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Pollutants**

Persistent Organic Pollutants Review Committee

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Agenda item 4 (d)

**Technical work: consolidated guidance on alternatives to
perfluorooctane sulfonic acid and its related chemicals**

**Consolidated guidance on alternatives to perfluorooctane
sulfonic acid and its related chemicals**

Note by the Secretariat

The annex to the present note contains the consolidated guidance on alternatives to perfluorooctane sulfonic acid and its related chemicals as agreed at the twelfth meeting of the Committee. The present note, including its annex, has not been formally edited.

Annex

**Consolidated guidance on alternatives to
perfluorooctane sulfonic acid (PFOS) and its
related chemicals**

Persistent Organic Pollutants Review Committee

September 2016

Disclaimer

The present document is a status report based on available information on alternatives to perfluorooctane sulfonic acid (PFOS) and its related chemicals from various sources. It is important to note that data gaps remain with regard to potential alternatives to PFOS and its related chemicals. The data presented in the document are indicative with respect to possible alternatives and it is important that research continue with the aim of identifying possible alternatives and their risks. Concerning the hazards and risks of the identified alternatives, the document responds to specific issues related to the Stockholm Convention and does not address issues unrelated to persistent organic pollutants.

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List of abbreviations and acronyms

AFFF	Aqueous film-forming foams
AR-AFFF	Alcohol-resistant aqueous film-forming foams
AR-FFFP	Alcohol-resistant film-forming fluoroprotein foams
BCF	Bioconcentration factor
CAS	Chemical Abstract Service
CBI	Confidential Business Information
CCD	Charge-coupled device (technology for capturing digital images)
CEN	European Committee for Standardization
CoRAP	Community Rolling Action Plan
D4	Octamethyl cyclotetrasiloxane
D5	Decamethyl cyclopentasiloxane
D6	Dodecamethyl cyclohexasiloxane
diPAPs	Diesters of polyfluoroalkyl phosphonic acids and phosphoric acids
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
EEA	European Economic Area
ETFE	Ethylene tetrafluoroethylene
EtFOSA	<i>N</i> -ethyl perfluorooctane sulfonamide (sulfluramid)
EtFOSE	<i>N</i> -ethyl perfluorooctane sulfonamidoethanol
EtFOSEA	<i>N</i> -ethyl perfluorooctane sulfonamidoethyl acrylate
EtFOSEP	Di[<i>N</i> -ethyl perfluorooctane sulfonamidoethyl] phosphate
EU	European Union
F-53	Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate/perfluoro[hexyl ethyl ether sulfonate]
F-53B	Potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate
FC-80	Potassium perfluorooctane sulfonate
FC-98	Potassium perfluoroethyl cyclohexyl sulfonate
FC-248	Tetraethyl ammonium perfluorooctane sulfonate
FFFC	Fire Fighting Foam Coalition
FFFP	Film-forming fluoroprotein foams
FTOH	Fluorotelomer alcohol
GHS	Globally Harmonisation System
INCI	International Nomenclature of Cosmetic Ingredients
LD ₅₀	Lethal Dose, 50%
MeFOSA	<i>N</i> -methyl perfluorooctane sulfonamide
MeFOSE	<i>N</i> -methyl perfluorooctane sulfonamidoethanol
MeFOSEA	<i>N</i> -methyl perfluorooctane sulfonamidoethyl acrylate OECD
MDM	Octamethyl trisiloxane
MD2M	Decamethyl tetrasiloxane
MD3M	Dodecamethyl pentasiloxane
MM (or HMDS)	Hexamethyl disiloxane
NGLF	Norsk Galvanoteknisk Landsforening
NIP	National Implementation Plan
NOAEC	No Observable Adverse Effect Concentration
NOAEL	No Observable Adverse Effect Level
OECD	Organisation for Economic Co-operation and Development
PAPs	Polyfluoroalkyl phosphonic acids and phosphoric acids
PFAAs	Perfluoroalkylic acids

PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFBSF	Perfluorobutane sulfonyl fluoride
PFBSK	PFBS potassium salt
PFCs	Polyfluorinated chemicals
PFCA	Perfluoroalkyl carboxylic acid
PFDA	Perfluorodecanoic acid
PFDS	Perfluorodecane sulfonic acid
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFOSA	Perfluorooctane sulfonamide
PFOSF	Perfluorooctane sulfonyl fluoride
PFSA	Perfluoroalkane sulfonic acid
POPs	Persistent Organic Pollutants
POPRC	Persistent Organic Pollutants Review Committee
PTFE	Polytetrafluoroethylene
USEPA	United States Environmental Protection Agency
ZVO	German national metal plating association
QSAR	Quantitative-structure-activity-relationships

I. Introduction

A. History of the considerations on alternatives to PFOS and its related chemicals under the Stockholm Convention

1. Since perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) were listed in Annex B to the Stockholm Convention in 2009, substantive progress has been made in phasing out of the use of PFOS and its related chemicals. The use of PFOS and its related chemicals has been replaced in a number of applications, while some of the use in critical applications, where it is not currently possible without the use of PFOS, may need to continue. Below is a summary of the history of the work under the Stockholm Convention on alternatives to PFOS and its related chemicals.

2. At its first meeting (November 2005), the Persistent Organic Pollutants Review Committee examined the proposal submitted by Sweden to list perfluorooctane sulfonate and 96 potential perfluorooctane sulfonate precursors in Annex A to the Stockholm Convention (UNEP/POPS/POPRC.1/9, UNEP/POPS/POPRC.1/INF/9). By decision POPRC-1/7, the Committee decided that it is satisfied that the screening criteria have been fulfilled for perfluorooctane sulfonate, as set out in the evaluation contained in the annex to that decision.

3. At its second meeting (November 2006), by decision POPRC-2/5, the Committee decided that perfluorooctane sulfonate is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and environmental effects such that global action is warranted. The Committee adopted the risk profile for perfluorooctane sulfonate as set out in document UNEP/POPS/POPRC.2/17/Add.5.

4. At its third meeting (November 2007), the Committee concluded that one of the substances included in the original proposal to list PFOS in Annexes A, B or C to the Stockholm Convention, PFOSF, is the most common starting material for different PFOS derivatives, that the probability that PFOSF will degrade to PFOS is very high and that therefore listing PFOSF together with PFOS acid and its salts would be the most effective measure to reduce releases of PFOS to the environment. By decision POPRC-3/11, the Committee concluded that PFOSF fulfills the criteria in Annex D, and that PFOSF, through its transformation product PFOS, is likely, as a result of long-range environmental transport, to lead to significant adverse effects on human health and/or the environment such that global action is warranted. By decision POPRC-3/5, the Committee adopted the risk management evaluation for perfluorooctane sulfonate as set out in document UNEP/POPS/POPRC.3/20/Add.5 and recommended to the Conference of the Parties that it consider listing PFOS (CAS No: 1763-23-1), its salts and PFOSF (CAS No: 307-35-7) in Annexes A or B to the Convention.

5. Furthermore, at its fourth meeting (October 2008), the Committee adopted the addendum to the risk management evaluation as set out in document UNEP/POPS/POPRC.4/15/Add.6. The addendum included a summary of new information on perfluorooctane sulfonate submitted during the intersessional period between the third and fourth meetings of the Committee. Also, at its fourth meeting, the Committee established the first intersessional working group on substitution and alternatives (UNEP/POPS/POPRC.4/15, para 123).

6. The Conference of the Parties at its fourth meeting (May 2009), by decision SC-4/17, decided to list PFOS, its salts and PFOSF in Annex B to the Convention with following acceptable purposes and specific exemptions:¹

- (a) Acceptable purposes:
 - (i) Photo-imaging;
 - (ii) Photoresist and anti-reflective coatings for semiconductors;
 - (iii) Etching agent for compound semiconductors and ceramic filters;
 - (iv) Aviation hydraulic fluids;
 - (v) Metal plating (hard metal plating) only in closed-loop systems;

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<http://chm.pops.int/Implementation/Exemptionsandacceptablepurposes/SpecificExemptionsAcceptablePurposes/tabid/790/Default.aspx>.

- (vi) Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters);
- (vii) Fire fighting foam;
- (viii) Insect baits for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp.;
- (b) Specific exemptions:
 - (i) Photo masks in the semiconductor and liquid crystal display (LCD) industries;
 - (ii) Metal plating (hard metal plating);
 - (iii) Metal plating (decorative plating);
 - (iv) Electric and electronic parts for some colour printers and colour copy machines;
 - (v) Insecticides for control of red imported fire ants and termites;
 - (vi) Chemically driven oil production;
 - (vii) Carpets;
 - (viii) Leather and apparel;
 - (ix) Textiles and upholstery;
 - (x) Paper and packaging;
 - (xi) Coatings and coating additives;
 - (xii) Rubber and plastics.

7. In addition, by decision SC-4/19, the Conference of the Parties established indicative elements of a work programme to facilitate the elimination of listed brominated diphenyl ethers and the restriction or elimination of PFOS and its salts, PFOSF and other chemicals listed in Annexes A or B of the Convention at the fourth meeting of the Conference of the Parties.

8. At its fifth meeting (October 2009), the Committee considered the work undertaken by the intersessional working group on substitution and alternatives. By decision POPRC-5/2, the Committee adopted the general guidance on considerations related to alternatives and substitutes for persistent organic pollutants and candidate persistent organic pollutants as set out in document UNEP/POPS/POPRC.5/10/Add.1 and requested the intersessional working group to continue to develop guidance on PFOS alternatives based on the annotated outline set out in annex V to document UNEP/POPS/POPRC.5/10.

9. At its sixth meeting (October 2010), the Committee considered the outcome of the work programme on new POPs adopted in decision SC-4/19 and reviewed the information on PFOS, its salts and PFOSF submitted by parties and observers. By decision POPRC-6/2, the Committee decided that the recommendations on how to fill the identified information gaps and the recommendations on the elimination of brominated diphenyl ethers from the waste stream and on risk reduction for PFOS, its salts and PFOSF as contained in the annex to that decision should be submitted to the Conference of the Parties at its fifth meeting for its consideration. The recommendations on risk reduction for PFOS, its salts and PFOSF were set out in part II of the annex to decision POPRC-6/2.

10. Furthermore, by decision POPRC-6/5, the Committee endorsed the guidance on alternatives to PFOS and its derivatives as set out in document UNEP/POPS/POPRC.6/13/Add.3 and agreed that the guidance document should be revised regularly as necessary to take into account available information on alternatives to PFOS and its derivatives.

11. The Conference of the Parties at its fifth meeting (May 2011), by decision SC-5/5, encouraged parties and other relevant stakeholders to implement where appropriate, taking into account national circumstances, the recommendations set out in the annex to decision POPRC-6/2 on the elimination from the waste stream of brominated diphenyl ethers that are listed in Annex A to the Convention and on risk reduction for PFOS, its salts and PFOSF and requested the Committee to prepare a technical paper on the identification and assessment of alternatives to the use of PFOS in open applications.

12. At its seventh meeting (October 2011), by decision POPRC-7/5, the Committee adopted the terms of reference for a technical paper on the identification and assessment of alternatives to the use of PFOS in open applications as set out in the annex to that decision. Furthermore, the Committee considered the comments on the guidance on alternatives to PFOS and its derivatives and information on experience in replacing PFOS and its derivatives with additional alternative products and/or

processes, including information about their health and environmental effects submitted by parties and observers (UNEP/POPS/POPRC.7/INF/13). The Committee revised the guidance as set out in UNEP/POPS/POPRC.6/13/Add.3/Rev.1 and requested the Secretariat to further collect comments on the guidance from parties and observers.

13. At its eighth meeting (October 2012), the Committee reviewed the technical paper on the identification and assessment of alternatives to the use of PFOS, its salts, PFOSF and their related chemicals in open applications set out in document UNEP/POPS/POPRC.8/INF/17/Rev.1. By decision POPRC-8/8, the Committee adopted the recommendations on alternatives to the use of PFOS, its salts, PFOSF and their related chemicals in open applications, prepared on the basis of the technical paper and contained in the annex to that decision, for consideration by the Conference of the Parties at its sixth meeting. Furthermore, by decision POPRC-8/9, having considered the comments on the guidance received from parties and observers (UNEP/POPS/POPRC.8/INF/19) and decided to revise the guidance on the basis of those comments and any additional information made available to the working group.

14. The Conference of the Parties at its sixth meeting (May 2013), by decision SC-6/7, took note of the information provided by parties on their experiences in implementing the recommendations set out in the annex to decision POPRC-6/2 and took note of the recommendations set out in the annex to decision POPRC-8/8. Based on the recommendations, the Conference of the Parties encouraged parties to consider stopping their use of PFOS, its salts and PFOSF and related chemicals for the applications for which safer alternatives have been identified and are commercially available, which have been identified as follows:

- (a) Fire-fighting foams;
- (b) Insecticides for the control of imported red fire ants and termites;
- (c) Decorative metal plating;
- (d) Carpets;
- (e) Leather and apparel;
- (f) Textiles and upholstery.

15. The Conference of the Parties also invited parties that still use PFOS, its salts, PFOSF and their related chemicals for the control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. to undertake studies, including pilot projects, to obtain peer-reviewed information on the feasibility of using alternatives to PFOS, its salts, PFOSF and their related chemicals within an integrated pest management approach and to submit any results to the Secretariat.

16. The Conference of the Parties requested the Committee to revise the guidance on alternatives to PFOS, its salts, PFOSF and their related chemicals to incorporate the information contained in the technical paper on alternatives to PFOS, its salts, PFOSF and their related chemicals in open applications and any other pertinent information.

17. By decision SC-6/4, the Conference of the Parties adopted the process for the evaluation of the continued need for PFOS, its salts and PFOSF for the various acceptable purposes and specific exemptions in accordance with paragraphs 5 and 6 of part III of Annex B to the Convention. The process mandated the Committee to undertake the assessment of alternatives of PFOS, its salts and PFOSF.

18. Furthermore, by decision SC-6/10, the Conference of the Parties adopted the workplan for revising the guidance on best available techniques and best environmental practices (BAT/BEP) relevant to the newly listed POPs including for the use of PFOS and related chemicals listed under the Stockholm Convention (2012).²

19. At its ninth meeting (October 2013), by decision POPRC-9/5, the Committee endorsed the terms of reference for the assessment of alternatives to PFOS, its salts and PFOSF and the preparation of a report for the evaluation of information on PFOS, its salts and PFOSF. Furthermore, by decision POPRC-9/6, the Committee endorsed the revised guidance on alternatives to PFOS, its salts, PFOSF and their related chemicals as amended at its ninth meeting (UNEP/POPS/POPRC.9/INF/11/Rev.1).

20. At its tenth meeting (October 2014), by decision POPRC-10/4, the Committee submitted the summary of the report on the assessment of alternatives to PFOS, its salts and PFOSF set out in the annex to that decision, together with the full assessment report (UNEP/POPS/POPRC.10/INF/7/Rev.1)

² <http://chm.pops.int/tabid/3170/Default.aspx>.

and fact sheets on nine of the alternatives assessed (UNEP/POPS/POPRC.10/INF/8/Rev.1), to the Conference of the Parties for consideration at its seventh meeting.

21. Furthermore, the Committee concluded that the guidance on alternatives to PFOS, its salts, PFOSF and their related chemicals should be revised to incorporate pertinent information contained in the report on the assessment of alternatives to PFOS, its salts and PFOSF, in addition to the information contained in the technical paper on the identification and assessment of alternatives to the use of PFOS, its salts, PFOSF and their related chemicals in open applications and, as so revised, should be submitted to the Conference of the Parties to the Stockholm Convention at its eighth meeting, in 2017.

22. The Conference of the Parties at its seventh meeting (May 2015), by decision SC-7/1, noted that as there are no longer any parties registered for the specific exemptions for the production and use of PFOS, its salts and PFOSF for carpets, leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives and rubber and plastics, no new registrations may be made with regard to them. By decision SC-7/5, the Conference of the Parties welcomed the report on the assessment of alternatives to PFOS, its salts and PFOSF carried out by the Persistent Organic Pollutants Review Committee (UNEP/POPS/POPRC.10/INF/7/Rev.1) and the report by the Secretariat (UNEP/POPS/COP.7/INF/11) on the evaluation of the information on PFOS, its salts and PFOSF; took note of the information provided by parties on their experiences in implementing the recommendations set out in the annex to decision POPRC-6/2 (UNEP/POPS/COP.7/INF/12) and the report by the Secretariat on the main challenges encountered by parties in implementing the recommendations with regard to PFOS, its salts and POF SF (UNEP/POPS/COP.7/8, annex IV).

23. The Conference of the Parties concluded that parties may need to continue to produce and/or use PFOS, its salts and PFOSF for acceptable purposes as provided in Annex B to the Convention and consequently need to notify the Secretariat of their intention to produce and/or use those chemicals for those purposes.

24. By decision SC-7/8, the Conference of the Parties took note of the revised draft guidance on BAT/BEP for the use of PFOS and related chemicals listed under the Stockholm Convention (UNEP/POPS/COP.7/INF/21) and adopted workplan for the ongoing review and update of the guidelines on best available techniques and provisional guidance on best environmental practices as set out in the annex to that decision.

25. According to the workplan, the expert group on BAT/BEP was mandated to collect and evaluate new information on areas of concern identified by parties regarding the management of stockpiles and products and articles in use consisting of or containing PFOS, the assessment and remediation of PFOS-contaminated sites and success stories regarding the implementation of alternatives and revise and supplement the guidance document as appropriate, including through the development of case studies. With regard to the guidance on BAT/BEP relevant to the POPs listed in Annex A or Annex B to the Convention, supplement with new information on available alternatives as identified by the POPs Review Committee.

26. At its eleventh meeting (October 2015), by decision POPRC-11/6, the Committee decided to prepare revised guidance on alternatives to PFOS, its salts, PFOSF and their related chemicals, based on the proposal set out in the annex to document UNEP/POPS/POPRC.11/INF/11/Rev.1, for consideration at its twelfth meeting.

27. All the above-mentioned relevant decisions and documents can be found in appendix 9 to the present document and available on the website of the Stockholm Convention³.

B. Objectives

28. The current document is a consolidated guidance on alternatives to PFOS and its related chemicals. The document was prepared on the basis of the guidance on alternatives to PFOS and its related chemicals⁴ and the proposal for revising that document.⁵

29. The objective of the current document is to provide a summary of information on currently known alternatives to PFOS, its salts, PFOSF and their related chemicals. The ultimate goal is to enhance the capacity of developing countries and countries with economies in transition to phase-out those chemicals, taking into account the need for time to phase-in alternatives to some of the uses and the fact that alternatives to certain uses may not be currently readily available in all countries.

³ <http://chm.pops.int/Implementation/PFOS/Guidance/tabid/5225/Default.aspx>.

⁴ UNEP/POPS/POPRC.9/INF/11/Rev.1.

⁵ UNEP/POPS/POPRC.11/INF/11.

C. Information source

30. The information in this document is based on the submissions by parties and others on alternatives to PFOS and its related chemicals received before 21 July 2016.
31. As outlined above, the information on alternatives to PFOS, its salts, PFOSE and their related chemicals has been reported by the POPs Review Committee in several documents with different objectives. As such, the Conference of the Parties, by decision SC-6/7, requested the Committee to revise the guidance on alternatives to PFOS, its salts, PFOSE and their related chemicals⁶ to incorporate the information contained in other sources.
32. The current document consolidates the information from the following documents:
- (a) Guidance on alternatives to PFOS, its salts, PFOSE and their related chemicals (UNEP/POPS/POPRC.9/INF/11/Rev.1);
 - (b) Technical paper on the identification and assessment of alternatives to the use of PFOS, its salts, PFOSE and their related chemicals in open applications (UNEP/POPS/POPRC.8/INF/17/Rev.1);
 - (c) Report on the assessment of alternatives to PFOS, its salts and PFOSE (UNEP/POPS/POPRC.10/INF/7/Rev.1);
 - (d) Fact sheets on alternatives to PFOS, its salts and PFOSE (UNEP/POPS/POPRC.10/INF/8/Rev.1);
 - (e) Report for the evaluation of information on PFOS, its salts and PFOSE (UNEP/POPS/COP.7/INF/11);
 - (f) Any other pertinent information submitted by parties and observers including through national reporting in accordance with Article 15 and experiences in implementing the recommendations set out in decision POPRC-6/2.
33. The technical paper on the identification and assessment of alternatives to the use of PFOS, its salts, PFOSE and their related chemicals in open applications was prepared by a consultant in response to the request in decision SC-5/5 and used by the Committee to develop recommendations set out in decision POPRC-8/8.
34. The report on the assessment of alternatives to PFOS, its salts and PFOSE and the fact sheets on alternatives to PFOS, its salts and PFOSE were developed by the Committee and the report for the evaluation of information on PFOS, its salts and PFOSE was prepared by the Secretariat as part of the process for the evaluation of the continued need for PFOS, its salts and PFOSE for the various acceptable purposes and specific exemptions set out in decision SC-6/4. Based on those reports and other information, the Conference of the Parties conducted the evaluation at its seventh meeting and adopted decision SC-7/5. In accordance to this decision, POPRC will undertake a new assessment of alternatives to PFOS, its salts and PFOSE in 2018.
35. Comments from parties and others on the previous versions of the guidance on alternatives to PFOS, its salts, PFOSE and their related chemicals have also been taken into consideration.⁷
36. All the information on alternatives to PFOS and its related received from parties and others are available on the Convention website.⁸
37. The workplan of the expert group on BAT/BEP set out in the annex to decision SC-7/8 should also be noted as described in paragraph 26 above.
38. While publically available scientific data on some alternatives listed in the document are lacking, there is extensive data on other alternatives such as perfluorobutanoic acid (PFBA), perfluorobutane sulfonic acid (PFBS), perfluorohexanoic acid (PFHxA) and perfluorohexane sulfonic acid (PFHxS), for which studies are peer reviewed and published in journals. In addition, United States Environmental Protection Agency (USEPA) has been reviewing substitutes for PFOS,

⁶ UNEP/POPS/POPRC.9/INF/11/Rev.1.

