently toxic to aquatic organisms		

Appendix 2

A selection of alternatives to the use of PFOS in some major open applications

Table A2-1: A selection of alternatives to the use of PFOS fluoro surfactants in fire-fighting foams [2]

Composition	Trade names	Manufacturer
Fluorosurfactants		
Perfluorohexane ethyl sulfonyl betaine and C_6-fluorotelomers often used in combination with hydrocarbons.	FORAFACTM- products	DuPont
Dodecafluoro-2-methylpentan-3-one	NOVEC 1230	3M
Trade secret	STHAMEX AFFF 3%	Dr. Sthamer
Trade secret	Fomtec AFFF 3% and 6%	Dafo Formtec
Trade secret	Ansulite 3x3 low viscosity AFFF	Ansul Inc.
Trade secret	Hydral AR 3-3	Sabo-Foam
Information gaps	BIO HYDROPOL 6	Bio-Ex
Trade secret	Filmfoam 813 (3%) - 816 (6%) AFFF	
	Comment: Filmfoam 813 is an aqueous film forming foam concentrate (AFFF) consisting of fluorocarbon and hydrocarbon surfactants[53]	
Information gaps	Towalex AFFF 3%	Tyco Fire integrated Solutions
Fluorine-free fire-fighting foams[54]		
Protein-based foams	Sthamex F-15	Dr. Sthamer
Products that contain glycols	Hi Combat ATM, "Trainol"[55]	AngusFire
	Comment: Synthetic detergent foams, often used for forestry, high-expansion applications and for training e.g marine uses	
Information gaps	PROFOAM 806G	Kroda Kerr
Trade secret	Moussol FF 3/6	Dr. Sthamer
Information gaps	Re-healing foam RF3X6 ATC 3% - 6%	Alf Lea Co
Information gaps	BIO FOR N	Bio-Ex
Information gaps	Centrifoam _Hi_foam	Kroda Kerr
Trade secret	HotFoam Meteor P+ Foam	Tyco
Information gaps	Moussol APS 3%	Dr. Sthamer
Information gaps	STHAMEX – SVM – P	Dr. Sthamer
Exact chemical composition is trade secret	Solberg foam HI-EX	Solberg
	Comment: Content is known for those ff foams. See the data security sheets or Solberg's web site.[56]	
Exact chemical composition is trade secret	Arctic foam 603EF ATC 3% - 3%	Solberg
	Comment: Content is known for those ff foams. See the data security sheets or Solberg's web site	
Exact chemical composition is trade secret	Arctic foam 201AF AFFF 1%	Solberg
	Comment: Content is known for those ff foams. See the data security sheets or Solberg's web site	
Information gaps	Towalex MB 3	Tyco Fire integrated Solutions
Information gaps	Arctic foam 602 ATC 3% - 6%	Solberg
	Comment: Content is known for those ff foams. See the data security sheets or Solberg's web site	
Information gaps	Arctic foam 203 AFFF 3%	Solberg
	Comment: Content is known for those ff foams. See the data security sheets or Solberg's web site	
Information gaps	Orchidex ME 3% eco	Angus Fire
Information gaps	Expandol	Angus Fire

53 www.kidde.com.ar/utcfs/ws-639/Assets/Filmfoam%20813%20-%20DS%20-%2004%20.pdf

54 www.kidde.com.ar/utcfs/ws-639/Assets/Filmfoam%20813%20-%20DS%20-%2004%20.pdf

eral Trainol products and actually a variety of fluorine free foams are shown on the AngusFire site here: http://www.angusfire.co.uk/utcfs/Templates/Pages/Template-53/0,8062,pageId%3D1410%26siteId%3D404,00.html

56 http://www.solbergfoam.com/

Table A2-2: A selection of fluorine-free products, fluorine bearing non-PFOS and PFOS and related substances for metal plating.[57]

Composition	Trade names	Manufacturers	Comments
Fluorine-free products			
Mainly alkane sulfonates	Sureact CR-H Slotochrom SV31[58] Antifog CR SurTec 850 SK4 Ankor Wetting Agent FF TIB Suract CRH	TIB Schlötter Chemisol SurTec Enthone Inc. TIB	Some of the products in this section are not resistant in chrome sulfuric acid pickling and hard chrome baths[59]
Fluor-based non-PFOS[60]			
6:2 FTS (=H4PFOS)	Capstone FS10 Proquel OF	DuPont Kiesow	Not resistant to hard chromium plating, less effective in decorative chromium plating
Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxo) ethane sulfonate	FC-53	China product	
Potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetraflouroethane sulfonate	FC-53b	China product	
1H,1H,2H,2H-perfluorooctane sulfonic acid	Fumetrol®21	Atotech	

Table A2-3: A selection of alternatives to the use of PFOS for carpets, leather and apparel, textiles and upholstery [2] [3].