⁷ UNEP/POPS/POPRC.6/INF/9, UNEP/POPS/POPRC.7/INF/13/Rev.1, UNEP/POPS/POPRC.8/INF/18, UNEP/POPS/POPRC.8/INF/19, UNEP/POPS/POPRC.9/INF/12/Rev.1, UNEP/POPS/POPRC.10/INF/9, UNEP/POPS/POPRC.11/INF/12, UNEP/POPS/POPRC.12/INF/[...].

⁸ <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC8/POPRC8Followup/SubmissionBDEsPFOS/tabid/3064/Default.aspx>.

<http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC9/POPRC9Followup/AlternativesPFOSSubmission/tabid/3565/Default.aspx>.

perfluorooctanoic acid (PFOA) and other long-chain perfluorinated substances since 2000, including over 150 alternatives of various types. Similarly, other government agencies have received and reviewed information on alternatives. Organisation for Economic Co-operation and Development (OECD) has established a web portal on perfluorinated chemicals to facilitate information exchange on perfluorinated chemicals.⁹

D. Other available information

39. The following related information and guidance is available:

- (a) Register of acceptable purposes and specific exemptions for PFOS, its salts and PFOSF (see <http://chm.pops.int/tabid/794/Default.aspx> and <http://chm.pops.int/tabid/4644/Default.aspx>);
- (b) Guidance on best available techniques and best environmental practices for the use of PFOS and related chemicals listed under the Stockholm Convention (see document UNEP/POPS/COP.7/INF/21; <http://chm.pops.int/tabid/3170/Default.aspx>);
- (c) Guidance for the inventory of PFOS and related chemicals listed under the Stockholm Convention on POPs (see document UNEP/POPS/COP.7/INF/26; <http://chm.pops.int/tabid/3169/Default.aspx>);
- (d) National regulatory actions related to PFOS, its salts and PFOSF reported by parties (see chapter IV of document UNEP/POPS/COP.7/INF/11);
- (e) Capacities for countries to transfer to reliance on alternatives to PFOS, its salts and PFOSF (see chapter V of document UNEP/POPS/COP.7/INF/11);
- (f) National reviews of the continued need for the specific exemption(s) and/or acceptable purpose(s) (see chapter VI of document UNEP/POPS/COP.7/INF/11);
- (g) Report on the assessment of alternatives to PFOS, its salts and PFOSF (Identification, prioritization, methodology, results, conclusions, information gaps) (see document UNEP/POPS/POPRC.10/INF/7/Rev.1);
- (h) Results of the prioritization of alternatives to PFOS (see appendix II of document UNEP/POPS/POPRC.10/INF/7/Rev.1);
- (i) Results of the prioritization of manufacturing intermediates for alternatives to PFOS (see appendix III of document UNEP/POPS/POPRC.10/INF/7/Rev.1);
- (j) Results of the screening assessment for 9 alternatives to PFOS (see appendix IV of document UNEP/POPS/POPRC.10/INF/7/Rev.1).

⁹ <http://www.oecd.org/ehs/pfc>.

II. Characteristics of PFOS and its related chemicals

A. PFOS and its related chemicals

40. Annex B to the Stockholm Convention lists PFOS, its salts and PFOSE. The following examples of salts are also listed: potassium perfluorooctane sulfonate; lithium perfluorooctane sulfonate; ammonium perfluorooctane sulfonate; diethanolammonium perfluorooctane sulfonate; tetraethylammonium perfluorooctane sulfonate; didecyltrimethylammonium perfluorooctane sulfonate (Table 1).

41. PFOS-related chemicals are chemicals that contain the structural element PFOS in their molecular structure and are or were produced with PFOSE as starting or intermediate material. Many of those PFOS-related chemicals are not mentioned in Annex B but are covered by the listing of PFOSE. Since PFOSE is the parent precursor to all PFOS related substances, therefore the present document includes descriptions of alternatives to all PFOS-related chemicals.

42. For more information, please refer to the risk profile¹⁰ and risk management evaluation¹¹ developed by the POPs Review Committee and the revised draft guidance on best available techniques and best environmental practices for the use of PFOS and related chemicals listed under the Stockholm.¹²

43. The chemical names, acronyms and CAS numbers of PFOS, its salts, and PFOSE listed in Annex B to the Stockholm Convention are summarized in Table 1 and other PFOS-related chemicals that are not listed in the Stockholm Convention are summarized in Table 2.

Table 1: Chemical names, acronyms and CAS numbers of PFOS, its salts, and PFOSE listed in Annex B to the Stockholm Convention

Chemical names	Acronyms	CAS No:
Perfluorooctane sulfonic acid	PFOS	1763-23-1
Perfluorooctane sulfonyl fluoride	PFOSE	307-35-7
Potassium perfluorooctane sulfonate	PFOSK	2795-39-3
Lithium perfluorooctane sulfonate	PFOSLi	29457-72-5
Ammonium perfluorooctane sulfonate	PFOSENH ₄	29081-56-9
Diethanolammonium perfluorooctane sulfonate	PFOSEDEA	70225-14-8
Tetraethylammonium perfluorooctane sulfonate	PFOSETEA	56773-42-3
Didecyltrimethylammonium perfluorooctane sulfonate	PFOSEDDA	251099-16-8

Table 2: Other PFOS-related chemicals that are not listed in the Stockholm Convention

Chemical names	Acronyms	CAS No:
Perfluorooctane sulfonamide	FOSA	754-91-6
<i>N</i> -Methyl perfluorooctane sulfonamide	MeFOSA	31506-32-8
<i>N</i> -Methyl perfluorooctane sulfonamidoethanol	MeFOSE	2448-09-7
<i>N</i> -Methyl perfluorooctane sulfonamidoethyl acrylate	MeFOSEA	25268-77-3
Ammonium bis[2- <i>N</i> -ethyl perfluorooctane sulfonamidoethyl] phosphate ¹³		30381-98-7
<i>N</i> -Ethyl perfluorooctane sulfonamide (sulfloramid)	EtFOSA	4151-50-2

¹⁰ UNEP/POPS/POPRC.2/17/Add.5.

¹¹ UNEP/POPS/POPRC.3/20/Add.5.

¹² UNEP/POPS/COP.7/INF/21, sections 1.3-1.5.

¹³ Alternative CAS name: 1-Octanesulfonamide, *N,N'*- [phosphinicobis(oxy-2,1-ethanediy)]bis[*N*-ethyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptafluoro-, ammonium salt.

Chemical names	Acronyms	CAS No:
<i>N</i> -Ethyl perfluorooctane sulfonamidoethanol	EtFOSE	1691-99-2
<i>N</i> -Ethyl perfluorooctane sulfonamidoethyl acrylate	EtFOSEA	432-82-5
Di[<i>N</i> -ethyl perfluorooctane sulfonamidoethyl] phosphate	EtFOSEP	67969-69-1
3-[[[(Heptadecafluorooctyl)- sulfonyl]amino]- <i>N,N,N</i> -trimethyl-1-propanaminium iodide/perfluorooctyl sulfonyl quaternary ammonium iodide	Fluorotenside -134	1652-63-7
Potassium <i>N</i> -ethyl- <i>N</i> -[(heptadecafluorooctyl) sulfonyl] glycinate		2991-51-7
<i>N</i> -Ethyl- <i>N</i> -[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide		61660-12-6

44. The proposal submitted by Sweden to list perfluorooctane sulfonate in the Annexes to the Convention included 96 potential perfluorooctane sulfonate precursors.¹⁴ The report published by the United Kingdom in 2004 contained a draft list of 98 compounds that have the potential to degrade to PFOS in the environment.¹⁵ The report published in China in 2009 indicated that 66 PFOS-related chemicals have been identified in a national inventory in China.¹⁶ In Denmark in 2007, 92 polyfluorinated substances, including 13 PFOS-related chemicals were registered as being used in products.¹⁷ In Canada in 2006, more than 60 PFOS-related chemicals have been listed.¹⁸ Many more PFOS-related chemicals were listed in the preliminary lists published by OECD in 2007.¹⁹

B. Chemicals structurally similar to PFOS

45. Perfluoroalkyl sulfonate (PFSA) is a generic term used to describe any fully fluorinated carbon chain length sulfonic acid, including PFOS and other higher and lower homologues.²⁰ There are several PFSA and derivatives thereof with shorter or longer alkyl chain lengths than PFOS that are used for applications similar to those for which PFOS is used – in other words as PFOS alternatives, though not necessarily safer alternatives. Some examples of PFSA are shown in Table 3.

Table 3: Examples of perfluoroalkyl sulfonate (PFSA)

Chemical names	Acronyms	CAS No:
Potassium perfluoroethyl cyclohexyl sulfonate	FC-98	67584-42-3
Perfluorobutane sulfonic acid	PFBS	59933-66-3
Potassium perfluorobutane sulfonate	K PFBS	29420-49-3
Perfluorohexane sulfonic acid	PFHxS	432-50-7
Perfluorodecane sulfonic acid	PFDS	335-77-3
Perfluorodecane sulfonate		67906-42-7

¹⁴ UNEP/POPS/POPRC.1/9, UNEP/POPS/POPRC.1/INF/9.

¹⁵ Risk and Policy Analysts and Building Research Environment. 2004. Perfluorooctane sulphonate: risk reduction strategy and analysis of advantages and drawbacks. United Kingdom Department for Environment, Food and Rural Affairs and Environment Agency for England and Wales.

¹⁶ <http://www.unep.org/chemicalsandwaste/Portals/9/CiP/InformalWorkshop2009/WorkshopMgmtChemicals/HWenya%20-%20PFOS%20in%20China.pdf>.

¹⁷ Jensen, A.A., Poulsen, P.B., Bossi, R. 2008. Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. Survey of Chemical Substances in Consumer Products, 99. Danish Environmental Protection Agency.

¹⁸ <http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=98B1954A-1>

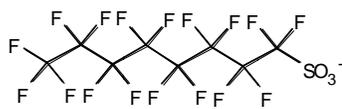
Ecological Screening Assessment Report on Perfluorooctane Sulfonate, Its Salts and Its Precursors that Contain the C8F17SO2 or C8F17SO3, or C8F17SO2N Moiety, 2006.

¹⁹ Preliminary lists of PFOS, PFAS, PFOA, PFCA, related compounds and chemicals that may degrade to PFCA, OECD, 2007 (ENV/JM/MONO(2006)15).

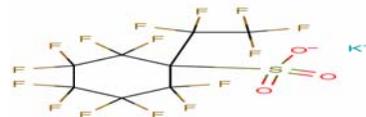
²⁰ <http://www.oecd.org/ehs/pfc/glossary.htm>.

46. As there are the restrictions on the use of PFOS, it is expected that chemicals that are structurally similar to PFOS and are not regulated, such as perfluoro[hexyl methyl ether sulfonate] and perfluoro[hexyl ethyl ether sulfonate] (F-53) are commercialized F-53 and is used as mist suppressant by Chinese metal plating enterprises.^{21, 22}

47. The similarity of these substances to PFOS is illustrated by the structure formulas below.



Perfluorooctane sulfonate (PFOS)



Potassium perfluoroethyl cyclohexyl sulfonate

C. Properties of PFOS and its related chemicals

48. The strong carbon-fluorine bond makes the perfluoroalkyl chain present in PFOS extremely stable and nonreactive. PFOS resists even strong acids and high temperatures and is not degradable in the environment. The basic PFOS structure is persistent, and the more complex PFOS-related chemicals will degrade to the basic PFOS structure during use or in the environment.

49. The surfactant properties of PFOS give extremely low surface tension. The perfluorocarbon chain is both oleophobic and hydrophobic; thus it repels water, oil and dirt and insulates electricity. According to fluorochemical producers these are considered critical properties of PFOS and perfluorinated surfactants polymers in a number of applications.²³

50. PFOS as a salt is more hydrophilic and soluble in water. The non-dissociated acid and the sulfonamides are less hydrophilic but more volatile than the salts, and can therefore be transported long distances by air or ocean currents. More information can be found in the PFOS risk profile.²⁴

D. Production and use of PFOS and its related chemicals

51. The information on production and use of PFOS, its salts and PFOSE has been provided by parties as follows: during the development of risk profiles and risk management evaluation; reviewed national implementation plans (NIPs);²⁵ national reporting under Article 15;²⁶ follow-up to decision POPRC-8/11;²⁷ and follow-up to decision POPRC-9/5. The collected information was summarized and reported by the Secretariat in document UNEP/POPS/COP.7/INF/11 at the seventh meeting of the Conference of the Parties as part of the process for the evaluation of the continued need for PFOS, its salt and PFOSE set out in decision SC-6/4.

52. It is important to note that many parties are still in the process of updating their NIPs through which information on the national situation will be described based on the inventory of PFOS, its salts and PFOSE once established. Revised draft guidance for the inventory of PFOS and related chemicals listed under the Stockholm Convention is available in document UNEP/POPS/COP.7/INF/26.

Production

53. The global production of PFOSE by 3M, the main producer of the chemical until the production ceased in 2003, is estimated to have been 13,670 metric tonnes²⁸ (1985 to 2002), with the largest yearly production volume, 3700 metric tonnes of PFOS and PFOS related substances, in 2000. On 16 May 2000, 3M announced that the company would phase-out the manufacture of PFOS and PFOS-related substances voluntarily from 2001 onwards. By the end of 2000, about 90 % of 3M's production of these substances had stopped and in the beginning of 2003 the production ceased completely.

²¹ <http://poppub.bcr.cn/col/1413428117937/index.html> (F-53).

²² Presentation by Jun Huang, Tsinghua University, at the national workshop on nine new persistent organic pollutants and the implementation of the Stockholm Convention in China, Beijing, 1–2 July 2010.

²³ Information provided by FluoroCouncil in 2011.

²⁴ UNEP/POPS/POPRC.2/17/Add.5.

²⁵ <http://chm.pops.int/tabid/253/Default.aspx>.

²⁶ UNEP/POPS/COP.7/INF/36, <http://chm.pops.int/tabid/3668/Default.aspx>.

²⁷ <http://chm.pops.int/tabid/2542/Default.aspx>.

²⁸ In this document, "tonnes" refers to "metric tonnes".

Quantitative data on production have only been available from 3M so far, but it is considered that the combined capacity of the other producers was very much less than that of 3M.²⁹

54. The estimated global production of PFOSF between 1970 and 2002 was 96,000 tonnes.³⁰

55. The company 3M voluntarily phased out PFOS production in 2002 and changed to production of shorter-chain polyfluorinated chemicals.

56. Some national information on production and use of PFOS and its related chemicals has been submitted to the POPs Review Committee. In 2003, China initiated the production of PFOS and PFOSF after manufacturers in the United States voluntarily suspended the production. In 2006, annual production of PFOSF in China exceeded 200 tonnes, of which about 100 tonnes was exported to other countries including Brazil³¹ and the member States of the European Union. In 2003, Germany and Italy produced < 60 tonnes and < 22 tonnes of PFOS, respectively. The estimated total use of PFOS in the United States in 2006 was < 8 tonnes a year.³² Ireland reported import and use of 10 kg of PFOS in 2006. Switzerland provided estimates for relatively recent use of PFOS (March 2007), ranging from 0.23 to 5 tonnes per year.

57. A survey on the production and use of PFOS and its related chemicals is ongoing in China, as reported under Article 15. In its announcement made in March 2014 about the ratification of the amendments to Annexes A, B and C to Convention to list nine new POPs, it specified that as from 26 March 2014, with regard to specific exemptions for PFOS and its related chemicals, efforts should be made to develop substitutes as soon as possible in order to eliminate all of their use before the exemptions expire, and the management and risk control should be reinforced to gradually eliminate their production and use.³³

58. According to the information submitted by parties in 2012, PFOS is still produced in Germany with no production quantities reported and that the information on tonnages has to take into account the production of 1H,1H,2H,2H-perfluorooctanesulfonic acid; CAS No: 276-19-97-2 (6:2 FTS) is not considered a suitable substitution chemical for PFOS by Germany, given its persistence and estimated substance characteristics, which are similar to PFOS.³⁴ German producers only sell PFOS for the remaining legal uses in electroplating (>95%) and in photo industry (< 5%) in Europe. Other producers include various Chinese companies.³⁵ Please see appendix 1, register of specific exemptions and acceptable purposes for PFOS, its salts and PFOSF (as of 1 March 2016).

Use

59. The information on the use of PFOS, its salts and PFOSF for the various acceptable purposes / specific exemptions under the Convention has been provided by parties as part of the national reporting under Article 15. A summary of information submitted by 2014 is available in document UNEP/POPS/COP.7/INF/11.

60. In 2011, the European Union reported uses as follows:³⁶ metal plating (6,500 kg/y), aviation hydraulic fluids (730 kg/y); photographic industry (562 kg/year used +~1,280 kg from historical storage); semiconductor industry (9.3 kg/year); fire-fighting foams (90 tonnes in stocks); and total sources 163 tonnes/year and 1,730 tonnes of perfluorooctane sulfonate and derivatives (PFOS) and not

²⁹ UNEP/POPS/POPRC.10/INF/10.

³⁰ Paul, A.G., Jones, K.C., Sweetman, A.J. 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. *Environmental Science and Technology* 43: 386–392.

³¹ From 2003 to 2013, Brazilian Sulfluramid manufacturing increased from 30 to 60 tonnes per year. <http://pubs.acs.org/doi/abs/10.1021/acs.est.5b04544?journalCode=esthag>.

³² Carloni D. "Perfluorooctane Sulfonate (PFOS) Production and Use: Past and Current Evidence" Prepared for UNIDO, UNIDO Regional Office in China, (2009)

³³ UNEP/POPS/POPRC.10/INF/10.

³⁴

<http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC9/POPRC9Followup/PFOSSubmission/tabid/3565/Default.aspx> (submission by Germany).

³⁵ UNEP/POPS/COP.6/INF/7,

<http://chm.pops.int/Convention/POPsReviewCommittee/LatestMeeting/POPRC8/POPRC8Followup/SubmissionBDEsPFOS/tabid/3064/Default.aspx>.

³⁶ Consortium ESWI Expert Team to Support Waste Implementation 2011. Study on waste related issues of newly listed POPs and candidate POPs. Service requests under the framework contract No ENV.G.4/FRA/2007/0066. Draft final report. 13 April 2011.

only unreacted PFOS in product (mainly from carpets).³⁷ The import and export of finished articles containing PFOS in photographic industry account for 150 kg/year and 250 kg/year, respectively.

61. Germany reported estimated annual use in 2010 as 75 kg in photo-imaging, 1.87 kg in photo-resist and anti-reflective coatings for semi-conductors, 50 kg in aviation hydraulic fluids, 3400 kg in metal plating (hard metal plating) in closed-loop systems, and 25000 kg in fire-fighting foam. Total use of PFOS in Germany in 2010 was 28.527 tonnes.³⁸

62. The Netherlands reported, according to the RHDHV (2013), the estimated amount of PFOS used in mist suppressants in the metal plating industry was 145-150 kg, photo-resist or anti-reflecting coatings in the semi-conductor industry was several kg, photolithographic procedures in the photographic industry was 0 kg, and hydraulic fluids in the aviation industry was 0 kg.

63. Belgium reported the estimated use in non-decorative metal plating (hard chromium plating) only in closed-loop systems is of 229 kg/year. The use is supposed to be ended by 2015.³⁹

64. Ireland reported estimated use for photo-resist and anti-reflective coatings for semi-conductors as of 2.6 kg in 2010, 0.4 kg in 2011, 0.3 kg in 2012 and 0 kg in 2013.

65. Slovenia reported estimated use of 480 kg in metal plating (hard metal plating) only in closed-loop systems before 2009.

66. Finland reported an estimated use for hard metal plating is approximately 50 kg per year from 2009 to 2014.⁴⁰

67. Sweden reported the estimated use of PFOS in aviation hydraulic fluids as 10 kg/year prior to 2013 as an alternative with another PFAS has been phased in by the supplier. Sweden has an ongoing use of PFOS in hard metal plating. The estimated use was 200 kg/year prior to 2010, approximately 180 kg/year in the period 2011-2013 and from 2014 reduced to 30 kg/year.

68. Norway reported the total amount of a PFOS related substance, glycine, N-ethyl-N-((heptadecafluorooctyl)sulfonyl)-, potassium salt also called potassium N-ethyl-N-((heptadecafluorooctyl)sulphonyl)glycinate (CAS No: 2991-51-7), and potassium heptadecafluoro-1-octanesulfonate (CAS No: 2795-39-3) that has been imported in the period 2010 – 2013 are estimated as listed in Table 4.

Table 4: Imported quantities of Potassium N-ethyl-N-((heptadecafluorooctyl)sulphonyl)glycinate (CAS No: 2991-51-7), and Potassium heptadecafluoro-1-octanesulfonate (CAS No: 2795-39-3) to Norway 2010 - 2013⁴¹

Chemical name	CAS No:	Imported quantity [kg/year]			
		2010	2011	2012	2013
Glycine, N-ethyl-N-((heptadecafluorooctyl)sulfonyl)-, potassium salt also called Potassium N-ethyl-N-((heptadecafluorooctyl)sulphonyl)glycinate	2991-51-7	3.4	6.8	2.2	0.18
Potassium heptadecafluoro-1-octanesulfonate	2795-39-3	0.17	0.018	1.1	No data

69. Switzerland reported in its national implementation plan that apart from import, stocks of PFOS may still be present in particular as fire-fighting foams. In 2005, estimates for stocks of PFOS in fire-fighting foams amounted to a total of approximately 15 - 18 tonnes. By the end of April 2012, the reports of the amounts of PFOS used for exempted purposes and stocks of PFOS containing fire-fighting foams for 2011 were received by the Federal Office for the Environment (FOEN). Based on a first evaluation of these data, 1000 tonnes of PFOS-containing firefighting foams and thus roughly 10 tonnes of PFOS were still stored in Switzerland in 2010. The difference to the estimates from 2005 may be due to notifications that are still missing and stocks that have been disposed of recently. In 2010 and 2011 respectively 100 kg of PFOS related substances were imported into Switzerland for the purpose of chromium plating. The estimates for 2012 amounted to 600 kg.

³⁷ Email communication with Mr. Juergen Helbig, European Union OCP & NFP Stockholm Convention.

³⁸ UNEP/POPS/POPRC.10/INF/10.

³⁹ <https://ec.europa.eu/transparency/regdoc/rep/1/2015/EN/1-2015-137-EN-F1-1.PDF>

⁴⁰ <https://ec.europa.eu/transparency/regdoc/rep/1/2015/EN/1-2015-137-EN-F1-1.PDF>.

⁴¹ UNEP/POPS/POPRC.10/INF/10.

70. Brazil reported estimated use of PFOS in insect baits for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. at a constant level of around 50,000 kg per year from 2009 to 2014; 1,876 kg/year was used in 2011 for hard metal plating.

71. Canada reported estimated use of PFOS in metal plating (hard metal plating) only in closed-loop systems at levels of 28.78 kg in 2009, 25.82 kg in 2010, 5.64 kg in 2011, 8.75 kg in 2012, 1.64 kg in 2013 and 0 in 2014. According to Canada's national implementation plan, there are no stockpiles consisting of pure PFOS. However, there are stockpiles of aqueous film forming foams (AFFFs) containing PFOS manufactured or imported before May 2008. The import of PFOS and products containing PFOS is prohibited under the PFOS Regulations with certain exceptions (e.g., laboratory use and incidental presence).

72. Japan reported past use of PFOS for photo-resist and anti-reflective coatings for semi-conductors (3.318 kg in 2010) and in etching agent for compound semiconductors and ceramic filters (12.4 kg in 2010). Japan's NIP⁴² cites a survey conducted in 2011, according to which approximately 1.5 tonnes (approximately 30 kg in PFOS equivalent) of PFOS or its salts in stock were identified for use in the etching agent and photosensitive film of semiconductors. According to the survey conducted by the relevant ministry, a total of approximately 12 tonnes (amount of PFOS or its salts contained) of the foam extinguishing agents containing PFOS were identified.

73. Turkey reported that PFOS and related substances are imported to the country under the 2923.90.00.90.19 HS Code. However, the exact amount of PFOS imported under the 2923.90.00.90.19 HS Code is not known.

74. Morocco reported import of sulfonic compounds potentially containing PFOS as 36,000 kg between 2010 and 2012.

E. Waste streams likely to contain PFOS, its salts and PFOSE and recommended management/destruction options

75. For the environmental sound management of wastes, "Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with PFOS, its salts and PFOSE"⁴³ adopted by the Conference of the Parties to the Basel Convention at its twelfth meeting, as well as the "General technical guidelines on the environmentally sound management of consisting of, containing or contaminated with persistent organic pollutants"⁴⁴ and the "Guidance on BAT and BEP for the use of PFOS and related chemicals listed under the Stockholm Convention"⁴⁵ should be consulted.

⁴² Japan. 2012. The National Implementation Plan of Japan under the Stockholm Convention on Persistent Organic Pollutants. August 2012.

⁴³ UNEP/CHW.12/5/Add.3/Rev.1.

⁴⁴ UNEP/CHW.12/5/Add.2/Rev.1.

⁴⁵ UNEP/POPS/COP.7/INF/21,

<http://chm.pops.int/Implementation/NIPs/Guidance/GuidanceonBATBEPfortheuseofPFOS/tabid/3170/Default.aspx>

III. Alternatives to the use of PFOS and its related chemicals

76. This chapter presents currently known chemical and non-chemical alternatives to the various uses of PFOS. The next chapter contains a brief description of the alternatives and their environmental, safety and health properties. For some of these alternatives, a general discussion of properties might be all that is possible owing to a lack of specific information. For each of the chemical groups discussed, a more comprehensive compilation of information was beyond the scope of the present Guidance. More detailed information on the properties of the alternatives is provided in the Technical Paper on the Identification and Assessment of Alternatives to PFOS in Open Applications.^[1]

77. The POPRC's 2014 alternatives screening assessment was based on information available to the POPRC at that time. There may be new information that was not available for consideration by the POPRC for some of the chemical groups. Some new information made available during this revision of the Guidance on Alternatives was included, for example in the section on siloxanes. This information – and any other relevant data that is submitted in the future -- may be considered in any future assessment.

78. According to the “General guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals”,⁴⁶ a safer alternative is one that either reduces the potential for harm to human health or the environment or has not been shown to be a potential persistent organic pollutant. The guidance cautions against selecting alternatives with hazardous properties such as mutagenicity, carcinogenicity, adverse effects on the reproductive, developmental, endocrine, immune, and nervous systems, or those that use, contain or lead to the formation of other chemicals with the characteristics of persistent organic pollutants.

79. Chemical alternatives may provide different levels of functionality than PFOS and may have different toxic properties. Information has not always been sufficient to determine whether the certain chemical alternatives are more suitable from both the functionality and environmental health and safety perspectives.

80. Non-chemical alternatives include alternative technology, industrial processes and innovative practices. It might be that a particular use or product is obsolete and not essential or that a process or product could be changed so that it does not require the use of PFOS. Such non-chemical alternatives are described in the “Guidance on best available techniques and best environmental practices for the use of PFOS and related chemicals listed under the Stockholm Convention on Persistent Organic Pollutants”.⁴⁷

81. The current document also addresses alternatives to the use of PFOS, its salts and PFOSF in open applications. The following uses are considered open applications conform document UNEP/POPS/POPRC.7/INF/22/Rev.1: 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.⁴⁸

82. There is no longer any parties registered for specific exemptions for the production and use of PFOS, its salts and PFOSF for carpets, leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives and rubber and plastics and no new registrations may be made with respect to them.⁴⁹ This will be emphasized in conjunction with descriptions of any existing option in each coming chapter of uses below.

A. Photo-imaging

83. Photo-imaging is listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. As at January 2016, the following parties are registered for this use: Canada, China, Czech Republic, European Union, Japan, Norway, Switzerland, and Vietnam. This use is not considered as an open application.

^[1] UNEP/POPS/POPRC.8/INF/17/Rev.1.

⁴⁶ UNEP/POPS/POPRC.5/10/Add.1.

⁴⁷ <http://chm.pops.int/tabid/3170/Default.aspx>.

⁴⁸ UNEP/POPS/POPRC.7/INF/22/Rev1.

⁴⁹ Decision SC-7/1: Exemptions.

84. In the photographic industry, the following PFOS-related compounds have been used in manufacturing film, paper and plates: tetraethylammonium perfluorooctane sulfonate and perfluorooctyl sulfonamidopropyl quaternary ammonium iodide. They function as dirt rejecters and friction control agents and to reduce surface tension and static electricity. Imaging materials that are very sensitive to light (e.g., high-speed films) benefit particularly from these properties. The concentration of PFOS-related chemicals in coatings of films, paper and plates is in the range of 0.1–0.8 µg/cm².

85. As the spread of digital cameras has reduced film use, the use of PFOS in this area is not expected to grow. World consumption of PFOS for colour film production fell from 23 tonnes in 2000 to 8 tonnes in 2004.⁵⁰

86. According to the 2006 OECD survey, up to 20 tonnes of lithium perfluorooctane sulfonate and PFOS were used annually in the photographic industry as anti-reflective agents.⁵¹

87. Small quantities of PFOS are still used in X-ray film for photo-imaging for medical and industrial uses e.g. inspection by non-destructive testing. It is also used in film for other industries such as the movie industry due to the lower quality of the alternatives.

88. Use of PFOS in industrial photographic coatings is exempt from the PFOS ban in the European Union. In Canada, the use, sale, offer for sale and import of photographic films, papers or printing plates containing PFOS, its salts or its precursors is permitted.⁵²

89. PFOS-related compounds have also been used in developers for photographic film. According to Commission Regulation (EU) No 757/2010 of 24 August 2010, this application has been banned in EU member states. Japan's photographic industry reported that PFOS is no longer used for photographic processing in Europe, Japan, North America or elsewhere. Since photographic processing solutions using PFOS were highly sophisticated products, they were produced and supplied by a limited number of manufacturers, which have stopped using PFOS for their photographic processing products.

90. The possible alternatives identified for the photographic industry are:

- (a) Digital techniques;
- (b) Fluor telomer-based products of various perfluoroalkyl chain length; C3- and C4-perfluorinated compounds;
- (c) Hydrocarbon surfactants;
- (d) Silicone products.⁵³

91. Desirable properties for chemical alternatives in these uses include dynamic surface tension capability, static inhibition, solubility, photo-inactivity and stability when subjected to heat and chemicals.

B. Semi-conductors (Photo-resist and anti-reflective coatings for semiconductors, etching agent for compound semi-conductors and ceramic filters, photo masks in the semiconductor and liquid crystal display industries)

92. Photo-resist and anti-reflective coatings for semiconductors and etching agent for compound semi-conductors and ceramic filters are listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. As at January 2016, the following parties are registered for this use: Canada, China, Czech Republic,⁵⁴ European Union, Japan, Norway, Switzerland, and Vietnam. Photo masks in the semiconductor and liquid crystal display industries is listed as specific exemptions for the production and use of PFOS, its salts and PFOSF in Annex B. As at January 2016, Canada, China and the Republic of Korea are registered for this use. Those uses are not considered as

⁵⁰ UNEP/POPS/POPRC.9/INF/11/Rev.1

⁵¹ [www.oecd.org/officialdocuments/displaydocumentpdf/?cote=ENV/JM/MONO\(2006\)36&doclanguage=en](http://www.oecd.org/officialdocuments/displaydocumentpdf/?cote=ENV/JM/MONO(2006)36&doclanguage=en)

⁵² UNEP/POPS/POPRC.10/INF/10.

⁵³ There are considerable datagaps of siloxane compounds used on the market for photographic applications, see UNEP/POPS/POPRC.8/INF/17/Rev.1.

⁵⁴ Czech Republic is not registered for etching agent for compound semi-conductors and ceramic filters.

open applications. Semiconductor manufacturing comprises up to 500 steps. The technology primarily involves four fundamental physical processes:⁵⁵

- (a) Implant;
- (b) Deposition;
- (c) Etch/polish;
- (d) Photolithography.

93. Photolithography is the most important of the four processes. It is essential for the successful implementation of the other three processes and, indeed, the overall production process. It shapes and isolates the junctions and transistors, it defines the metallic interconnects and it delineates the electrical paths that form the transistors; and it joins them together. Photolithography reportedly represents 150 of the total 500 steps. Photolithography is also integral to the miniaturization of semiconductors.^{56, 57}

94. Photo resist and anti-reflectant products are either water based⁵⁸ or solvent-based solutions containing up to 80% solvents with the remaining components being acrylic or other polymer resins, PFOS-derived cross-linking agents, stabilizers and/or PFOS-derived surfactants. Typical use concentrations are in the range of 0.02 to 0.1 wt%.^{59, 60}

95. Photoresists are photosensitive polymeric materials used for making circuit patterns.⁶¹ Photo resists for fine patterning need to contain a substance called photo acid generator (PAG) that include PFOS. PAG generates hydrogen ions by exposure to laser light which causes an anisotropic chain reaction that increases focal depth. Therefore, PAGs are essential to fine patterning. In subsequent steps photo resist agent is rinsed out during the photolithographic process and does not remain in semiconductors.

96. Since diffused reflection would possibly disorder the shape of a circuit in design, therefore an anti-reflective coating (ARC) is necessary to avoid disturbance during photolithographic processes. PFOS is used in anti-reflective coating agents to give surface activity and regulate reflective characteristics of the coating between the metal and resist layers.

97. A number of resist suppliers sell top anti-reflective coating (TARC) and bottom anti-reflective coating (BARC), which are used in combination with deep ultra violet (DUV) photo resist. The process involves placing a thin, top coating on the resist to reduce reflective light, in much the same way and for the same purposes that eyeglasses and camera lenses are coated. Since anti-reflective coating agents are rinsed out during the photolithographic process, PFOS does not remain in the semiconductors.⁶²

98. The manufacture of advanced semiconductor devices is not currently possible without the use of PFOS in critical applications such as photo resistant and anti-reflective coatings. The semiconductor industry in Austria has replaced PFOS by 2015 by another PFOS-free photoresistant. However no specific details besides the Web link on the used alternative were provided based on the claim of business confidentiality. PFOS can also be used as a surfactant in etching processes in the manufacture of compound semiconductors.⁶³ PFOS is then added as part of an etching agent, and

⁵⁵ UNEP/POPS/COP.7/INF/21.

⁵⁶ Risk & Policy Analysts Limited (RPA) in association with BRE Environment. 2004. PerfluorooctaneSulfonate: Risk reduction Strategy and Analysis of Advantages and Drawbacks, Final Report. Prepared for Department for Environment, Food and Rural Affairs and Environment Agency for England and Wales, April 2004.

⁵⁷ Draft guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on Persistent Organic Pollutants, UNEP, Stockholm Convention, Revised March 2014.

⁵⁸ http://signupmonkey.ece.ucsb.edu/wiki/images/b/bb/AZ_Aquatar_VIII-A_45_MSDS.pdf

⁵⁹ http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_090c/0901b8038090c227.pdf?filepath=productsafety/pdfs/noreg/233-00873.pdf&fromPage=GetDoc.

http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08fb/0901b803808fb12.

⁶⁰ http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_090c/0901b8038090c227.pdf?filepath=productsafety/pdfs/noreg/233-00873.pdf&fromPage=GetDoc.

http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08fb/0901b803808fb12.

⁶¹ <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC2/AnnexFinformationYear2007/tabid/466/Default.aspx>.

⁶² UNEP/POPS/COP.7/INF/21.

⁶³ UNEP/POPS/COP.7/INF/21.

rinsed out during the subsequent washing treatment. PFOS is a process chemical that does not remain in the final article, the semiconductor device.

99. PFOS reduces the surface tension and reflection of etching solutions, properties that are important for precise photolithography in the semiconductor industry (compound semiconductors and ceramic filters and photo masks and LCD displays). Small amounts of PFOS-based compounds are required during the following critical photolithography applications, which are crucial for achieving the accuracy and precision required to manufacture miniaturized high-performance semiconductor chips:⁶⁴

- (a) Ultra-fine patterning/photo resists as photo-acid generators and/or surfactants;
- (b) Anti-reflective coatings as uniquely performing surfactants.

100. The exact PFOS derivative used is not publicly known.

101. The annual use of PFOS in the European Union's semiconductor industry before 2000 was 470 kilograms, with emissions of 54 kilograms. Due to the European industry's successful efforts to reduce uses of PFOS, the annual use in 2010 for the remaining critical uses was 10 kilograms with emissions of less than 0.5 of a kilogram.⁶⁵

102. According to the industry, no alternatives are currently available that would allow for the comprehensive substitution of PFOS in these particular and essential applications.⁶⁶ The World Semiconductor Council (WSC), an industry body of Semiconductor Industry Associations, was committed to ending non-critical uses of PFOS in member countries of the United Nations Economic Commission for Europe by May 2007 and globally in May 2009. The WSC agreed to this voluntary agreement on PFOS in 2006 and subsequently implemented it.

103. The industry continues to work towards developing comprehensive PFOS substitutes for current and future semiconductor manufacturing. The WSC (World Semiconductor Council) manufacturers have agreed not to seek new uses of photolithography chemicals containing PFOS and the suppliers have publically stated that they will not provide PFOS-containing chemicals for any new uses. Additionally, semiconductor companies are replacing remaining use of PFOS as the feasibility and capability are proven. A few semiconductor companies will be required to continue to use PFOS blends until these feasibility issues are overcome. The amount left in use is highly controlled. WSC, 2011 Report.⁶⁷

104. The estimated global annual PFOS use (2010 data) for the three remaining applications is as follows, WSC, 2011 Report:⁶⁸

- (a) Photo resists: 46.4kg;
- (b) BARC: 4.5kg;
- (c) TARC: 893.5kg.

105. Although the Japanese electronic industry had used less than 5 kilograms of PFOS annually for the etching of high-frequency compound semiconductors and piezoelectric ceramic filters before 2013, the alternative methods yielding comparable quality are currently available and being used in Japan.

106. According to information submitted by the Chinese delegation to the fourth meeting of the Conference of the Parties, the semiconductor industry in China uses 30–40 kilograms of PFOS yearly for photo resists, as an anti-reflective coating, as a de-gluing agent and as a developing agent, and in 2007 industry sales were ¥100 billion.⁶⁹ The WSC has announced publicly in 2011 that the global semiconductor industry has successfully eliminated all non-critical uses of PFOS and identified substitutes for most other uses, although continued use of very small quantities of PFOS remains

⁶⁴ UNEP/POPS/POPRC.9/INF/11/Rev.1.

⁶⁵

<http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC8/POPRC8Followup/SubmissionsPFOsdraftguidance/tabid/3233/Default.aspx>. (submission by ESIA)

<http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC8/POPRC8Followup/SubmissionsPFOsdraftguidance/tabid/3233/Default.aspx>

⁶⁶ 20th WSC Joint Statement May 2016 Seoul FINAL.

⁶⁷ http://www.semiconductorcouncil.org/wsc/uploads/WSC_2011_Joint_Statement.pdf

Annex 2 page 16 – 23.

⁶⁸ http://www.semiconductorcouncil.org/wsc/uploads/WSC_2011_Joint_Statement.pdf Annex 2 page 16 – 23

⁶⁹ http://chm.pops.int/Portals/0/Repository/addinfo_2008/UNEP-POPS-POPRC-SUB-F08-PFOS-ADIN-CHI.English.pdf.

critical in a few remaining processes (the critical applications in manufacturing semiconductor chips such as photo resist and anti-reflective coatings for semiconductors). The remaining critical uses of PFOS are limited and highly controlled, and emissions of PFOS by the entire global semiconductor industry have been reduced to approximately 6 kg/year. The acceptable purpose exemptions under the Stockholm Convention are still required. In 2011 the WSC also announced that, the semiconductor industry has reduced global emissions of PFOS from semiconductor use to approximately 6kg/year which represents a 99% reduction from semiconductor emissions in 2005. These emissions will continue to reduce as technology and feasibility permit replacement of critical uses.

107. New photolithography technologies use less photo resist per wafer than older technologies, and the new photo resist formulations contain much lower concentrations of PFOS. Thus, the total use of PFOS is decreasing, lowering the total amount of releases. In 2002, effluent releases for these critical uses for the whole of Europe totalled an estimated 43 kilograms of PFOS. As PFOS does not break down, this represents an ongoing accumulative load to the environment. PFOS has been found to be the major constituent in semiconductor manufacturing plant wastewaters along with other PFCs and perfluoroalkyl carboxylates including PFOA and PFDA.⁷⁰

108. The cost of developing a new photo-resist system is estimated to be US\$700 million (0.3 % of annual sales) for an industry which had global sales of US\$248 billion in 2006.⁷¹ This indicates that cost is not a barrier to develop a new photo-resist system.