Composition	Trade names	Traders	Comments
Fluorine-free products			
Hyperbranched hydrophobic polymers (dendritic i, e. highly branched polymers) and specifically adjusted comb polymers as active components. Glycols are added as solvents and cationic surfactants in small amounts act as emulsifiers.	RUCO-DRY ECO	Rudolf GmbH (Germany)	Superhydrophobic surfaces, meaning.contact angles larger than 150°. Rudolf Chemie describes the coating as a bionic Lotus coating addressed after the Lotus plant leaves. Applied in coatings, textile and leather.
Siloxanes and silicone polymers Mixtures of silicones and stearamidomethyl pyridine chloride, sometimes together with carbamide (urea) and melamine resins;	Advantex™	Bluestar Silicones	Impregnation of all-weather textiles. Surfactants for the impregnation of textile fabrics, leather, carpets, rugs and upholstery and similar articles
Fluor-based non-PFOS			
Perfluorobutane sulfonate (PFBS) derivatives or other alternatives based on various C_4-perfluorocompounds Fluorotelomer alcohols and esters	Scotchgard TM Zonyl® Capstone®	3M Du Pont	Applied in coatings, printing, and textiles
Fluorinated polymers	Foraperle® 225, etc.	Du Pont	Impregnation of leather and indoor car upholstery

57 Additional information on the use of PFOS and alternatives is available from the National Association for Surface Finishing (http://www.nasf.org/).

58 This product is only usefull for decorative chrome plating [5].

59 Communication with Lanxess.

60 There are many more fluorinated substances listed in the Danish Ministry of Environment report [5].

Table A2-4: A selection of alternatives to the use of PFOS for coating and coating additives [2] [3].

Composition	Trade names	Traders	Comments
Fluorine-free products			
Hyperbranched hydrophobic polymers (dendritic i, e. highly branched polymers) and specifically adjusted comb polymers as active components. Glycols are added as solvents and cationic surfactants in small amounts act as emulsifiers.	RUCO-DRY ECO	Rudolf GmbH (Germany)	Superhydrophobic surfaces, meaning.contact angles larger than 150°. Rudolf Chemie describes the coating as a bionic Lotus coating addressed after the Lotus plant leaves. Applied in coatings, textile and leather.
Siloxanes and silicone polymers Mixtures of silicones and stearamidomethyl pyridine chloride, sometimes together with carbamide (urea) and melamine resins;	Advantex™	Bluestar Silicones	Impregnation of all-weather textiles.
Sulfosuccinates, for example the sodium salt of di-(2-ethylhexyl) sulfosuccinate dissolved in ethanol and water Silicone polymers, such as polyether-modified polydimethyl siloxane, mixed with di-(2-ethylhexyl) sulfosuccinate in ethanol and water or fatty alcohol polyglycol ether sulfate	WorléeAdd®		Surfactants for the impregnation of textile fabrics, leather, carpets, rugs and upholstery and similar articles Wood primers and printing inks
Propylated naphthalenes and propylated biphenyls	Ruetasolv®	Rütgers Kureha Solvents	Water repelling agents for applications such as rust protection systems, marine paints, resins, printing inks and coatings in electrical applications
Fluor-based non-PFOS			
Perfluorobutane sulfonate (PFBS) derivatives or other alternatives based on various C_4-perfluorocompounds	Scotchgard	3M	Applied in coatings, printing, and textiles
Fluorotelomer alcohols and esters Fluorinated polyethers	Zonyl® Capstone TM® PolyFox™	Du Pont	
Fluorinated polymers	Foraperle® 225, etc.	Du Pont	Impregnation of leather and indoor car upholstery