109. PFOS was used to produce developers and edge bead removers. No alternative substances have been commercialized for existing uses in PAG, BARC and TARC that would allow for the comprehensive substitution of PFOS in these critical applications.⁷² Substitutes do exist for these non-critical uses, and the semiconductor industry has phased out these uses e.g Fuji describes photo-resists that are “PFOS & PFAS free.”⁷³ The scientific literature indicates that it should be possible to develop a PFOS-free photo-resist system.⁷⁴ The patent literature also indicates active work in this area. For example, patents describe fluorine-free photoresist compositions as an alternative to PFOS/PFAS use.^{75, 76, 77} In the photolithography industry, it is considered that few alternatives are available that would allow for the comprehensive substitution of PFOS in critical applications. Thus the new photolithography technologies, which in detail are trade secrets, use less photoresist per wafer, and the new photoresist formulations contain much lower concentrations of PFOS. Non-critical uses of PFOS are as edge bead removers, de-gluing agents and developing agents. Substitution requires varying lengths of time. According to the industry, smooth substitution often requires more than 10 years, and substitution without approval from customers tends to halt the latter’s production lines. Customers expect alternatives to perform comparably to PFOS-containing items.⁷⁸

110. There may be one additional specialized application for which, according to industry sources, there is currently no substitute for PFOS: use in liquid etchant in the photo mask rendering process. For photo mask etching with strong acids non-fluorosurfactants are not stable enough, and shorter-chain fluorosurfactants do not have sufficiently low surface tensions.⁷⁹

C. Aviation hydraulic fluids

111. Aviation hydraulic fluids are listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. As at January 2016, the following parties are registered for this use: Canada, China, Czech Republic, European Union, Norway, Switzerland, Vietnam, and Zambia. This use is considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

⁷⁰ Lin AY, Panchangam SC, Lo CC (2009). The impact of semiconductor, electronics and optoelectronic industries on downstream perfluorinated chemical contamination in Taiwanese rivers. *Environ Pollut.* 2009 Apr;157(4):1365-72. doi: 10.1016/j.envpol.2008.11.033. Epub 2008 Dec 30.

⁷¹ UNEP/POPS/POPRC.9/INF/11/Rev.1

⁷² UNEP/POPS/COP.7/INF/21.

⁷³ http://www.fujifilmusa.com/products/semiconductor_materials/photoresists/krf/index.html.

⁷⁴ Ayothi R, Chang SW, Felix N, Cao HB, Deng H, Yueh W, Ober CK (2006) New PFOS free photoresist systems for EUV lithography, *Jour Photopolymer Science and Technol* 19:515-520.

⁷⁵ <https://www.google.com/patents/US20090181319>.

⁷⁶ <https://www.google.com/patents/US8034533>.

⁷⁷

<http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC11/POPRC11Followup/PFOSInfoRequest/tabid/4814/Default.aspx> (submission by SIA)

⁷⁸ UNEP/POPS/POPRC.9/INF/11/Rev.1.

⁷⁹ UNEP/POPS/COP.7/INF/21.

112. Aviation Hydraulic fluids with a perfluoroethylcyclohexyl sulfonate content of about 0.1% have been used in civil and military airplanes since the 1970s (United States patent 3679587 dates from 1972). The total global market for fluorinated compounds in aircraft hydraulic fluids is about 2 tonnes per year. Annual PFOS consumption in the European Union for this use was about 730 kilograms/year in 2009.⁸⁰

113. In the manufacturing process for aviation hydraulic fluids, a PFOS-related compounds such as potassium perfluoroethylcyclohexyl sulfonate, was used as an additive to the aviation hydraulic fluids with a content of about or less than 0.1%.⁸¹ According to the manufacturers, this formulation helps prevent evaporation, fires, and corrosion

114. The potassium salt of perfluoroethylcyclohexyl sulphonate (CAS No: 67584-42-3)⁸² is not a PFOS precursor, but a PFOS related substance,⁸³ and it has been used in hydraulic oils⁸⁴ instead of PFOS in the past. However, like other C₈ compounds it is likely to be persistent and 3M which formerly produced this chemical has ceased to do so. 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.

115. Alternative hydraulic fluid additives must undergo extensive testing to qualify for use in the aviation industry to sustain severe conditions during use. Aviation hydraulic fluids without fluorinated chemicals but based on, for example, phosphate esters exist,⁸⁵ and fluorinated chemicals other than PFOS can be used as already mentioned potassium perfluoroethylcyclohexyl sulfonate. These substances can absorb water and the subsequent formation of phosphoric acid can damage metallic parts of the hydraulic system. For this reason, phosphate ester-based hydraulic fluids are routinely examined for acidity as this determines its useful lifetime.

116. An anti-erosion agent added to the hydraulic fluid contains an unidentified residual organic fluorochemical which is most likely a by-product of the manufacturing process.⁸⁶ It is possible that this residual substance could be PFOS.

117. The fire-resistant aviation hydraulic fluids principally contain tri-alkyl phosphates, tri-aryl phosphates, and mixtures of alkyl-aryl-phosphates.] 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 the product characteristics since these characteristics are important to aviation security.

118. The known trade names from traders on the market are as follows: Arnica, Tellus, Durad, Fyrquel, Houghto-Safe, Hydrauncoil, Lubritherm Enviro-Safe, Pydraul, Quintolubric, Reofos, Reolube, Valvoline Ultramax, Exxon HyJet, and Skydrol.⁸⁷

119. Spain and Norway reported that fluorinated phosphate esters are used as alternatives to PFOS in aviation hydraulic fluids, but there is no detailed information available about their chemical composition and technical performance.^{88, 89}

120. Since very little is published concerning the chemical composition of these aviation hydraulic oils, currently it is not possible to assess their environmental and health impact.

⁸⁰ UNEP/POPS/POPRC.9/INF/11/Rev.1.

⁸¹ 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.boeing.com/environmental/TechNotes/TechNotes2001-02.pdf>

⁸² In the U.S. this chemical is considered a C8 PFOS equivalent 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>

⁸³http://www.pops.int/documents/meetings/poprc/submissions/Comments_2006/sia/pfos.uk.risk.eval.report.2004.pdf

⁸⁴ https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/183154/pfos-riskstrategy.pdf

⁸⁵ www.freepatentsonline.com/6319423.html and www.freepatentsonline.com/WO2006138081.html.

⁸⁶ UNEP/POPS/POPRC.8/INF/17/Rev.1

⁸⁷ <http://www.atsdr.cdc.gov/toxprofiles/tp99-c3.pdf>.

⁸⁸ National report from Spain to the Stockholm Convention on PFOS, 2014.

⁸⁹ PFOS_Norway_8 Jan 2016_HYJET V Data sheet (003).pdf.

D. Metal plating

121. Metal plating (hard metal plating) only in closed-loop systems is listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. As at January 2016, the following parties are registered for those uses: Canada, China, Czech Republic, European Union, Norway, Switzerland, and Vietnam. Metal plating (hard metal plating) and (decorative plating) are listed as specific exemptions for the production and use of PFOS, its salts and PFOSF in Annex B. As at January 2016, China and the Republic of Korea are registered for those uses. Those uses are considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1, unless used in closed-loop systems.

122. There are two main technologies in metal plating namely hard and decorative metal plating. The difference between hard and decorative metal plating is thickness, hardness and deposition of the chrome layer on the plated object where the hard metal plating is addressed as functional against e.g. corrosion, abrasion etc and the decorative metal plating main function is primarily a decorative surface finish.

123. PFOS is used as a surfactant, wetting agent and mist suppressing agent for chrome plating to create protective foam and decrease aerosol emissions and improve the work environment. It was previously used for both decorative chrome plating and hard chrome plating processes, but new technology using chromium (III) instead of chromium (VI) for certain decorative chrome plating has made PFOS use in decorative chrome plating obsolete. However, chromium (III) does not work for hard chrome plating⁹⁰. In hard chrome plating, PFOS works by lowering the surface tension of the plating solution and forming a single foamy film barrier of a thickness of about 6 nanometres on the surface of the chromic acid bath, which mitigates its aerosol (fog) formation, thus reducing airborne loss of chromium (VI) from the bath and decreasing exposure of workers to this carcinogenic agent. Chromium (VI) is currently in an ongoing REACH authorization process.

124. The PFOS derivative most frequently used in hard chrome plating is the quaternary ammonium salt tetraethylammonium perfluorooctane sulfonate (sold under trade names such as Fluorotenside-248 and SurTec 960), typically in a 5–10% solution. The potassium, lithium, diethanolamine and ammonium salts of PFOS may also be used.

125. In Europe, and also in Canada ATOTECH markets Fumetrol[®] 140 with PFOS and Fumetrol[®] 21 without PFOS but with the fluorotelomer derivatives 1*H*,1*H*,2*H*,2*H*-perfluorooctane sulfonic acid (CAS No: 27619-97-2). 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 or H4PFOS).

126. There is some uncertainty about its efficacy although some trials show equivalent results with 6:2FTS as with PFOS.⁹¹ There is some uncertainty about its efficacy and suitability for certain metal finishing applications. For example, in the aerospace industry, Fumetrol 21 LF was tested to the same chromic acid anodize qualification standards as Fumetrol 140. This included salt spray, paint adhesion, coating weights, bend fracture SEM analysis, and other tests. The addition of Fumetrol 21 LF to the chromic acid anodize bath interfered with coating weight development. This resulted in the inability to meet specification requirements for coating weight and corrosion resistance performance⁹².

Metal plating (hard metal plating) only in closed-loop systems

127. The term “hard” refers to the process of electrodepositing a thick layer (0.2 mm or more) of certain types of metal directly onto substrates. In terms of hard metal plating, for example, the deposited chrome layer provides the following desirable properties:

- (a) Hardness;
- (b) Wearability;
- (c) Corrosion resistance;
- (d) Lubricity;

⁹⁰ Blepp M., Willand W., Weber R. (2015) Verwendung von PFOS in der Galvanik - Kennzeichen eines geschlossenen Kreislaufs, Verwendung von Ersatzstoffen. Umweltbundesamt Projektnummer [55 567], TEXTE 63/2016 <http://www.umweltbundesamt.de/publikationen/verwendung-von-pfos-in-der-galvanik-kennzeichen>

⁹¹ Poulsen et al. *Substitution of PFOS for use in nondecorative hard chrome plating*, 2011, Environmental Project No. 1371 2011, Danish Ministry of Environment.

⁹² UNEP-POPS-POPRC8FU-SUBM-PFOS-Boeing_130621.En.doc.

(e) Low coefficient of friction.

128. Examples of hard metal plated parts are:

- (a) Hydraulic cylinders and rods;
- (b) Railroad wheel bearings and couplers;
- (c) Molds for the plastic and rubber industry;
- (d) Tool and die parts.

129. In hard metal plating, PFOS is still used because other mist suppressants degrade more or less rapidly under the prevailing, strongly acidic and oxidizing conditions: PFOS works by lowering surface tension and forming a single foamy barrier on the surface of the chromic acid bath, which maintains its aerosol (fog) formation, thus reducing airborne loss of chromium (VI) from the bath and decreasing exposure to this carcinogenic agent.^{93, 94}

130. Closing the material loop for hexavalent chromium (VI) hard plating means using suitable combinations of techniques such as cascade rinsing, ion exchange and evaporation that aims to avoid environmental releases of chromium (VI). When hot electrolytes with high evaporation rates are used, closing of the material loop can sometimes already be achieved by simple methods such as using a single static rinse in combination with seven rinsing steps in a pumped, very slowly flowing, and rinse cascade. But in most cases, an evaporator is required to regain the electrolyte from the rinse water.⁹⁵

131. Regional weather patterns may affect applicability of evaporation. Cat ion exchanger resins with high resistance to strong oxidants are used to selectively remove unwanted metal ions. Closing the loop for process chemicals does not mean being free of wastewater. In fact no loop can be held completely closed all the time. Current BAT/BEP for PFOS means that PFOS is to be used in closed loop so no emissions.

132. Current BAT/BEP for PFOS means that PFOS is used in closed loop so that hardly any emissions take place.⁹⁶ By selecting suitable activated carbon and optimized flow rates, up to 99% of PFOS can be removed from wastewater by adsorption onto activated carbon. The PFOS waste from the metal plating process should be collected and disposed in an environmentally sound manner. Sources for PFOS can be regeneration of ion exchangers, air scrubber effluents, floor water of the plating plant and carry-over effects.⁹⁷

133. The aerosol can also be reduced through optimized covering of the chromic acid bath and optimized exhaustion, or enclosure of the baths.⁹⁸

134. There is more extensive information is provided in the draft guidance on best available techniques (BAT) and best environmental practices (BEP) on releases of perfluorooctane sulfonic acid (PFOS) and PFOS-related substances from production and use under the specific exemptions and acceptable purposes listed in the Convention.⁹⁹

Metal plating (hard metal plating and decorative plating) – not in closed-loop systems

135. The term “decorative” refers to a different process than described above, whereby only a thin layer (0.05 to 0.5µm) of metal is deposited onto substrates. In terms of decorative metal plating, for example, the deposited chrome layer provides the following desirable properties:

- (a) Appearance (aesthetically pleasing);
- (b) Non-tarnishing.

136. Examples of decorative chrome plated parts are:

- (a) Car and truck pumpers;
- (b) Motorcycle parts;

⁹³ UNEP/POPS/POPRC.9/INF/11/Rev. 1, “Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals”.

⁹⁴ UNEP/POPS/COP.7/INF/21.

⁹⁵ UNEP/POPS/COP.7/INF/21.

⁹⁶ UNEP/POPS/COP.7/INF/21

⁹⁷ UNEP/POPS/COP.7/INF/21.

⁹⁸ Blepp M. (2015) Berichterstattung an die Europäische Kommission nach Artikel 12 der EU-POP-Verordnung (EU-POP-VO). Umweltbundesamt Projektnummer [55 567].

⁹⁹ UNEP/POPS/COP.7/INF/21.

- (c) Kitchen appliances;
- (d) Smart phones and tablets.

137. In hard and decorative metal plating, PFOS is still used because other wetting agents degrade more or less rapidly under the prevailing, strongly acidic and oxidizing conditions. In hard chrome plating and chromium (VI) anodizing tank operations, the plating bath consists of chromium (VI) acid. This acid is a highly oxidative, strong acid that decomposes most types of surfactants.

138. As mentioned earlier, chromium (VI) is a known human carcinogen and therefore chromium (VI) emissions are regulated to protect workers from occupational exposure and to protect the environment. Emissions to the atmosphere can be reduced by either limiting the amount of chromium (VI) through use of add-on air pollution control devices or utilizing a chemical mist suppressant. PFOS works by lowering surface tension and forming a single foamy barrier on the surface of the chromic acid bath, which maintains its aerosol (fog) formation, thus reducing airborne loss of chromium (VI) from the bath and decreasing exposure to this carcinogenic agent.¹⁰⁰

139. PFOS was previously used for decorative metal plating, but new technology using chromium (III) instead of chromium (VI) has made this use mostly obsolete. Although the use of chromium (III) does not work for hard metal plating, some kinds of non-PFOS agents are being used in both decorative and hard metal plating. Non-fluorinated alternatives for decorative metal plating are available on the European market.¹⁰¹

The price of the chemicals

140. An economic assessment of the non-PFOS alternatives depends on:

- (a) The price of the chemicals and or physical alternatives;
- (b) The amount needed during use;
- (c) The expenses during substitution;
- (d) Expenses to possible continuous addition of chemicals;
- (e) Expenses related to possible break down of a continuous addition system, due to problems related to non-sufficient or excess additions of chemicals.

141. In Danish study conducted 2011,¹⁰² suppliers of PFOS and non-PFOS alternatives were contacted in order to learn more about the price of the chemicals. However, only price information was received about the price for a few of the chemicals and mostly for the PFOS products.

142. The information received in this Danish study from the suppliers, suggests that the price of the PFOS products used as mist suppressant for non-decorative hard metal plating is around 100 to 200 DKK (13 EUR to 27 EUR) per kilo/liter. The price is dependent on the concentration of PFOS in the chemical. The cheaper products contain about 2-3 % PFOS whereas the more expensive products contains 3-7 % PFOS.

143. In comparison one of the alternatives was found to cost 120 DKK (16 EUR) per kilo/liter. The price is not fully comparable as no information was received on the amounts to be used compared to a PFOS product. However, the supplier informed that the product was cheaper than using PFOS. Other information about the price of the non-PFOS alternatives was sparse. One supplier informed that their non-PFOS alternative is more expensive than PFOS (but not how much more expensive).

144. In conclusion, the economic assessment of the non-PFOS alternatives based on the price alone is inconclusive. Some alternatives may be cheaper and some may be more expensive.

145. Non-fluorinated alternatives for hard metal plating are available on the European market but are new, and some are still being tested. These alternatives (whose chemical description and CAS numbers have not been released by the private sector) appear functional with some slight process changes including stirring the chromium bath.¹⁰³

¹⁰⁰ Blepp M. (2015) Berichterstattung an die Europäische Kommission nach Artikel 12 der EU-POP-Verordnung (EU-POP-VO). Umweltbundesamt Projektnummer [55 567]

¹⁰¹ UNEP/POPS/COP.7/INF/21.

¹⁰² Poulsen et al. *Substitution of PFOS for use in nondecorative hard chrome plating*, 2011, Environmental Project No. 1371 2011, Danish Ministry of Environment.

¹⁰³ Poulsen et al. *Substitution of PFOS for use in nondecorative hard chrome plating*, 2011, Environmental Project No. 1371 2011, Danish Ministry of Environment.

146. Non-fluorinated surfactants are used during the production process for hard metal plating and decorative metal 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 surfactants¹⁰⁴. Trivalent chromium is formed by chemical degradation in the bath, which has to be oxidized to hexavalent chromium by membrane electrolysis.

147. During the electroplating process, the protective foam layer that prevents misting of chromic acid is eventually broken down. Then there is a need to refill the bath with additional wetting and mist suppressant agent to maintain a stable protective foam layer over the chrome bath, and after about 7 months only about 1% of the original content is left.¹⁰⁵ Thus, the bath must be refilled with PFOS once the foam layer is insufficient to withhold the chromium (VI) aerosols. Alternatives to the PFOS derivatives are considered to be less stable and durable in the chrome bath than PFOS since they may not reach the necessary surface tension and additionally they degrade further through oxidation which is not the case for PFOS. This is due to the extreme persistence of PFOS which is considered as one of the most stable chemicals in fluoro chemistry.

148. When the metal plating solution is spent, the bath is exhausted and the plating solution liquid must be disposed of. However it must be taken into account that, due to the high ability of PFOS to absorb to the surface of most materials and “memory effect”, PFOS can be found in the wastewater stream of electroplating plants for months (or, in some cases, more than a year) after being substituted. Ion exchangers, washing water from exhausters and every contact surface must be purified or exchanged as well as the electrolyte liquid itself.¹⁰⁶ The solution is sent to a chemical waste water plant, where the chromium is precipitated as chromium (III) hydroxide. In the European Union, the resulting dewatered sludge is sent to specially prepared landfills, engineered to prevent leakage, where the sludge is stored.¹⁰⁷

149. The sludge is sometimes used as a fertilizer for agricultural soil which can result in broad scale contamination of agricultural fields with PFOS and provide a major emission source to food and water.¹⁰⁸ A great part of the PFC used in this industry therefore probably ends up in the environment. The recent discovery of high levels of PFOS in agricultural soils in the United States and Germany could result from such use of sludge as a fertilizer, but the source of the sludge was not identified in this study.¹⁰⁹ In 2009, the German national metal plating association (ZVO) stated that in Germany 20% of PFC is lost to the environment.¹¹⁰

150. In the European Union the annual PFOS use for metal plating was about 10 tonnes in 2003 but has declined recently. According to data from the European Commission (2010) the total use in the European Union today is estimated to be around 4 tonnes.¹¹¹

151. China reported that its metal plating industry uses 25 tonnes of PFOS a year. The PFOS-containing mist suppressants used in China are FC-80 (CAS No: 2795-39-3 – PFOS potassium salt) and FC-248 (CAS No: 56773-42-3 – PFOS tetraethyl ammonium salt). The industry turnover is €30 billion. A phase-out without an effective alternative could worsen the health of 100,000 Chinese workers through exposure to chromium (VI), according to Chinese authorities. In China the available PFOS alternatives used for chrome plating are F-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate, CAS No: 756426-58-1), F-53B (potassium 2-(6-chloro-

¹⁰⁴ Poulsen et al. *Substitution of PFOS for use in nondecorative hard chrome plating*, 2011, Environmental Project No. 1371 2011, Danish Ministry of Environment.

¹⁰⁵ Personal communication from Carsten Ree Jørgensen, CEO, Nichro, 2009.

¹⁰⁶ Breidenbach H. 2009. Substitution von perfluorierten Netzmitteln in Chrombädern 2009 Oberflächen Polysurfaces No. 6/2009. http://www.polymedia.ch/htdocs/Files/Polysurfaces/OP-archives/2009/OP_2009-06.pdf.

¹⁰⁷ IPPC BREF BAT for the Surface Treatment of Metals and Plastics European Commission, 2006.

¹⁰⁸ Krofges P, Skutlarek D, Farber H, Baitinger C, Godeke I, Weber R., PFOS/PFOA Contaminated Megasites In Germany Polluting The Drinking Water Supply Of Millions Of People Organohalogen Compounds Vol. 69 (2007).

¹⁰⁹ Renner R. 2009. EPA finds record PFOS, PFOA levels in Alabama grazing fields. *Environmental Science and Technology* 43: 1246–1247.

¹¹⁰ Personal communication from Christoph Matheis, Zentralverbandes Oberflächentechnik e. V. (ZVO), 6 March 2009.

¹¹¹ European Commission. 29 January 2010. Implementation of the restriction on PFOS under the Directive 2006/122/EC – electroplating applications and fire fighting foams containing PFOS stocks.

1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate, CAS No: 73606-19-6) and Fumetrol® 21 (1H,1H,2H,2H-perfluorooctane sulfonic acid).¹¹²

152. Canada reports having imported an estimated 3 metric tonnes of PFOS from the United States in 2004 for use in metal plating. Since the implementation of the *Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations* in 2008, the quantities imported into Canada for this use have decreased significantly. The use of PFOS containing substances in this application was prohibited in May 2013. Of the suppliers of fume suppressants to the metal finishing (chromium plating/anodizing) industry in Canada, many report that PFOS-free fume suppressants are now already in use. Atotech Canada reports that all Canadian accounts are now using PFOS free fume suppressants or other control technologies. Other Canadian suppliers report approximately an 85 – 90% change to PFOS free fume suppressants.¹¹³ France reports having used 200 kilograms of PFOS for metal plating in 2006. All these figures are for chromium plating, including decorative plating. A comprehensive report by the United States Environmental Protection Agency on the detectable levels of PFOS in the effluent of decorative chromium electroplating facilities is available.¹¹⁴

153. There are promising emerging technologies to replace the hazardous chromium (VI) in hard metal plating with the less hazardous chromium (III).¹¹⁵ To what extent this technology would eliminate the need for PFOS as mist suppressant is not clear, but looking at decorative metal plating where chromium (III) is already applied in commercial scale, there is currently no need for PFOS as mist suppressant.

154. The German national metal plating association (ZVO) describes the availability of PFOS-free alternative products from 10 German suppliers.¹¹⁶ While information is lacking about the exact identity of these chemical compounds, three of them were fluorinated chemicals and seven were fluorine-free. The non-fluorinated alternatives were not stable enough in the hard chrome plating bath. It is stated that all 10 products could be used for decorative chrome plating, for which alternative chromium (III) processes seem to exist already. Alternative surfactants for this process are being studied at the University of Wuppertal, Germany.¹¹⁷ One possible non-fluorinated surfactant alternative for decorative plating may be Enthone® (ethoxylated oleyl amine, CAS No: 26635-93-8).

155. The Norwegian association of electroplaters (Norsk Galvanoteknisk Landsforening (NGLF)), reports that the industry has phase out the use of PFOS-containing wetting/anti-mist agent by using the chromium (III) process instead of the chromium (VI) process where possible (decorative chrome plating). At present the use of PFOS hard metal plating in closed-loop is low. A yearly use of less than 10 kg of a PFOS-containing product is estimated by NGLF.¹¹⁸

156. In Japan the use of PFOS in hard chrome plating has also been reported as discontinued.¹¹⁹

157. The use of control devices, such as Composite Mesh Pads (CMP) or Packed Bed Scrubbers (PBS), to catch aerosols from chromium plating baths offers an alternative to the use of PFOS. CMP operate at over 99% efficiency on 1 micron sized particles while PBS operate with over 98% efficiency removal of chromium (VI) aerosols. CMP are currently considered to be maximum achievable control technology of chromium (VI) aerosols. Closed tanks with increased ventilation have been suggested as alternative solutions to CMP and PBS for applications where use of chromium (III) is not yet possible. However, such systems need further improvement to be as effective as control devices in getting rid of chromium emissions. There is some concern that increased ventilation will also result in increased energy consumption and loss of some chromium from baths.¹²⁰ Other methods

¹¹² Presentation by Jun Huang, Tsinghua University, at the national workshop on nine new persistent organic pollutants and the implementation of the Stockholm Convention in China, Beijing, 1–2 July 2010.

¹¹³ Personal communication from P. J. Paine, Environment Canada, July 2012.

¹¹⁴ http://www.in.gov/idem/ctap/files/plating_chromium_pfos_study.pdf

¹¹⁵ E. Jennings Taylor, “Functional chrome coatings electrodeposited from a trivalent chromium plating electrolyte (FARADAYIC®, 1 TriChrome Plating)” (2013).

¹¹⁶ Personal communication from Christoph Matheis, Zentralverbandes Oberflächentechnik e. V. (ZVO), 6 March 2009.

¹¹⁷ Personal communication from Jutta Hildenbrand, University of Wuppertal, 15 October 2009.

¹¹⁸ Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2016.

¹¹⁹ Poulsen et.al, Substitution of PFOS for use in nondecorative hard chrome plating (2011), Danish Ministry of Environment, p 32. <http://www2.mst.dk/udgiv/publications/2011/06/978-87-92779-10-6.pdf>.

¹²⁰ http://eippcb.jrc.es/reference/BREF/stm_bref_0806.pdf.

such as using physical covers (netting, balls) for baths to diminish hydrogen burst and reduce misting currently do not work but should be further investigated.¹²¹

158. Fluorinated surfactants (including PFOS) are not used in other metal plating applications besides metal plating with chromium (VI),^{122, 123} Such applications not based on chromium (VI) are:

- (a) Agents to prevent haziness of plated copper by regulating foam and improving its stability;
- (b) Non-foaming surfactants in nickel-plating baths to reduce surface tension;
- (c) Agents added to tin-plating baths to ensure that plating has uniform thickness;
- (d) Alkaline zinc and zinc alloy plating;
- (e) Electroless nickel dispersion coating and strong acid electrolytes with insoluble anodes, such as precious metal electrolytes (e.g. gold, palladium and rhodium);
- (f) Agents to impart a positive charge to fluoropolymer particles and to aid electroplating of polymers (e.g. PTFE) onto steel for surface protection.

159. A lot of products have been tried for the application in hard metal 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 metal plating due to its slightly higher surface tension when compared to PFOS.

160. Shortchain fluorosurfactant products appear to be less effective, less stable in chromium baths and need more product/replenishment.

Technical feasibility and efficacy

161. CMP¹²⁴ and PBS¹²⁵ are alternatives already on the Canadian market and are the most commonly used control devices.¹²⁶ 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.

162. Control devices such as CMP operate at over 99% efficiency on 1 micron sized particles. PBS are over 98% efficient. CMP's are considered to be maximum achievable control technology.

163. 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.

164. There are currently available alternatives for metal hard plating and decorative plating.¹²⁷ The compliance date for eliminating use of PFOS-based fume suppressants for chromium electroplating and chromium anodizing was 19 September 2015.¹²⁸

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

166. 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.¹²⁹

¹²¹ Poulsen et al. *Substitution of PFOS for use in nondecorative hard chrome plating*, 2011, Environmental Project No. 1371 2011, Danish Ministry of Environment.

¹²² The Canadian *Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations* prohibit PFOS-based fume suppressants in electroless nickel-polytetrafluoroethylene plating and etching of plastic substrates prior to their metalization.

¹²³ <http://chm.pops.int/tabid/4814/Default.aspx> (submission by Germany).

¹²⁴ <http://www.faculty.ait.ac.th/visu/images/pdf/Romchat%20Dissertation1.pdf>.

¹²⁵ <http://archive.defra.gov.uk/environment/quality/chemicals/documents/pfos-riskstrategy.pdf>.

¹²⁶ <https://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=208517F9-1>.

¹²⁷ "Blepp M. (2015) Berichterstattung an die Europäische Kommission nach Artikel 12 der EU-POP-Verordnung (EU-POP-VO). Umweltbundesamt Projektnummer [55 567].

¹²⁸ EPA-HQ-OAR-2010-0600; FRL-9709-9 at <https://www.gpo.gov/fdsys/pkg/FR-2012-09-19/pdf/2012-20642.pdf>.

¹²⁹ Poulsen et. al, *Substitution of PFOS for use in nondecorative hard chrome plating* (2011), Danish Ministry of Environment, p 32. <http://www2.mst.dk/udgiv/publications/2011/06/978-87-92779-10-6.pdf>.

Health and environmental effects including toxicological and ecotoxicological information

167. There is little independent and reliable information from publically available sources 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.¹³⁰

168. It must be taken into account that it is much more difficult to remove alternatives such as 1H,1H,2H,2H-perfluorooctanesulfonic acid, CAS No: 27619-97-2 (6:2 FTS) or perfluorobutanesulfonic acid CAS No: 375-73-5 (PFBS) out of the wastewater by adsorption than for PFOS.¹³¹

169. 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.¹³² Therefore, it is crucial that the most recent BAT/BEP guidance is applied in order to reduce emissions to its lowest level possible.¹³³

170. 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 whether they are appropriate safer alternatives.

171. 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.

In China an alternative to PFOS exist, namely F53-B (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy) ethane sulfonate), where only one independent scientific study has been performed on environmental impact and ecotoxicity.

Cost-effectiveness

172. 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 m³/minute) to ~ \$200,000 for 50,000 cfm airflow (1416 m³/minute).

173. 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.

174. 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).

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

Availability, accessibility and socio-economic consideration

176. 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.

177. 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 tonnes per year.

E. Certain medical devices

178. Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio-opaque ETFE production, in-vitro diagnostic medical devices and CCD colour filters) are listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. As at

¹³⁰ UNEP/POPS/POPRC.10/INF/7/Rev.1, UNEP/POPS/POPRC.10/INF/8/Rev.1.

¹³¹ <http://www.ncbi.nlm.nih.gov/pubmed/23883102>.

¹³² Danish Ministry of Environment, "Short-chain Polyfluoroalkyl Substances (PFAS).

A literature review of information on human health effects and environmental fate and effect aspects of short-chain PFAS" Environmental project No. 1707, 2015, <http://www2.mst.dk/Udgiv/publications/2015/05/978-87-93352-15-5.pdf>.

¹³³ UNEP/POPS/COP.7/INF/21.

January 2016, the following parties are registered for those uses: China, Japan, and Vietnam. This use is not considered as an open application.

179. Video endoscopes are used to examine and treat patients at hospitals. Around 70% of the video endoscopes used worldwide, or about 200,000 endoscopes, contain a charge-coupled device (CCD, technology for capturing digital images) colour filter that contains a small amount (150 ng) of PFOS. According to a submission from the Japanese delegation, repairing such video endoscopes requires a CCD colour filter containing PFOS.

180. It is technically possible to produce PFOS-free CCD filters for use in new equipment. There are, however, 200,000 existing endoscopes that use PFOS-containing filters. Gradual phase-out of existing endoscopes will permit the use of PFOS-free equipment.

181. PFOS is also used as an effective dispersant when contrast agents are incorporated into an ethylene tetrafluoroethylene (ETFE) copolymer layer. PFOS plays an important role in radio-opaque ETFE production, allowing the achievement of the levels of accuracy and precision required in medical devices (e.g., radio-opaque catheters, such as catheters for angiography and in-dwelling needle catheters).

182. Since about 2000, when the harmful environmental effects of PFOS were identified, manufacturers of radio-opaque ETFE have been working with chemical materials suppliers to find alternatives. The 2006 OECD survey identified the use of PFBS as a surfactant in coating products. In some cases this substance can be used as a dispersant for inorganic contrast agent when it is mixed into ETFE.

F. Fire-fighting foams

183. Fire-fighting foam is listed as acceptable purpose for the production and use of PFOS, its salts and PFOF in Annex B. As at January 2016, the following parties are registered for this use: Canada, China, Switzerland, Vietnam and Zambia. This use is considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

184. In 2012, the POPRC recommended that since alternatives are available, “encouraged parties should stop using PFOS” for this use¹³⁴ as a recommendation to COP.

185. The performance of fire extinguishing foams is improved in several ways by the aqueous film and hence by the property determining surfactant. The water film, which is located between the fuel and the foam, cools the surface of the fuel, acts as a vapor barrier, supports the spreading of the foam on the fuel and promotes the self-healing of the foam blanket after injuries.¹³⁵ Because of these unique properties, AFFF is one of the most valuable tools in fighting hydrocarbon fuel fires so called Class B fires.¹³⁶ However AFFF is that the formation of the water film is exclusively provided by polyfluorinated surfactants.¹³⁷

186. Fluorosurfactants are a key ingredient in aqueous film forming foams (AFFF) have been manufactured by different processes and have many different chemical structures especially for extinguishing Class B (flammable liquids) fires.

187. Aqueous film forming foam (AFFF), sometimes referred to as aqueous fire-fighting foam, is a generic term for fire-fighting and/or vapor suppression products used globally to extinguish fires. AFFFs were designed to be especially effective in extinguishing Class B (flammable liquids) fires. AFFFs are unique amongst other fire-fighting foams in that they contain a small percentage of fluorinated surfactant (fluorosurfactant). This ingredient brings certain 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.

¹³⁴ Annex to decision POPRC-8/8.

¹³⁵ <http://www.mfs-fire-extinguishers.co.uk/types.htm>.

¹³⁶ http://www.iafss.org/publications/fss/11/1261/view/fss_11-1261.pdf.

¹³⁷ http://www.iafss.org/publications/fss/11/1261/view/fss_11-1261.pdf.

188. 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 as well as short-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 no longer available in industrialized countries¹³⁸.

189. Over the past decade, AFFF manufacturers have been replacing PFOS based products with fluorotelomer-based fluorosurfactants. There was a concern that these fluorotelomer-based products would lead to higher exposures to perfluorooctanoic acid (PFOA) which has similar hazard characteristics as PFOS.¹³⁹ The current effort is to complete the replacement of any remaining long-chain fluorosurfactants with shorter-chain fluorosurfactants such as perfluorohexylethanol (6-2 FTOH) derivatives^{140, 141}. In addition, alternative fluorosurfactants based on perfluorobutane sulfonate (PFBS) and related substances have also been considered along with various non-fluorinated alternatives. The short chain perfluoroalkyl sulphonates perfluorobutane sulfonate (PFBS) has never been applied or successfully used in fire fighting foams due to its non dispersive properties.¹⁴² This is also the case for perfluorohexane sulfonate (PFHxS) that currently is considered as a long chain PFC according to the OECD definition.¹⁴³ Measurement in fire fighters however, show equal levels of PFHxS and PFOS, which suggest the use of PFHxS in fire fighting foam.¹⁴⁴ PFHxS is currently under evaluation as a PBT (persistent, bioaccumulative, toxic) substance under REACH in Europe.¹⁴⁵

190. Fire-fighting foams with fluorosurfactants are very effective for extinguishing liquid fuel fires at airports and oil refineries and storage facilities (Class B fires). However, they also represent a direct release of fluorosurfactants to the environment. Types of fire-fighting foams include:

- (a) Fluoro-protein foams (FP) used for hydrocarbon storage tank protection and marine applications;
- (b) Aqueous film-forming foams (AFFF) developed in the 1960s and used for aviation, marine and shallow spill fires;
- (c) Film-forming fluoroprotein foams (FFFP) used for aviation and shallow spill fires;
- (d) Alcohol-resistant aqueous film-forming foams (AR-AFFF), which are multi-purpose foams;
- (e) Alcohol-resistant film-forming fluoroprotein foams (AR-FFFP), which also are multi-purpose foams; developed in the 1970s.

191. Normally, a mixture of fluorinated surfactant and a hydrocarbon-based surfactant is used in AFFF, as this combination is more cost-effective and performs better than either surfactant separately. The concentration of perfluorinated compounds in fire-fighting foams is about 0.9–1.5%.¹⁴⁶

192. The fluorinated surfactant used in AFFF forms an aqueous film covering the surface of oil and is used for stopping fires at chemical plants (Class B fires), fuel storage facilities (Class B fires), airports, underground parking facilities and tunnels. A PFOS-related compound used in the past was 3-[[[(Heptadecafluorooctyl)-sulfonyl]amino]-N,N,N-trimethyl-1-propanaminium iodide.

193. Today most fire-fighting foams are manufactured with fluorochemicals/telomers based on a perfluorohexane (C₆) chain. However, more than 50 enterprises in China that produce AFFF still consume more than 100 tonnes of PFOS per year.

¹³⁸ UNEP/POPS/COP.7/INF/21.

¹³⁹ PFOA meets the Annex D screening criteria, and is currently under evaluation by the POPRC as a candidate for listing in the Stockholm Convention.

¹⁴⁰ <http://www.fffc.org/images/APFarticle08.pdf>.

¹⁴¹ Carl Einar Amundsen, Roald Sørheim, Ingunn Forfang, Thomas Hartnik, Roald Aasen, Kristoffer Næs, Trine Eggen, 2008, Statens forurensningstilsyn (SFT), report TA-2444/2009. <http://www.klif.no/publikasjoner/2444/ta2444.pdf>.

¹⁴² Communication with Mr. Roger Klein.

¹⁴³ <http://www.oecd.org/ehs/pfc/>.

¹⁴⁴ Seow, J. 2013. Fire fighting foams with perfluorochemicals-review. 5th International Fire fighting foam conference.

¹⁴⁵ <http://echa.europa.eu/addressing-chemicals-of-concern/substances-of-potential-concern/pact/-/substance-rev/8834/term>.

¹⁴⁶ Pabon M, Corpart JM. 2002. Fluorinated surfactants: synthesis, properties, effluent treatment. *Journal of Fluorine Chemistry* 114: 149–156.

194. As fire-fighting foams have a long shelf life (10–20 years or longer), PFOS-containing fire-fighting foams such as Light Water (FC-600) may still be used around the world in accidental oil fires. In 2004 European Union stocks of fire-fighting foams with PFOS totalled 122 tonnes. According to Commission Regulation (EU) No 757/2010 of 24 August 2010, fire extinguishing foam placed on the EU/EEA market before 27 December 2006 may be used until 27 June 2011. In Norway in 2005 the stocks of fire-fighting foams containing PFOS were estimated to be 21 tonnes, with their main use in the off-shore oil industry.¹⁴⁷ In Switzerland stocks of PFOS in 2007 were estimated to be 13 tonnes, with consumption of 15–20% annually.¹⁴⁸ In 2006, Canada reported an estimated 300 tonnes of stockpiles of PFOS-containing fire-fighting foams, which represents approximately 3 tonnes of PFOS. These stockpiles have partially been destroyed following the coming into force of the *Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations* in 2008. In Japan stocks of AFFF amount to 19,000 tonnes (50% of which are stored in 23,000 underground parking areas), and the maximum annual production capacity for alternative fire-fighting foams without PFOS is 2,100 tonnes.

195. Collecting and destroying these stocks of PFOS instead of using them will avoid considerable pollution from this persistent organic pollutant (for example, around airports). The cost of replacement and destruction of the PFOS currently found in fire-fighting foam stores in the European Union has been estimated at €6,000 per tonne, or about €700,000 in total. Replacing PFOS throughout Japan with alternatives in an environmentally appropriate way (including collection, refilling, transportation, storage and incineration) would cost ¥1.7 million (€13,000) per tonne, or ¥22 billion (€170 million) in total. In Canada, in 2006, disposal and replacement costs for PFOS-based fire-fighting foams were estimated to be Can\$ 700,000 (€500,000).

196. The alternatives to the use of PFOS fluorosurfactants in fire-fighting foams are:

- (a) Non-PFOS-based fluorosurfactants with shorter chain length such as:
 - (i) C6-fluorotelomers such as perfluorohexane ethyl sulfonyl betaine, often used in combination with hydrocarbons such as ®Capstone® products (Chemours) and products from Chemguard and Dynax;
 - (ii) Dodecafluoro-2-methylpentan-3-one (3M);
- (b) A return to the previously used technology, which employed fluorine-free fire-fighting foams. Examples include:
 - (i) Silicone-based surfactants,¹⁴⁹ often used in combination with fluorosurfactants;
 - (ii) Hydrocarbon-based surfactants, often used in combination with fluorosurfactants;
 - (iii) Synthetic detergent foams, often used for forestry and high-expansion applications and for training (“Trainol”); new products with glycols (Hi Combat ATM from AngusFire),¹⁵⁰
 - (iv) Protein-based foams (e.g. Sthamex F-15), which are less effective for flammable liquid fuel fires and are mainly used for training but also have some marine uses.

197. In Norway, the offshore oil industry voluntarily and systematically phased out the use of PFOS before the ban in 2007. PFOS containing fire-fighting foam has also been phased out by other users in Norway. While the most used alternatives in Norway are now PFOS-free telomer-based fluorosurfactants, there are also fluorine-free alternatives on the market, such as Arctic Re-Healing Foam™ RF, developed by 3M Australia. The Norwegian producer Solberg Scandinavian AS states that this fluorine-free alternative is not quite as effective as AFFF and will not be an alternative at offshore installations or for the petroleum industry, but that its fire-fighting performance is close to that of AFFF and that it is a good alternative for other uses.¹⁵¹ It has been approved for the control and extinguishing of class B flammable liquid hydrocarbon and polar fuel fires. Arctic Re-healing Foam

¹⁴⁷ Climate and Pollution Agency (former SFT), Norwegian Ministry of the Environment. 2005. Kartlegging av PFOS i brannskum [Survey of PFOS use in fire-fighting foam]. TA-2139.