Appendix 3

List of abbreviations and acronyms

ADHD	Hyperactivity disorder
AFFF	Aqueous Film Forming Foam
BAT	Best Available Technology
BEP	Best Environment Practice
BREF	BAT Reference Document
CAS RN	Chemical Abstracts Service Registration Number
CMP	Chemical-mechanical polishing
D4	Octamethyl cyclotetrasiloxane
D5	Decamethyl cyclopentasiloxane
D6	Dodecamethyl cyclohexasiloxane
diPAPs	Diesters of polyfluoroalkyl phosphonic acids and phosphoric acids
CBI	Confidential business information
COP	Conference of the Parties
6:2 FTS	6:2 fluorotelomer sulfonate
FTOH	Fluor telomere alcohol
MDM	Octamethyl trisiloxane
MD2M	Decamethyl tetrasiloxane
MD3M	Dodecamethyl pentasiloxane
MM (or HMDS)	Hexamethyl disiloxane
MSDS	Material Safety Data Sheet
NH4PFHx	,Ammonium perfluorohexanoate
OECD	Organisation for Economic Co-operation and Development
PBT	Persistence, Bioaccumulation and Toxicity
PBS	Packed Bed Scrubber
PAPs	Polyfluoroalkyl phosphonic acids and phosphoric acids
PFAS	Perflouroalkyl Sulphonate
PFBS	Perfluorobutane sulphonate
PFC	Perfluorinated Compound
PFCA	Perfluoroalkyl carboxylic acid
PFOS	Perfluorooctane Sulfonic Acid
PFOSA	Perfluorooctanesulphonic Acid
PFOSF	Perfluorooctanesulphonyl Fluoride
PFHxS	Perfluorohexane sulfonic acid
PFHxA	Perfluorohexanoic acid
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
POPRC	POP Review Committee
POPs	Persistent Organic Pollutants
THPFOS	Tetra Hydro PFOS
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency

Appendix 4

Guidance to assist Parties in updating their NIP to address the new POPs: Draft terminology

The definitions and regulatory terms provided in this appendix were developed for use with a set of guidance documents on updating national implementation plans with information on newly listed persistent organic pollutants (see the website of the Stockholm Convention) and they should be considered within the context of the provisions established by the Stockholm Convention for each substance.

Chemical terms

Agent
Any physical, chemical, or biological entity that can induce an adverse response (synonymous with stressor) (vocabulary handbook of POPs Contaminated sites).

Article
An object which during production is given a special shape, surface or design, which determines its function to a greater degree than does its chemical composition. Examples of articles are a car, battery, computer, telephone, printer, clothes, and refrigerator. Articles can contain liquids (e.g. car: brake fluid) and gases (e.g. refrigerator: compressed cooling gas).

Chemical good/good
A substance or a mixture/preparation or an article.

Chemical identity
A name that will uniquely identify a chemical. This can be a name that is in accordance with the nomenclature systems of the International Union of Pure and Applied Chemistry (IUPAC) or the Chemical Abstracts Service (CAS), or a technical name.

Chemical product/product[61]
A chemical substance and/or mixture/preparation of chemical substances with certain percentages or percentage ranges of the chemical substances.

Chemical substance/chemical/substance
Chemical elements and their compounds in the natural state or obtained by any production process, including any additive necessary to preserve the stability of the product and any impurities deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition.

Compound
Found something for “organic chemical/compound” – An organic chemical or compound is a substance that contains mainly carbon, hydrogen and oxygen...(vocabulary handbook of POPs Contaminated sites)

Contaminant
Any chemical substance whose concentration exceeds background concentrations or that does not naturally occur in the environment (vocabulary handbook of POPs Contaminated sites).

UNEP: Any physical, chemical, biological, or radiological substance or matter present in any media at concentrations that may result in adverse effects on air, water, or soil.

Generic name
A name that is not specific for a chemical substance, but describes a class of chemicals. A generic name is used by industry, for example, to protect confidential business information when the identity of the chemical should not be revealed through the chemical identity

61 The term product is sometimes used to include chemicals, mixtures and articles

Glycolysis / Chemical recovery
The creation of energy through the intramuscular combustion of glycogen. In other words, the muscles burning stored sugar for energy.