¹⁴⁸ Buser, A., Morf, L. 2009. Substance flow analysis of PFOS and PFOA in Switzerland. *Environmental Studies* 0922. Federal Office for the Environment, Bern.

¹⁴⁹ Generally, siloxanes such as polyther-modified siloxanes are called silicone surfactants in silicone industry.

¹⁵⁰ www.kiddecanada.com/utdfs/Templates/Pages/Template-50/0,8061,pageId%3D2587&siteId%3D463,00.html.

¹⁵¹ <http://www.solbergfoam.com/Foam-Concentrates/ARCTIC-Foam.aspx>

RF meets the requirements of parts 3 and 4 of the European Committee for Standardization (CEN) EN 1568 specifications.¹⁵²

Technical feasibility and efficacy

198. 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 and in-use for several years.

199. The specific identities of replacements or substitutes for PFOS, PFOS-related chemicals and mixtures have been claimed as CBI¹⁵³ to the extent they have been disclosed to the U.S. government. However, chemical structures of major fluorosurfactants used in AFFF have been analysed through an independent scientific study in 2015.¹⁵⁴ Results from this study indicate that these substances and mixtures have included short-chain PFAS and various fluorinated telomers.

200. Dodecafluoro-2-methylpentan-3-one (CAS No: 756-13-8) is manufactured and sold by 3M as an alternative to halon and other ozone depleting / substances with a high global warming substances. Applications for this fluorinated ketone include clean fire extinguishing agents (CEA). Although CAS No: 756-13-8 has been used as a clean extinguishing agent, it's not clear to what extent dodecafluoro-2-methylpentan-3-one (CAS No: 756-13-8) has replaced PFOS AFFF. Dodecafluoro-2-methylpentan-3-one would generally not be considered a viable alternative to PFOS AFFF, since it is used as a fire protection fluid.¹⁵⁵

201. There are varying views¹⁵⁶ on the efficacy of non-PFOS based AFFFs. In some circumstances, the non-PFOS based AFFFs were found to retain similar fire suppression capabilities as PFOS containing agents and in others, variable efficacy is reported.

Health and environmental effects including toxicological and ecotoxicological information

202. The primary supply of AFFF has become 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 than long chain telomer based fluorosurfactants, but due to scarce publically available data for short chain 6:2 fluorotelomers more information is needed to confirm this hypothesis.¹⁵⁷

203. 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, a further assessment of health and environmental impacts for Class A foam extinguishing agents is scarcely done.¹⁵⁸

Cost-effectiveness

204. 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.¹⁵⁹

205. A British survey states that the fluorine-free alternatives to fire-fighting foams in the United Kingdom are approximately 5–10% more expensive than fluorosurfactant-based foams.¹⁶⁰ According to a manufacturer of fluorine-free alternatives, the price would fall if the market size

¹⁵² Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

¹⁵³ There are replacements in US but they are not publically disclosed.“

¹⁵⁴ Will J. Backe, Thomas C. Day, and Jennifer A. Field*, Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS; *Environ. Sci. Technol.*, 2013, 47 (10), pp 5226–5234

¹⁵⁵ <http://multimedia.3m.com/mws/media/1246880/3mtm-novectm-1230-fire-protection-fluid.pdf>.

¹⁵⁶ <http://chm.pops.int/tabid/2467/Default.aspx>

¹⁵⁷ UNEP/POPS/POPRC.10/INF/7/Rev.1, UNEP/POPS/POPRC.10/INF/8/Rev.1.

¹⁵⁸ <http://chm.pops.int/tabid/2467/Default.aspx> (submission by China, completed form).

¹⁵⁹ <http://chm.pops.int/tabid/2467/Default.aspx> (submission by Norway, completed form).

¹⁶⁰ Risk and Policy Analysts and Building Research Environment. 2004. Perfluorooctane sulphonate: risk reduction strategy and analysis of advantages and drawbacks. United Kingdom Department for Environment, Food and Rural Affairs and Environment Agency for England and Wales.

increased. A more deliberate shift towards fluorine-free fire-fighting foam alternatives would probably eliminate the difference in cost.

Availability, accessibility and socio-economic consideration

206. 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 and Chemguard (both Tyco companies), Chemours, , 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.

207. 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.¹⁶¹

208. 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.

G. Insect baits for control of leaf-cutting ants

209. Leaf cutting ants of the genera *Atta* spp and *Acromyrmex* spp. are native in a large part of Latin America and the southern part of the United States.¹⁶² Leaf-cutting ants are the dominant species in both natural and human-disturbed settings where they occur. They are considered to be a keystone species because of their influence on the environment, contributing to environmental diversity, productivity, and nutrient and energy flow. Their activities improve drainage and root penetration, increase organic matter and mineralization. They improve secondary seed dispersal and germination. Understanding the beneficial effects of leaf-cutting ants on the environment can help with making decisions, within the context of sustainable agriculture, forestry or land management, on what type of method might be chosen.¹⁶³

210. Insect baits for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. are listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. As at January 2016, the following parties are registered for this use: Brazil and Vietnam. Those uses are considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

211. *N*-Ethyl perfluorooctane sulfonamide (known as sulfluramid; EtFOSA; CAS No: 4151-50-2) has been used as an active ingredient in ant baits to control leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. in many countries in South America (see appendix 7) as well as for control of red imported fire ants, and termites.¹⁶⁴

212. According to information from the 2006 OECD survey sulfluramid was used in insecticides at a concentration of 0.01-0.1% at an annual volume of up to 17 tonnes.

213. Fluorosurfactants may also be used as “inert” surfactants (enhancers used in pesticide formulations but not constituting active ingredients) in pesticide products. Sulfluramid is used in Brazil in more than 95% of baits for the control of leaf-cutting ants, although the amount of PFOS used was not reported. Since 10% of sulfluramid is degraded to PFOS, its use represents a direct release of PFOS to the environment.^{165, 166, 167}

214. According to the Brazilian delegation, the use of sulfluramid in Brazil prevents damage corresponding to losses of up to 14.5 % of trees per hectare. Other agricultural products likely to suffer

¹⁶¹ <http://chm.pops.int/tabid/2467/Default.aspx> (submission by China, completed form).

¹⁶² <http://www.antweb.org/antblog/2011/03/geographic-range-of-leaf-cutter-ants-don-indianapolis-in-usa.html>

¹⁶³ Terezinha MC Della Lucia, Lailla C Gandra, Raul NC Guedes. 2013. Managing leaf-cutting ants: peculiarities, trends and challenges. *Pest Manag Sci* 70:14-23.

¹⁶⁴ UNEP/POPS/POPRC.6/13/Add.3/Rev.1.

¹⁶⁵ UNEP/POPS/POPRC.3/20/Add.5.

¹⁶⁶ <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+7100>.

¹⁶⁷ Löfstedt et al., “Is Ongoing Sulfluramid Use in South America a Significant Source of Perfluorooctanesulfonate (PFOS)? Production Inventories, Environmental Fate, and Local Occurrence” *Environ. Sci. Technol.*, 2016, 50 (2), pp 653–659 DOI: 10.1021/acs.est.5b04544, <http://pubs.acs.org/doi/abs/10.1021/acs.est.5b04544?journalCode=esthag>

costly losses are soybean and maize. Also, the per-hectare capacity to support livestock is likely to decrease if forage for grazing is reduced by ants.¹⁶⁸

215. Currently, the active ingredients registered in Brazil for producing bait to control leaf-cutting ants are sulfluramid, fipronil and chlorpyrifos. The latter two, however, are considered more acutely toxic to humans and the environment than sulfluramid. Furthermore, the effectiveness of these substances has been questioned; thus new alternatives are being studied in Brazil. According to the Brazilian Annex F information, sulfluramid cannot currently be efficiently replaced in Brazil by any other registered products commercialized for the same purpose.¹⁶⁹

216. In the EU, PFOS-related substances are not used in the manufacture of pesticides.¹⁷⁰ Ant baits containing S-methoprene and pyriproxifen are registered in New Zealand for the control of exotic ants by aerial and ground applications.¹⁷¹

217. According to Brazil 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. Additionally according to Brazil, fenoxycarb, pyriproxifen, diflubenzuron, teflubenzuron, silaneafone, thidiazuron, tefluron, prodron, abamectin, methoprene, Hydramethylnon, boric acid, some insecticides from the group of neonicotinoids, pyrethroids, Spinosyns, etc., had been tested for leaf-cutting ants, but they were not effective.¹⁷² An adequate insecticide used to formulate bait for the control of leaf-cutting ants should be lethal at low concentrations or otherwise prevent the ant feeding or reproducing and act by ingestion and present a delayed toxic action. Additionally, it should be odorless and non-repellent, so as to be dispersed by trophallaxis to most workers in the colony. Since 1958, over 7,500 chemical compounds for ant control have been studied in many countries. Fewer than 1% of those 7,500 compounds have shown promise.¹⁷³

218. Leaf-cutting ants have mechanical and chemical defenses that help them to counterbalance the effect of some control measures. Studying the adaptation mechanisms of leaf-cutting ants is recommended to improve effectiveness of strategies for their ecological management.¹⁷⁴ Exocrine glands and symbiotic bacteria are the main sources of antimicrobials in leaf-cutting ants, and are used to counter biological control agents. Studying the adaptation mechanisms of leaf-cutting ants is recommended to improve effectiveness of strategies for their ecological management. However biological control can be effective under some conditions. In laboratory studies, the entomopathogenic *Metarrhizium anisopliae* can cause the decline and ultimate death of small colonies 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 to 5 days.^{175, 176} Effective natural products include limonoids extracted from the roots of the South Brazilian endemic plant *Raulinoa echinata*.¹⁷⁷ Further research is required to verify the effectiveness of these interventions under field conditions. Input from Brazil indicated that no effective biological control methods have been identified yet.

¹⁶⁸ Oficio Oficio DFIA/SDA/MAPA nº 123/2008 from Ministry of Agriculture, Livestock and Food Supply, Animal and Plant Protection Secretariat Agriculture Inputs Inspection Department.

¹⁶⁹ UNEP/POPS/COP.7/INF/21.

¹⁷⁰ <http://archive.defra.gov.uk/environment/quality/chemicals/documents/pfos-riskstrategy.pdf>.

¹⁷¹ Environmental Risk Management Authority of New Zealand (ERMA NZ) (2007), Decision, 2007-11-11.

¹⁷² UNEP/POPS/COP.7/INF/11.

¹⁷³

<http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC3/AdditionalInformationonPFOS/ta/bid/353/Default.aspx> (submission by Leaf-Cutting Ant Baits Industries Association, Note-1)

¹⁷⁴ Madelen Herrera y Nurys Valenciaga. Peculiarities of leaf-cutter ants (Attini: Acromyrmex y Atta) that make difficult their control, 2011, Cuban Journal of Agricultural Science, Volume 45, Number 3.

¹⁷⁵ D.B. Jaccoud, W.O.H. Hughes and C.W. Jackson, *The epizootiology of a Metarrhizium infection in mini-nests of the leaf-cutting ant Atta sexdens rubropilosa*, 1999, ENTOMOLOGIA EXPERIMENTALIS ET APPLICATA, Volume 93, Number 1, 51-61, DOI: 10.1023/A:1003830625680.

¹⁷⁶ Myriam M. R. Ribeiro, Karina D. Amaral, Vanessa E. Seide, Bressane M. R. Souza, Terezinha M. C. Della Lucia, Maria Catarina M. Kasuya, and Danival J. de Souza, *Diversity of Fungi Associated with Atta bisphaerica (Hymenoptera: Formicidae): The Activity of Aspergillus ochraceus and Beauveria bassiana*, Psyche Volume 2012, 2012, Article ID 389806, 6 pages, doi:10.1155/2012/389806.

¹⁷⁷ Maique W. Biavatti, I; Rosângela WesterlonI; Paulo C. Vieira; M. Fátima G. F. da Silva; João B. Fernandes; M. Fernanda G. V. Peñaflo; Odair C. Bueno; Javier Ellena, *Leaf-cutting ants toxicity of limonexic acid and degraded limonoids from Raulinoa echinata*. X-ray structure of epoxy-fraxinellone, Journal of the Brazilian Chemical Society, *Print version* ISSN 0103-5053. Chem. Soc. vol.16 no.6b São Paulo Nov./Dec. 2005.

219. 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 viability¹⁷⁸. However research is continuing.

220. With the development of synthetic insecticides, chemical methods have been effectively used to control *Atta* spp. and *Acromyrmex* spp.¹⁷⁹

221. There are a number of chemical alternatives to *N*-Ethyl perfluorooctane sulfonamide (known as sulfluramid), with a multitude of uses¹⁸⁰ and/or tested as alternatives to sulfluramid. Chlorpyrifos, Cypermethrin, mixture of Chlorpyrifos and Cypermethrin, Fipronil, Imidacloprid,¹⁸¹ Abamectin, Deltamethrin, Fenitrothion, mixture of Fenitrothion and Deltamethrin. Chlorpyrifos used to be considered as an alternative, but due to the severe toxicological and environmental characteristics of this pesticide it can no longer be considered as an alternative for effective control of *Atta* spp. and *Acromyrmex* spp.¹⁸²

Non-chemical control methods for leaf-cutting ants

222. Leaf-cutting 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 some others methods to control leaf-cutting ants that are not based on chemical pest control. These methods are biological, physical or natural control.¹⁸³ However leaf-cutting ants have developed defensive mechanisms against some of these control measures.

223. Defense against biological control includes the following:

(a) Leaf-cutting ants are provided with spines that serve as means of protection against their natural enemies;

(b) When infected with a symbiotic fungus, the contaminated parts of the ant colony are disinfected, pruned, and isolated, reducing the impact of the fungus.

224. Leaf-cutting 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-cutting ants, and are used to counter biological control agents. Studying the adaptation mechanisms of leaf-cutting ants is recommended to improve effectiveness of strategies for their ecological management.¹⁸⁴

225. However biological control can be effective. The entomopathogenic *Metarrhizium anisopliae* can cause the decline and ultimate death of small colonies¹⁸⁵ 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.¹⁸⁶ One of the largest studies of parasites associated with leaf-cutting ants demonstrates a new possible non-chemical control method for these two species

¹⁷⁸ D.B. Jaccoud, W.O.H. Hughes and C.W. Jackson, *The epizootiology of a Metarrhizium infection in mini-nests of the leaf-cutting ant Atta sexdens rubropilosa*, 1999, ENTOMOLOGIA EXPERIMENTALIS ET APPLICATA, Volume 93, Number 1, 51-61, DOI: 10.1023/A:1003830625680.

¹⁷⁹ Information from Brazil.

¹⁸⁰ Information from Argentina and China.

¹⁸¹ Information from China.

¹⁸² UNEP/POPS/POPRC.10/INF/7/Rev.1.

¹⁸³ BRITTO, J. S.; FORTI, L. C.; OLIVEIRA, M. A.; ZANETTI, R.; WILCKEN, C. F.; ZANUNCIO, J. C.; LOECK, A. E.; CALDATO, N.; NAGAMOTO, N. S.; LEMES, P. G. and CAMARGO, R. S., 2016. Use of alternatives to PFOS, its salts and PFOSF for the control of leaf-cutting ants *Atta* and *Acromyrmex*, International Journal of Research in Environmental Studies (2016) 3(2): pp.11-92. p.51, 68.

¹⁸⁴ Madelen Herrera y Nurys Valenciaga. Peculiarities of leaf-cutter ants (*Atta*: *Acromyrmex* y *Atta*) that make difficult their control, 2011, Cuban Journal of Agricultural Science, Volume 45, Number 3.

¹⁸⁵ D.B. Jaccoud, W.O.H. Hughes and C.W. Jackson, *The epizootiology of a Metarrhizium infection in mini-nests of the leaf-cutting ant Atta sexdens rubropilosa*, 1999, ENTOMOLOGIA EXPERIMENTALIS ET APPLICATA, Volume 93, Number 1, 51-61, DOI: 10.1023/A:1003830625680.

¹⁸⁶ Myriam M. R. Ribeiro, Karina D. Amaral, Vanessa E. Seide, Bressane M. R. Souza, Terezinha M. C. Della Lucia, Maria Catarina M. Kasuya, and Danival J. de Souza, Diversity of Fungi Associated with *Atta bisphaerica* (Hymenoptera: Formicidae): The Activity of *Aspergillus ochraceus* and *Beauveria bassiana*, Psyche Volume 2012, 2012, Article ID 389806, 6 pages, doi:10.1155/2012/389806.

of leaf cutting ants in the form of specialized parasites.¹⁸⁷ *Escovopsis* is a group of parasites that attack the fungal crops raised by the ants. Interestingly, a variety of forms of *Escovopsis* are present in the same ant colony and the parasite has the capability to invade distantly-related fungus-growing ant species, including those found in Brazil. Since 1999, no significant progress was made in order to operationally enable its use for the control of leaf-cutting ants.¹⁸⁸

226. Effective natural products include limonoids extracted from the roots of the South Brazilian endemic plant *Raulinoa echinata*.¹⁸⁹ Baits prepared with neem oil (Azadirachtin) reduced ant foraging by 75.5% for *Atta* spp, and 83.5% for *Acromyrmex* spp. in a field trail in Brazil. Baits prepared with sesame oil reduced ant foraging by 55.9% and 67.6% of *Atta* spp. and *Acromyrmex* spp., respectively.¹⁹⁰ Baits prepared with neem and sesame, in fact explain that do not control or kill leaf-cutting ants' colonies, they simply reduce the forage activity in trails for a period. After this time the leaf-cutting ants return to activities causing damages. Plants extracts including neem and sesame are not as effective as sulfluramid.¹⁹¹

227. In 2011 a new natural ant bait called Cocapec was registered in Brazil¹⁹². The baits, based on saponins and flavones from the plant *Tephrosia candida*, also contain an extract from the plant *Psychotria marcgravii*, organic soybean oil and citrus pulp. The baits were developed by a cooperative of farmers and ranchers of the High Mogiana region, based in Franca/SP, which has more than 2,200 members and a total area of 60,000 hectares of coffee. The herbal formulation is highly attractive to ants, which carry it inside the nest without intoxication, inserting it into the internal food system. Its fungicidal action eliminates the fungus that coexists with the ants, spoiling the food base of the nest resulting in its extinction. Cocapec is approved for use on organic farms, without efficacy studies. Since the new protocol for leaf cutting ants control was established by Ministry of Agriculture in 2009 to prove the efficacy for a regular registration of pesticides use the register of this product was cancelled, because they didn't provide the new studies of efficacy. However it is recommended for organic farms, assuming its efficiency.¹⁹³ More research is needed to verify if this product can be efficient in the leaf cutting ant control.

228. Defense against physical control includes the following: Leaf-cutting 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.

229. Research in Costa Rica showed that increasing plant diversity in coffee plantations reduced leaf loss to leaf cutting ants from 40% in monocultures to <1% in farms with complex plant diversity.¹⁹⁴

¹⁸⁷ Meirelles LA, Solomon SE, Bacci M, Wright AM, Mueller UG, Rodrigues A (2015) Shared *Escovopsis* parasites between leaf-cutting and non-leaf-cutting ants in the higher attine fungus-growing ant symbiosis, R. Soc. Open Sci 2:15027 – 15038.

¹⁸⁸ Britto, J. S.; Forti, L. C.; Oliveira, M. A.; Zanetti, R.; Wilcken, C. F.; Zanuncio, J. C.; Loeck, A. E.; Caldato, N.; Nagamoto, N. S.; Lemes, P. G. and Camargo, R. S., 2016. Use of alternatives to PFOS, its salts and PFOSE for the control of leafcutting ants *Atta* and *Acromyrmex*, International Journal of Research in Environmental Studies (2016) 3(2): pp.48

¹⁸⁹ Maique W. Biavatti, I; Rosângela WesterlonI; Paulo C. Vieira; M. Fátima G. F. da Silva; João B. Fernandes; M. Fernanda G. V. Peñaflor; Odair C. Bueno; Javier Ellena, Leaf-cutting ants toxicity of limonexic acid and degraded limonoids from *Raulinoa echinata*. X-ray structure of epoxy-fraxinellone, Journal of the Brazilian Chemical Society Print version ISSN 0103-5053. Chem. Soc. vol.16 no.6b São Paulo Nov./Dec. 2005.

¹⁹⁰ P Boff, A Giesel, MIC Boff. 2016. No-residual baits and farmer perception to manage leaf-cutting ants. *Agroecology and Sustainable Food Systems* 40(5):451-465.

¹⁹¹ Britto, J. S.; Forti, L. C.; Oliveira, M. A.; Zanetti, R.; Wilcken, C. F.; Zanuncio, J. C.; Loeck, A. E.; Caldato, N.; Nagamoto, N. S.; Lemes, P. G. and Camargo, R. S., 2016. Use of alternatives to PFOS, its salts and PFOSE for the control of leafcutting ants *Atta* and *Acromyrmex*, International Journal of Research in Environmental Studies (2016) 3(2): pp.48

¹⁹² http://www.bioisca.com.br/?page_id=318

¹⁹³ Britto, J. S.; Forti, L. C.; Oliveira, M. A.; Zanetti, R.; Wilcken, C. F.; Zanuncio, J. C.; Loeck, A. E.; Caldato, N.; Nagamoto, N. S.; Lemes, P. G. and Camargo, R. S., 2016. Use of alternatives to PFOS, its salts and PFOSE for the control of leafcutting ants *Atta* and *Acromyrmex*, International Journal of Research in Environmental Studies (2016) 3(2): pp.48

¹⁹⁴ Edgar H. Varón, Sanford D. Eigenbrode, Nilsa A. Bosque-Pérez and Luko Hilje. 2007. Effect of farm diversity on harvesting of coffee leaves by the leaf-cutting ant *Atta cephalotes*. *Agricultural and Forest Entomology* (2007), 9, 47–55.

Technical feasibility and efficacy

230. The reported chemical alternatives to sulfluramid as pesticides for leaf cutting ants are: fipronil, deltamethrin, fenitrothion and hydramethylnon.¹⁹⁵

231. In principle these pesticides are available on the world market. However, they are not all freely available everywhere. Deltamethrin may be a vPvB substance. In general, it should be noted that substances which have been identified as not likely to be a POP, may still exhibit hazardous characteristics, such as imidacloprid and chlorpyrifos. As indicated in the General guidance¹⁹⁶ on considerations related to alternatives and substitutes for POPs, where possible, efforts should be made to collect information to ensure that alternatives do not exhibit hazardous properties and that the risk of alternatives is considerably lower than that of the POP they replace. It is therefore strongly recommended that further assessment of alternatives to PFOS, its salts and PFOSF identified, is carried out by Parties within their national framework of authorization before considering such substances as suitable alternatives.¹⁹⁷

232. Some of these pesticides listed above are all available as commercial products on the Argentinean market. Argentina has prohibited the import, production, trading and use of chlorpyrifos in formulations of household sanitary products¹⁹⁸ 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 sulfluramid in Argentina can be divided in two main groups namely chemical alternatives (synthetic insecticides) and non-chemical alternatives (non-chemical products). The common chemical alternatives are Fipronil, applied on the total surface or as a component of a bait and Chlorpyrifos, applied using fogging machines in all main principal entries of the nest.

233. The non-conventional are Entomopathogenic fungi are: (a) organic bait consisting of rice grains with *Beauveria sp.*; (b) Diatomaceous earth mixed with waste water in the principal entry of each anthill; (c) Vegetal substances with insecticide effect: extract of eucalyptus, castor-oil plant and “Palo Amargo” (“Bitter stick”, *Aeschirium crenata Vell.* Simaroubaceae); (d) Natural enemies: parasitoids known as “Moscas descapitadotas” (“Decapitating flies”, Diptera: Phoridae); and (e) organic baits based on yeast and rice. All these alternatives have been tested in Argentina with promising results.^{199, 200}

234. 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 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 primary exposure to humans.²⁰¹

235. 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, has already rendered unsatisfactory and inconsistent results, and has offered no indication of any technical, economic, or operational viability. However field trials in 2016 have shown considerable promise. For example, neem baits reduced ant foraging by 75.5% for *Atta* spp. and 83.5% for *Acromyrmex* spp. in a field trail in Brazil. PFOS-related chemicals 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, PFOS-related chemicals and mixtures have been claimed as confidential business information (CBI) to the extent they have been disclosed to the

¹⁹⁵ http://landscapeipm.tamu.edu/files/2012/09/AmdroAntBlockLeafcutting_fnl.pdf.

¹⁹⁶ UNEP/POPS/POPRC.5/10/Add.1.

¹⁹⁷ UNEP/POPS/POPRC.10/INF/7/Rev.1, UNEP/POPS/POPRC.5/10/Add.1

¹⁹⁸ For household sanitary products biocide uses are applied only.

¹⁹⁹ Comments from Argentina dated 3rd July 2012 publicly available on SC homepage.

²⁰⁰ UNEP/POPS/POPRC.8/INF/18.

²⁰¹ UNEP/POPS/POPRC.6/13/Add.3/Rev.1.

U.S. government. Generally speaking, however, these substances and mixtures have included short-chain PFAS and various fluorinated telomers.

236. The effectiveness of the substances mentioned in appendix 2 have been questioned thus new alternatives are being studied in Brazil. According to Brazil, fenoxycarb, pyriproxyfen, diflubenzuron, teflubenzuron, silaneafone, thidiazuron, tefluron, prodrone, abamectin, methoprene, Hydramethylnon, boric acid, some insecticides from the group of neonicotinoids, pyrethroids, Spinosyns, etc., had been tested for leaf-cutting ants, but they were not effective.^{202, 203}

Health and environmental effects including toxicological and ecotoxicological information

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

238. 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. The resistance to insecticides does not apply to leaf-cutting ants. In this case, the target of insecticides is the workers who are sterile, thus not allowing the selection of resistant individuals.²⁰⁴

239. Multiple resistances are 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.²⁰⁵

240. According to Brazil the active ingredients fipronil and chlorpyrifos present a much higher toxicity to mammals, water organisms, fish and bees than sulfluramid.²⁰⁶ Additionally Brazil consider not to 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.

Availability, accessibility and socio economic consideration

241. These alternatives mentioned, chlorpyrifos, cypermethrin, fipronil, abamectin, deltamethrin and fenitrothion²⁰⁷ are available as commercial products on the Argentinian market.

242. Currently, the active ingredients registered in Brazil for ant baits are sulfluramid, fipronil and chlorpyrifos. Chlorpyrifos as insect baits is no longer used in Brazil for control leaf cutting ants. 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.

H. Insecticides for control of red imported fire ants and termites

243. Insecticides for control of red imported fire ants (RIFA) and termites are listed as specific exemptions or the production and use of PFOS, its salts and PFOSF in Annex B. As at January 2016, China and the Republic of Korea are registered for this use. Those uses are considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

244. PFOS is no longer used to manufacture ant bait or insecticides against beetles and ants in the European Union, and the United States Environmental Protection Agency cancelled the manufacturing use-registration of sulfluramid in May 2008 and all product registrations by 2012.²⁰⁸ According to information submitted to the secretariat of the Stockholm Convention, sulfluramid had been used for pest control (to control cockroaches, white ants and fire ants) in China.

²⁰² UNEP/POPS/COP.7/INF/11.

²⁰³ <http://chm.pops.int/tabid/4814/Default.aspx> (submission by Brazil, English translation of “Review, analysis and discussion on the feasibility of the use of alternatives to PFOS, its salts and PFOSF for the control of leaf-cutting ants Atta and Acromyrmex within the integrated pest management approach”).

²⁰⁴ <http://chm.pops.int/tabid/4814/Default.aspx> (submission by Brazil, “Revisão, análise e discussão sobre a viabilidade do uso das alternativas ao pfos, seus sais e pfosf, no controle das formigas cortadeiras Atta e Acromyrmex dentro de uma abordagem de manejo integrado de pragas”).

²⁰⁵ Robert G. Bellinger, *Pest Resistance to Pesticides*, 1996, Department of Entomology, Clemson University.

²⁰⁶ http://echa.europa.eu/information-on-chemicals/cl-inventory-database?p_p_id=dissclinventory_WAR_dissclinventoryportlet&p_p_lifecycle=0&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=1&p_p_col_count=2.

²⁰⁷ UNEP/POPS/POPRC.8/INF/18.

²⁰⁸ www.epa.gov/fedrgstr/EPA-PEST/2008/May/Day-16/p10919.htm.

245. In the EU, PFOS-related substances are not used in the manufacture of pesticides.²⁰⁹ Ant baits containing S-methoprene and pyriproxifen are registered in New Zealand for the control of exotic ants by aerial and ground applications.²¹⁰

246. Red Imported Fire Ants, (RIFA) are a threat to human activity because of their painful stings, which may cause severe allergic reactions in venom sensitive people. Thus, efforts to prevent their spread are important to nurserymen, sod producers, landscape professionals, and homeowners throughout the infested areas. RIFA will aggressively attack anything that disturbs or threatens their mound. They are capable of stinging repeatedly and painfully, with each sting resulting in a long-lasting, itching pustule. Individuals sensitive to RIFA stings may go into anaphylactic shock. The RIFA are a threat to pets, newborn chicks and calves, wildlife, and sleeping or bed-ridden individuals. They damage electrical equipment and their unsightly mounds interfere with cutting and harvesting machinery in cattle operations and other landscape and agricultural functions.²¹¹

Technical feasibility and efficacy

247. In Australia pesticide products that contain Bifenthrin, Hydramethylnon, Pyriproxyfen, Alphacypermethrin, Fipronil, Indoxacarb and their mixtures thereof are registered and commercialized to manage RIFA and termites.²¹²

248. 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.

249. The two PFOS-related substances potassium *N*-ethyl-*N*-[(heptadecafluorooctyl) sulfonyl] glycinate (CAS No: 2991-51-7) and 3-[[[(heptadecafluorooctyl)sulfonyl]amino]-*N,N,N*-trimethyl 1-propanaminium iodide (CAS No: 1652-63-7) have been approved in pesticide formulations in the United States in the past.²¹³ However, 3-[[[(heptadecafluorooctyl)sulfonyl]amino]-*N,N,N*-trimethyl 1-propanaminium iodide (CAS No: 1652-63-7) is currently only approved for non-food use and potassium *N*-ethyl-*N*-[(heptadecafluorooctyl) sulfonyl] glycinate (CAS No: 2991-51-7) is no longer permitted.^{214, 215} Both chemicals have other uses, for example as cleaning agents²¹⁶. PFOS derivatives were used in pesticides because they were considered rather inert and non-toxic²¹⁷.

250. The specific identities of replacements or substitutes for PFOS, PFOS-related chemicals 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.

Health and environmental effects including toxicological and ecotoxicological information

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

Availability, accessibility and socio economic consideration

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

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

254. All substances except Hydranethylnon are approved for biocidal use in EU

²⁰⁹ <http://archive.defra.gov.uk/environment/quality/chemicals/documents/pfos-riskstrategy.pdf>.

²¹⁰ Environmental Risk Management Authority of New Zealand (ERMA NZ) (2007), Decision, 2007-11-11.

²¹¹ <http://www.fmcprosolutions.com/LinkClick.aspx?fileticket=bYPHKM4OFLk%3D&tabid=1253&mid=2103>

²¹² Australia Public Chemical Registration Information System Search - portal apvma.pdf.

²¹³ www.fluoridealert.org/pesticides/pfos.pfoas-page.htm.

²¹⁴ <http://iaspub.epa.gov/apex/pesticides>.

²¹⁵ Federal Register: June 24, 1998 (Volume 63, Number 121), Notices, Page 34384-34390.

²¹⁶ https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/183154/pfos-riskstrategy.pdf.

²¹⁷ UNEP/POPS/COP.7/INF/21.

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

255. 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.²¹⁸ At least 30 natural enemies have been identified in South America.

256. Biological controls for red imported fire ant (RIFA) include a group of decapitating phorid flies (*Pseudacteon* spp.) which parasitize the ants.²¹⁹ The microsporidian protozoan *Thelohania solenopsisae* and the fungus *Beauveria bassiana* are also promising controls for RIFA. *B. bassiana* has been shown to control RIFA under field conditions in Taiwan Province of China.

257. 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.²²⁰ Other potential biological controls include the endoparasitic fungi *Myrmecomycetes annellisae* and *Myrmecinosporidium durum*, and the parasite *Mattesia* spp.

258. Biological control options²²¹ for termites include *Beauveria bassiana* and *Metarhizium anisopliae*.

I. Electric and electronic parts for some colour printers and colour copy machines

259. Electric and electronic parts for some colour printers and colour copy machines are listed as specific exemptions for the production and use of PFOS, its salts and PFOSE in Annex B. As at January 2016, China and the Republic of Korea are registered for this use. This use is considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

260. Electrical and electronic equipment often requires hundreds of parts and thousands of processes. PFOS-based chemicals are used in the manufacturing of digital cameras, cell phones, printers, scanners, satellite communication systems, radar systems and the like. The PFOS-related compounds are used as process chemicals, and the final products are considered as mostly PFOS-free.²²²

261. PFOS has 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.²²³

262. 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.²²⁴

²¹⁸ Steven M. Valles, "Positive-Strand RNA Viruses Infecting the Red Imported Fire Ant, *Solenopsis invicta*," *Psyche*, vol. 2012, Article ID 821591, 14 pages, 2012. doi:10.1155/2012/821591

²¹⁹ Flanders K, Graham LCP. 2008. Biological Control of Imported Fire Ants. ANR-1149. Alabama Cooperative Extension System. <http://www.aces.edu/pubs/docs/A/ANR-1149/ANR-1149.pdf>

²²⁰ Steven M. Valles, Review Article, Positive-Strand RNA Viruses Infecting the Red Imported Fire Ant, *Solenopsis invicta*, *Psyche* Volume 2012, 2012, Article ID 821591, 14 pages doi:10.1155/2012/821591.

²²¹ Lenz M., Biological control in termite management: the potential of nematodes and pathogens. 2005, Proceedings of the Fifth International Conference on Urban Pests, Lee Y-L, Robinson WH (eds). <http://www.icup.org.uk/reports%5CICUP008.pdf>.

²²² UNIDO, Guidance for the inventory of perfluorooctane sulfonic acid (PFOS) and related chemicals under the Stockholm Convention on Persistent Organic Pollutants, 2012 (https://www.unido.org/fileadmin/user_media/Services/Environmental_Management/Stockholm_Convention/Guidance_Docs/UNEP-POPS-GUID-NIP-2012-PFOS-Inventory.En.pdf); UNIDO, Guidance on the Best Available Techniques (BAT) and Best Environmental Practice (BEP) for PFOS and its salts, 2012 ([https://www.unido.org/fileadmin/user_media/Services/Environmental_Management/Stockholm_Convention/Guidance_Docs/UNEP-POPS-GUID-NIP-2012-BATBEP/UNEP-POPS-GUID-NIP-2012-BATBEP.PFOS.Enx.pdf](https://www.unido.org/fileadmin/user_media/Services/Environmental_Management/Stockholm_Convention/Guidance_Docs/UNEP-POPS-GUID-NIP-2012-BATBEP/UNEP-POPS-GUID-NIP-2012-BATBEP/UNEP-POPS-GUID-NIP-2012-BATBEP.PFOS.Enx.pdf)).

²²³ UNIDO, Guidance for the inventory of perfluorooctane sulfonic acid (PFOS) and related chemicals under the Stockholm Convention on Persistent Organic Pollutants, 2012 (https://www.unido.org/fileadmin/user_media/Services/Environmental_Management/Stockholm_Convention/Guidance_Docs/UNEP-POPS-GUID-NIP-2012-PFOS-Inventory.En.pdf).

²²⁴ UNIDO, Guidance on the Best Available Techniques (BAT) and Best Environmental Practice (BEP) for PFOS and its salts, 2012

263. 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 chemicals, had been used as an additive in toner and printing inks.

264. PFOS-related chemicals are no longer used on color printers and color copy machines, although these parts may still be imported to the US according to information submitted in 2010.²²⁵ The specific identities of replacements or substitutes for PFOS, PFOS-related chemicals 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.²²⁶

265. No information about effects on the environment or human health, or about the level of PFOS in electronic waste, is available. Intermediate transfer belts of colour copiers and printers contain up to 100 ppm of PFOS, while an additive used in producing PFA (perfluoroalkoxy) rollers contains 8×10^{-4} ppm PFOS. Industry groups reported that alternatives are currently not available for those applications.²²⁷

J. Chemically driven oil production

266. Chemically driven oil production is listed as a specific exemption for the production and use of PFOS, its salts and PFOSF in Annex B. As at January 2016, China and the Republic of Korea are registered for this use. This use is considered open applications conform document UNEP/POPS/POPRC.7/INF/22/Rev1.

267. PFOS derivatives may be used as surfactants in the oil to enhance oil or gas recovery in wells, as evaporation inhibitors for gasoline, as jet fuel and hydrocarbon solvents. As late as 2009 and 2012, PFOS and its related substances were reportedly used as a surfactant in old oil fields in some regions to recover oil trapped in small pores between rock particles. At the same time, oil and gas production and mining were reportedly carried out without the use of PFOS and its related substances in other countries, including developing countries, thus indicating the existence of alternative processes that did not require PFOS.

268. According to information submitted by China at the fourth meeting of the Conference of the Parties, at the time PFOS was still used as a surfactant in old oil fields in China to recover oil trapped in small pores between rock particles. At the meeting, several representatives questioned this use of PFOS, saying that oil production and mining in their countries did not require the use of PFOS, which indicated that there were alternative processes.²²⁸

269. According to information from the 2006 OECD survey, tetraethylammonium perfluorooctane sulfonate and potassium perfluorooctane sulfonate were used in the mining industry in member countries as suppressing agents in an annual combined volume of up to 50 tonnes.²²⁹

270. Alternatives to PFOS in oil and mining industries are PFBS, fluorotelomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids, and thioether acids.^{230, 231} 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, aliphatic fluorocarbons for oil well stimulation. Oil well stimulation services also involve corrosion control, water

(https://www.unido.org/fileadmin/user_media/Services/Environmental_Management/Stockholm_Convention/Guidance_Docs/UNEP-POPS-GUID-NIP-2012-BATBEPFOS.Enx.pdf).

²²⁵ <http://chm.pops.int/tabid/2467/Default.aspx> (submission by USA)

²²⁶ <http://chm.pops.int/tabid/2467/Default.aspx> (submission by USA)

²²⁷ UNEP/POPS/COP.7/INF/21.

²²⁸ UNEP/POPS/POPRC.9/INF/11/Rev.1.

²²⁹ Organization for Economic Cooperation and Development. 2006. Results of the 2006 OECD Survey on Production and Use of PFOS, PFAS, PFOA, PFCA, Their Related Substances and Products/Mixtures Containing These Substances. ENV/JM/MONO(2006)36. Available at [www.oecd.org/officialdocuments/displaydocumentpdf/?cote=ENV/JM/MONO\(2006\)36&doclanguage=en](http://www.oecd.org/officialdocuments/displaydocumentpdf/?cote=ENV/JM/MONO(2006)36&doclanguage=en).

²³⁰ Information from OECD and the United States Environmental Protection Agency, 2009.

²³¹ 3M Gas Well Stimulant WS 1200:

http://multimedia.3m.com/mws/mediawebservlet?mwsId=SSSSSuUn_zu8l00xmxtG58mvlv70k17zHvu9lxtD7SSSSS--.

blocks/blockage control, iron control, clay control, paraffin wax and asphaltene removal and prevention of fluid loss and diverting.²³²

K. Uses not exempted: carpets, leather and apparel, textiles and upholstery

271. Carpets, leather and apparel, textiles and upholstery were listed as specific exemptions for the production and use of PFOS, its salts and PFOSF in Annex B. Currently there are no parties registered for specific exemptions for carpets, leather and apparel, textiles and upholstery. At its seventh meeting, the Conference of the Parties, by decision SC-7/1, noted that as there were no longer any parties registered for specific exemptions for those uses, no new registrations may be made with respect to them. Those uses are considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

272. Side-chain fluorinated polymers are used extensively by the textile industry and by consumers for the treatment of all-weather clothing, umbrellas, bags, sails, tents, parasols, sunshades, upholstery, leather, footwear, rugs, mats, carpets, medical fabrics, such as woven or nonwoven surgical drapes and gowns and the like to repel water, oil and dirt (stains).

273. The main PFOS derivatives (normally 2–3% of the fibre weight for textiles but 15% for carpets) previously used for textile and carpet surface treatment applications were the acrylate, methacrylate, adipate and urethane polymers of *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE).

274. Examples of well-known trademarked soil and dirt repellents are:

- (a) Scotchgard™ (3M);²³³
- (b) Capstone® (Chemours);²³⁴
- (c) Products from Daikin, Asahi Glass, Clariant, Rudolf Chemie and others.

275. Before 2000 these were the most important uses of PFOS derivatives. Since it was banned in many countries PFOS has been replaced mainly with shorter-chain analogues and fluorotelomers but also with non-fluorinated chemicals.