Intermediate
A substance that is manufactured for and consumed in or used for chemical processing in order to be transformed into another substance

Listed polybrominated diphenyl ethers (PBDEs) or POP-PBDEs
Polybrominated diphenyl ethers listed as POPs in Annex A of the Stockholm Convention –tetrabromodiphenyl ether and pentabromodiphenyl ether – and – hexabromodiphenyl ether and heptabromodiphenyl ether

Mixture/preparation
A mixture or a solution composed of two or more substances in which they do not react

Metabolism
The conversion or breakdown of a substance from one form to another by a living organism (vocabulary handbook of POPs Contaminated sites)

PFOS related chemicals
Chemicals that contain the structural element PFOS in their molecular structure as they are and were produced with perfluorooctane sulfonic acid (PFOS), its salts or perfluorooctane sulfonyl fluoride (PFOSF) as an intermediate or starting material

Plastic
A plastic material is any of a wide range of synthetic or semi-synthetic organic solids that are moldable

Polymer / Polymer fraction
A substance consisting of molecules characterised by the sequence of one or more types of monomer units.

Precursor
A chemical that can be transformed to produce another chemical. For example, some residual monomer chemicals from the telomer manufacturing process, such as telomer alcohols and telomer iodides, are PFOA precursors because they may remain in the final product and can be transformed into PFOA. (OECD)

Sample
Specimen or small quantity of something
Structural formula
Chemical elements and their compounds in the natural state or obtained by any production process, including any additive necessary to preserve the stability of the product and any impurities deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substances or changing its composition. (OECD)

Trade name
A name that is given to a chemical, a mixture or an article by the company that markets/ supplies it. The trade name normally specifically identifies the chemical, mixture, or article and sometimes gives information on the company

Common name
A name that is given to a chemical to be able to communicate more easily, especially with the public, than through the often complicated systematic chemical name

Recycling and Waste Management Terms

Bio-solids
Solid or semisolid material obtained from treated wastewater, often used as fertilizer.
Disposal
Final placement or destruction of toxic, radioactive, or other wastes; surplus or banned pesticides or other chemicals; polluted soils; and drums containing hazardous materials from removal actions or accidental releases. Disposal may be accomplished through use of approved secure landfills, surface impoundments, land farming, deep-well injection, ocean dumping, or incineration (vocabulary handbook of POPs Contaminated sites)

Downcycling
Downcycling is a term used to refer to the recycling process when the resultant material is below the quality of the original source. An example of this is the conversion of plastics into lower-quality plastics. (Posner)

Dumpsite (open / controlled)
An open dumpsite is any physical, chemical, biological, or radiological substance or matter present in any media at concentrations that may result in adverse effects on air, water, or soil. A controlled dumpsite is a non-engineered disposal site where improvement is implemented on the operational and management aspects rather then on the facility or structural requirements.

Effluent
An outflowing of water or gas from a natural body of water, or from a human-made structure

UNEP: Any solid, liquid or gas that enters the environment as a byproduct of human activities.

End product
The result of a completed series of processes or changes

Incineration
A treatment technique uses heat to remove contamination from solid, liquid, or gaseous materials. Hazardous organic compounds are converted to ash, carbon dioxide and water. Temperatures will vary depending on the type of contamination and the contaminated material (vocabulary handbook of POPs Contaminated sites)

Landfill
An engineered waste management facility at which waste is disposed by placing it on or in land in a manner that minimizes adverse human health and environmental effects (vocabulary handbook of POPs Contaminated sites)

Point source pollution / Diffuse pollution
A stationary location or fixed facility from which pollutants are discharged; any single identifiable source of pollution; e.g. a pipe, ditch, ship, ore pit, factor smokestack.(vocabulary handbook of POPs Contaminated sites) / Diffuse source/pollution : from widespread activities with no one discrete source, e.g. acid rain, pesticides, urban runoff, landfill sites, large industrial complexes containing a number of point sources,..(Vocabulary handbook of POPs Contaminated sites)

Pollutant
Generally, any substance intruded into the environment that adversely affects the usefulness of a resource or the health of humans, animals, or ecosystems (vocabulary handbook of POPs Contaminated sites)

Pyrolysis
Decomposition or transformation of a compound caused by heat.

Runoff
Also known as surface runoff, water from precipitation or irrigation that does not evaporate or seep into soil but flows into rivers, streams or lakes and that may carry sediment (vocabulary handbook of POPs Contaminated sites)

Recyclate
Recycled material that will be used to form new products

Sewage
Liquid and solid waste carried off in sewers or drains

Sludge
A semisolid residue from air or water treatment processes. Residues from treatment of metal wastes and the mixture of waste and soil at the bottom of a waste lagoon are examples of sludge, which can be a hazardous waste (vocabulary handbook of POPs Contaminated sites)

Stockpiles
A reserve of a chemical as a substance and/or preparation, and/or of articles containing the chemical accumulated within a country that are still allowed to be used under the Convention. If stockpiles are no longer to be used according to any specific exemption specified in Annex A or acceptable purpose specified in Annex B and if they are not allowed to be exported according to paragraph 2 of Article 3 they shall be deemed to be waste.

Waste
Substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law

Waste categories
Waste in many different forms e.g solid wastes; gaseous wastes etc

Waste hierarchy
The order of preference of waste management techniques, reduce, reuse, recycle, dispose etc.

Wastewater
Wastewater is spent or used water from an individual home, a community, a farm, or an industry that contains dissolved or suspended matter (vocabulary handbook of POPs Contaminated sites)

Water effluents
An outflowing of water from a natural body of water, or from a human-made structure

Regulatory terms

Notified acceptable purpose (DDT; PFOS, its salts, PFOSF and PFOS related chemicals)
An acceptable purpose listed in Annex B to produce or use a POP that has been notified by a Party to the Secretariat

Notified exemption for articles in use
An exemption for types of articles containing POPs provided the Party has notified to the Secretariat that a particular type of article remains in use within that Party

Notified use as site limited intermediate
An exemption for production and use of a POP as a closed-system site-limited intermediate provided the Party has notified this production and use to the Secretariat

POPs allowed for laboratory-scale research or as a reference standard
The POPs listed in Annex A and B can be used for laboratory-scale research or as a reference standard

Registered exemptions (lindane; endosulfan; PFOS, its salts, PFOSF and PFOS related chemicals)
A specific exemption listed in Annex A or B to produce or use a POP that has been notified by a Party to the Secretariat to be registered in the register of specific exemption

Unintentional trace contaminant
A chemical substance, mixture, or article that contains unintentionally a POP listed in Annex A or B in a concentration higher than a trace contaminant is regulated as POPs

Other terms

Best Available Technology /Technique
The most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques from providing in principle the basis for emission limit values designed to prevent and, where that is not practical, generally to reduce emissions and impact on the environment as a whole (vocabulary handbook of POPs Contaminated sites)

Best Environmental Practice
A method or technique that has consistently shown results superior to those achieved with other means, and that is used as a benchmark

Closed-loop systems
Closed system not relying on matter exchange outside of the system

End-of-life vehicle
An individual vehicle that is no longer suitable for use, and which is intended for dismantling and recovery of spare parts or is destined for material recovery and recycling or final disposal

End-of-use vehicle
A vehicle that is no longer used as intended by the previous owner, but may be fully functional and used appropriately by others

GHS
The Globally Harmonised System for Classification and Labelling of Chemicals (or the "GHS") and is an internationally agreed standard to classify hazardous chemical substances and mixtures and to label them according to their hazard and to provide a safety data sheet for professional use

Inventory
a complete listing of merchandise or stock on hand, work in progress, raw materials, finished goods on hand, etc., made each year by a business concern

Label
An appropriate group of written, printed, or graphic information elements concerning a hazardous product, selected as relevant to the target sector(s), that is affixed to, printed on, or attached to the immediate container of a hazardous product, or to the outside packaging of a hazardous product

Life cycle
Life cycle of a chemical means all stages of the life of a chemical with production of the chemical, mixtures, and articles containing the chemical, storage, transport, distribution, export, import, professional use, consumer use, recycling, and waste management of the chemical, mixtures, and articles containing the chemical

Material flow
An analytical method of quantifying flows and stocks of materials or substances in a well-defined system

Obsolete pesticides
Pesticides that cannot be used for legal or technical reasons, which may include the following:

- banned for use
- physically degraded
- chemically degraded
- ineffective as a pesticide
- expired
- not needed
- unidentified (e.g. no label or labelled in a foreign language)
- non-compliant with local regulations (e.g. wrong package)
- unsuitable formulation (e.g. cannot be used with available application equipment)

Pesticide
Any substance or mixture of substances intended for preventing, destroying, or controlling any pest. Pests include vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products, or animal feedstuffs. A pesticide is also any substance administered to animals for the control of insects, arachnids, or other pests in or on their bodies or substances intended for use as a plant growth regulator, defoliant, desiccant, or agent for thinning fruit or preventing the premature fall of fruit. The term can also be used for substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport

Production chain
The network of retailers, distributors, transporters, storage facilities and suppliers that participate in the sale, delivery and production of a particular product