276. Analyses of perfluorinated substances in textiles conducted by the Norwegian Institute for Air Research on behalf of the Norwegian Pollution Control Authority have shown very low concentrations or have failed to identify the presence of PFOS. The analyses indicate that perfluorinated acids and telomer alcohols are unintended byproducts and potential degradation products of currently used as alternatives to PFOS in impregnating agents.²³⁵

277. The alternative polymers for the impregnation of textile fabrics, leather, carpets, rugs and upholstery and similar articles are:

- (a) Other polyfluorinated compounds with shorter alkyl chain length such as:
 - (i) Substances based on perfluorobutane sulfonate (PFBS);
 - (ii) fluorotelomer-based substances, including polymers;
- (b) Silicone-based products;²³⁶
- (c) Mixtures of silicones and stearamidomethyl pyridine chloride, sometimes together with carbamide (urea) and melamine resins;

278. According to the information provided by Argentina in 2011, the leather industry used to use PFOS as water and oil repellent. Currently it has been replaced by perfluorobutane sulfonate.

279. Scotchgard® Protector product produced by 3M (universal spray) containing 1–5% of a perfluorobutane sulfonyl urethane (the identity of the chemical has not been provided by the company) has also been suggested as an alternative for stain-repellent impregnation of textiles, leather and carpets.

280. Chemours has introduced a brand name, Capstone®, for a series of alternative products for various applications based on short-chain fluorotelomers, mainly involving C₆ chemistry. Other

²³² UNEP/POPS/COP.7/INF/26.

²³³ http://solutions.3m.com/wps/portal/3M/en_US/Scotchgard/Home/.

²³⁴ www.chemours.com/Capstone/en_US/index.html.

²³⁵ Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

²³⁶ https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290565/scho0309bpqz-e-e.pdf.

Companies such as Daikin, Asahi Glass and Clariant (and maybe others) have introduced short-chain fluorotelomers as well.

281. Rudolph Group has introduced BIONIC-FINISH®ECO as a fluorocarbon-free, water-repellent treatment for textiles.²³⁷ BIONIC-FINISH®ECO is composed of a hydrocarbon matrix forming star-shaped, hyper-branched polymers, or dendrimers.²³⁸ The exact identity of the chemical has not been provided by the company.

282. There is a lack of information on the hazards associated with DWR hyper-branched polymers, or dendrimers.²³⁹

283. 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 electrochemical fluorination chemistry have been used. PFOS was not directly used to treat textiles but used to be present at up to 2 to 3 wt% in products.²⁴⁰ In addition, fluorotelomer-based polymers have also been used.

284. 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.

285. 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.²⁴¹ Dendrimers may be in the region of nano sized materials meaning features with an average diameter between 1 to 100 nm.²⁴²

286. There are considered five basic groups of organosiloxanes, of which two are outlined here: 1) R_2SiO_x are cyclic substances, in which R is usually a methyl group, but can also be hydrogen, vinyl group, phenyl group, or a trifluoropropyl ($CF_3CH_2CH_2-$) group, and $x = 3, 4, 5, 6$, etc (D4, D5 and D6 fall into this group); and 2) $R_3SiO(SiR_2O)_nSiR_3$ are linear substances in which R is usually a methyl group, but can also be a phenyl group, and $n = 0, 1, 2, 3, 4$, etc.²⁴³

287. The starting material for the manufacture of polydimethylsiloxanes (PDMS) is dimethyldichlorosilane derived from the manufacturing of either cyclic or linear siloxanes intermediates. The first step in the process is hydrolysis to form cyclic siloxanes and/or linear siloxanols. Such polymers could contain residual amounts of monomeric cyclic siloxanes such as D4, D5 or D6 and oligomeric siloxanes and, in some cases, could possibly break down to form small amounts of these cyclic siloxanes.²⁴⁴

288. The non-intermediate industrial uses of PDMS are numerous. Industrial uses include antifoams, softness and wetting agents in textile manufacturing, components of polishes and other surface-treatment formulations, lubricants, mould-release agents, paper coatings, and as dielectric fluids and heat-transfer liquids. PDMS is also used in consumer applications such as personal, household and automotive care products. High molecular weight PDMS are used as water repellents on textiles and leather.²⁴⁵

²³⁷ There are still data gaps but some data are available in UNEP/POPS/POPRC.8/INF/17/Rev.1.

²³⁸ www.rudolf.de/innovations/hydrophobic-future/bionic-finish/self-organisation.htm.

²³⁹ www.supfes.eu.

²⁴⁰ UNEP/POPS/COP.7/INF/26.

²⁴¹ Communication from Prof. Martin Möller, University of Aachen.

²⁴² <http://ec.europa.eu/environment/chemicals/nanotech/>

http://www.oecd.org/departement/0,3355,en_2649_37015404_1_1_1_1_1,00.html.

²⁴³ https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290565/scho0309bpqz-e-e.pdf.

²⁴⁴ Brooke D N, Crookes M J, Gray D and Robertson S. 2009. Environmental Risk Assessment Report: octamethylcyclotetrasiloxane. Environmental Agency. Available at:

https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290565/scho0309bpqz-e-e.pdf.

²⁴⁵ https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290565/scho0309bpqz-e-e.pdf.

Technical feasibility and efficacy

289. PFOS-related chemicals are no longer used on carpets. The specific identities of many but not all replacements or substitutes for PFOS, PFOS-related chemicals and mixtures have been claimed as CBI to the extent they have been disclosed during their registration to the U.S. government. These registered substances and mixtures have included short-chain PFAS and various fluorinated telomers.

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

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

Health and environmental effects including toxicological and ecotoxicological information

292. 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 due to their similar environmental hazards.

293. The OECD Working Party on Manufactured Nanomaterials is trying to address the gap in publically available safety information about different kinds of nanomaterials produced by man that do not 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.

294. 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.²⁴⁶

Cost-effectiveness

295. Perfluorohexane sulfonyl fluoride (PFHxSF) and its derivatives, which are not feasible alternatives to PFOS, used to cost are 10% higher more in 2012 in China than the prices of products containing PFOS.²⁴⁷ The current cost situation is not clear.

Availability, accessibility, socio-economic consideration

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

297. Perfluorohexane sulfonyl fluoride (PFHxSF) and its derivatives exist on the Chinese market and are commercialized with a production volume of 20 tonnes per year. Domestic production capacity in China is up to 50 tonnes per year. Another five companies have begun to study ifperfluorohexane 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.²⁴⁸

L. Uses not exempted: paper and packaging

298. Paper and packaging were listed as a specific exemption for the production and use of PFOS, its salts and PFOSF in Annex B. Currently there are no parties registered for specific exemptions for paper and packaging and rubber and plastics. At its seventh meeting, the Conference of the Parties, by decision SC-7/1, noted that as there were no longer any parties registered for the specific exemption for those uses, no new registrations may be made with respect to them. Those uses are considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

299. Fluorinated chemicals are used in the paper industry to produce waterproof and greaseproof paper. Concentration of 1.0–1.5% of fluorochemical, based on the dry weight of the fibres, is typically used.²⁴⁹ Following are the main suppliers and brand names of fluorochemicals in the paper industry:

²⁴⁶ Personal communication with Prof. Juan Carlos Flores (OECD).

²⁴⁷ UNEP/POPS/POPRC.8/INF/17/Rev 1.

²⁴⁸ UNEP/POPS/POPRC.8/INF/17/Rev 1.

²⁴⁹ UNEP/POPS/COP.7/INF/26.

- (a) Archroma Cartaguard(r)®;
- (b) Chemours Capstone®;
- (c) Daikin Unidyne®;
- (d) Asahi Glass Asahigard®;
- (e) Solvay Solvera®;
- (f) Rudolf Chemie Ruco-guard®.

300. PFOS derivatives have been used both in food contact applications such as plates, food containers, popcorn bags, pizza boxes and wraps and in non-food contact applications such as folding cartons, containers, carbonless forms and masking papers. Paper protection by PFOS derivatives has been achieved by using one of the following:

- (a) Mono-, di- or triphosphate esters of N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE);
- (b) N-Methyl perfluorooctane sulfonamidoethanol acrylate polymers.

301. 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 polyfluoroalkyl phosphonic acids (PAPs) may be still used in food-contact paper products and as leveling 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.²⁵⁰

302. Before 2000, about 32% of the total use of PFOS in the European Union was for paper coating; the use of PFOS for this purpose is no longer allowed and PFOS has been replaced mainly by other fluorinated chemicals. The United States revoked approval of three perfluorinated substances/substance categories for use in Food Contact Materials effective January 4, 2016 to include: Diethanolamine salts of mono- and bis (1 H, 1 H, 2 H, 2 H perfluoroalkyl) phosphates where the alkyl group is even-numbered in the range C8-C18 and the salts have a fluorine content of 52.4 percent to 54.4 percent as determined on a solids basis; Pentanoic acid, 4,4-bis [(gamma-omega-perfluoro-C8-20-alkyl)thio] derivatives, compounds with diethanolamine (CAS No: 71608-61-2); and 3-Perfluoroalkyl substituted phosphate ester acids, ammonium salts formed by the reaction of 2,2-bis[(gamma), [omega]-perfluoro C4-20 alkylthio) methyl]-1,3-propanediol, polyphosphoric acid and ammonium hydroxide.²⁵¹

303. The known alternative surfactants for impregnation of paper and cardboard for use in packaging are short-chain telomer-based substances and perfluoropolyethers (see appendix 2), and poly(dimethyl siloxane).

304. Grease-proof paper did exist before PFOS technology was introduced to the market, and other technologies can do the work. In a survey conducted by the Norwegian Food Safety Authority in 2006, it was concluded that no fluorinated substances were used in fast-food packaging in Norway. The

²⁵⁰ Handbook of Environmental Chemistry, Springer Verlag Vol 17, Editors: T.P. Knepper and F.T. Lange, Polyfluorinated Chemicals and Transformation Products, 2011, ISBN 978-3-642-21871-2.

²⁵¹ <https://www.federalregister.gov/articles/2016/01/04/2015-33026/indirect-food-additives-paper-and-paperboard-components>.

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.²⁵²

M. Uses not exempted: coatings and coating additives

305. Coatings and coating additives are listed as a specific exemption for the production and use of PFOS, its salts and PFOSF in Annex B. Currently there are no parties registered for specific exemptions for coatings and coating additives. At its seventh meeting, the Conference of the Parties, by decision SC-7/1, noted that as there were no longer any parties registered for the specific exemption for this use, no new registrations may be made with respect to it. This use is considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

306. PFOS derivatives have had several uses in coating, paint and varnishes to reduce surface tension, for example, for substrate wetting, for leveling, as dispersing agents and for improving gloss and antistatic properties. PFOS derivatives can be used as additives in dyes and ink, as pigment grinding aids and as agents to combat pigment flotation problems. The concentrations used were below 0.01% (w/w).

307. 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.²⁵³

308. 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. Dendrimers may be in the region of nano sized materials meaning features with an average diameter between 1 to 100 nm.

309. 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.²⁵⁴

310. The possible alternatives identified for use in paints and varnishes are surfactants based on the following:

- (a) Short chain fluorotelomer-based surfactants (e.g. Capstone™ products),²⁵⁵ or Chemguard.
- (b) C4-compounds based on perfluorobutane sulfonate, especially in the area of electronic coating;
- (c) Fluorinated polyethers (PolyFox®);
- (d) Sulfosuccinates, for example the sodium salt of di-(2-ethylhexyl) sulfosuccinate dissolved in ethanol and water, which is used as an alternative in wood primers and printing inks;
- (e) Silicone polymers, such as polyether-modified polydimethyl siloxane, mixed with di-(2-ethylhexyl) sulfosuccinate in ethanol and water (WorléeAdd®);
- (f) Propylated naphthalenes and propylated biphenyls, which can be used as water repelling agents for applications such as rust protection systems, marine paints, resins, printing inks and coatings in electrical applications;
- (g) Fatty alcohol polyglycol ether sulfate, sometimes together with a sulfosuccinate.

311. Information from suppliers in the paint and varnish industry suggests that fluorosurfactants are in general much more expensive than other alternative surfactants.²⁵⁶ They are therefore used in paint

²⁵² Information from Norwegian Pollution Control Authority (former Statens Forurensningstilsyn), 2009.

²⁵³ Handbook of Environmental Chemistry, Springer Verlag Vol 17, Editors: T.P. Knepper and F.T. Lange, Polyfluorinated Chemicals and Transformation Products, 2011, ISBN 978-3-642-21871-2.

²⁵⁴ UNEP/POPS/POPRC.6/13/Add.3/Rev.1.

²⁵⁵ Perfluorocarboxylic Acid Content in 116 Articles of Commerce, US EPA (2009) <http://www.oecd.org/env/48125746.pdf>.

and varnishes only in situations where very low surface tension is desired and no other (non-fluorinated) alternatives can achieve it (e.g., in products where an extremely smooth surface is desired).

M. Uses not exempted: rubber and plastics

312. Rubber and plastics were listed as a specific exemption for the production and use of PFOS, its salts and PFOSF in Annex B. Currently there are no parties registered for specific exemptions for rubber and plastics. At its seventh meeting, the Conference of the Parties, by decision SC-7/1, noted that as there were no longer any parties registered for the specific exemption for those uses, no new registrations may be made with respect to them. Those uses are considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

313. Perfluorobutane sulphonate (PFBS) derivatives or various C₄-perfluorocompounds are used as alternatives to PFOS in rubber moulding defoamers in electroplating and as additives in plastics.²⁵⁷

O. Other uses not exempted

314. PFOS derivatives have historically been used as surfactants to lower surface tension and improve wetting and rinse-off in a variety of industrial and household cleaning products such as automobile waxes, alkaline cleaners, denture cleaners and shampoos, floor polish, dishwashing liquids and car wash products. PFOS derivatives have also been used in carpet spot cleaners.

315. PFOS derivatives may be used as surfactants in the mining industry to enhance the amount of recovery of metals from the ores in copper and gold mines.

316. Tetraethylammonium perfluorooctane sulfonate and potassium perfluorooctane sulfonate have also been used as acid mist suppressing agents. There can be large-scale mining activities in developing countries, as well as mining operations of the artisanal-small scale type still using PFOS. Other activities also include quarrying operations by construction companies. Since the major challenge in many developing countries is addressing the problem of mercury and lead poisoning from artisanal small-scale gold mining, the use of PFOS has usually not been addressed.²⁵⁸

317. Cleaning agents, waxes and polishes for cars and floors are not listed as any exemptions for PFOS, its salts and PFOSF in Annex B. This use is considered as an open application.

318. A PFOS derivative that was often used in cleaning agents, floor polishes and auto polishes is potassium N-ethyl-N-[(heptadecafluorooctyl)sulfonyl] glycinate (CAS No: 2991-51-7). The concentration of that PFOS derivative in the final product was generally between 0.005% and 0.01% but might have been ten times as high.

319. The possible alternative chemicals identified for use in cleaning agents, waxes and floor polishes are:

(a) Short chain telomer-based surfactants and polymers;²⁵⁹

(b) Various C₄-perfluorinated compounds: Novec® (3M), for commercial and industrial cleaning, contains methyl nonafluorobutyl ether (CAS No: 163702-07-6) and methyl nonafluoroisobutyl ether (CAS No: 163702-08-7);

(c) Fluorinated polyethers: PolyFox® (OMNOVA Solutions Inc.), a line of fluorosurfactants that are polymers with a molecular weight greater than 1,000 based on ether links and with C₂F₅ or CF₃ as the starting material.

320. A shift to softer waxes that are more biodegradable or entirely biodegradable may completely eliminate the need for persistent polyfluorinated compounds. In these products, the fluorinated surfactants are replaced with non-ionic or anionic surfactants, which have good wetting properties.

321. Fluorotelomer silicones such as polyfluorooctyl triethoxy silane (1H,1H,2H,2H-perfluorooctyl triethoxy silane, a NanoCover® product) used in a bathroom floor spray product. This and similar substances were banned in Denmark in April 2010 because of toxic effects on mouse lungs.²⁶⁰

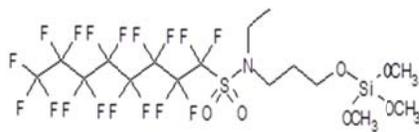
²⁵⁶ Poulsen, P.B., Jensen, A.A., Wallström, E. 2005. More environmentally friendly alternatives to PFOS-compounds and PFOA. Environmental Project no. 1013. Danish Environmental Protection Agency. www2.mst.dk/Udgiv/publications/2005/87-7614-668-5/pdf/87-7614-669-3.pdf.

²⁵⁷ UNEP/POPS/POPRC.6/13/Add.3/Rev.1.

²⁵⁸ UNEP/POPS/COP.7/INF/26.

²⁵⁹ Survey, screening and analyses of PFCs in consumer products, KLIF TA-2578/2009 (2009) <http://www.miljodirektoratet.no/old/klif/publikasjoner/2578/ta2578.pdf>.

322. Furthermore, according to information from the 2006 OECD survey less than 1 tonne of *N*-ethyl-*N*-[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide (CAS No: 61660-12-6) that is a silane, 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.



N-Ethyl-*N*-[3-(trimethoxysilyl)propyl] perfluorooctane sulfonamide

²⁶⁰ <http://mst.dk/75866>.

IV. Properties of alternative substances

A. Overview

323. This chapter contains a brief description of the environmental, safety and health properties of PFOS alternatives. For some of these alternatives, a general discussion of properties might be all that is possible owing to a lack of specific information. For each of the chemical groups discussed, a more comprehensive compilation of information was beyond the scope of the present study. More detailed information on the properties of the alternatives is provided in the Technical paper on the identification and assessment of alternatives to PFOS in open applications.²⁶¹

324. The key to the performance of fluorosurfactants is extremely low surface tension and for polymer surfaces extremely low surface energy. Because of environmental and health concerns, other surfactants could be used as alternatives where very low surface tension levels are not needed.

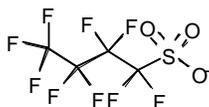
325. When production of PFOS ceased in the United States in 2002, other chemicals took their place in the US, but PFOS production rapidly increased in China.²⁶² The first U.S. PFOS substitutes were mainly derivatives of perfluoroalkyl sulfonates with a shorter alkyl chain and C₈-based fluorotelomers.

326. Since 2006, the major manufacturers of long-chain fluorotelomers (8:2 fluorotelomers) in the EU, Japan, and US have been working towards the elimination of C₈-based and longer-chain-based PFCs by year-end 2015, in accordance with the United States Environmental Protection Agency's voluntary 2010/2015 PFOA Stewardship Program.²⁶³ Global producers that did not sign up for the Stewardship Program are not included in the partnership. Currently, C₆-fluorotelomers increasingly dominate the trade. Thus Non-fluorinated alternatives have made some gains in the marketplace, especially in textile treatments and fire fighting foams. Further gains for the non-fluorinated alternatives will be based on their ability to provide the performance customers require as well as on due to regulatory policies that permit continued use of fluorinated chemicals in commerce.^{264, 265}

327. Appendix 4 is a non-exhaustive list of alternatives to the use of PFOS in some major open applications with trade names and company information where available.

B. Shorter-chain perfluoroalkyl sulfonates

328. After the phase-out of PFOS, 3M introduced a new generation of polymeric anionic fluorinated surfactants (Scotchgard[®] and Novec[®] products), which are based on perfluorobutane sulfonates (PFBS; C₄-chemistry):



329. These compounds are claimed to have a low dynamic surface tension or rather a rapid surface migration, which is important in high-speed coating processes and low-viscosity systems. Generally these surfactants have a lower surface tension than hydrocarbon and silicone surfactants. They can also be used in smaller amounts than hydrocarbon surfactants. The compounds are said to influence the adhesion of the second-layer coating less than silicon or conventional fluorinated surfactants.

330. These short-chain alternatives could provide the surfactant function in various applications including the paint and coatings industry; stain-repellent impregnation of textiles, leather and carpets; in electronic coating; in industrial commercial cleaning; and in cleaners for solder flux residue.

331. According to information from the 2006 OECD survey, 50–160 tonnes of potassium perfluorobutane sulfonate and 40–60 tonnes of perfluorobutane sulfonyl fluoride were produced in 2005 as intermediates for the production of catalysts, flame retardants, additives in plastics, industrial coatings, mist suppression systems, rubber molding defoamers for electroplating and the like.

²⁶¹ UNEP/POPS/POPRC.8/INF/17/Rev.1.

²⁶² http://chm.pops.int/Portals/0/Repository/addinfo_2008/UNEP-POPS-POPRC-SUB-F08-PFOS-ADIN-CHI.English.pdf.

²⁶³ <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/and-polyfluoroalkyl-substances-pfass-under-tsca#tab-3>

²⁶⁴ <http://www.ec.gc.ca/epe-epa/default.asp?lang=En&n=AE06B51E-1>.

²⁶⁵ <http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=6B9B6B28-1&xml=F68CBFF1-B480-4348-903D-24DF9D623DC>.

1. Health effects of shorter-chain perfluoroalkyl sulfonates

332. Information about PFBS, its potassium salt (PFBSK) and PFHxS (C6) is available. Including toxicity studies. However a variety of impacts of C6-C4 substances have been observed in peer-reviewed studies association with attention deficit hyperactivity disorder (ADHD) in children, negative impacts on development in animals, and modulation of immune system response. The substances have also been detected in cord blood, adult blood, house dust, sea mammals and in the Arctic.²⁶⁶

333. It has been claimed by the industry that PFBS does not have the particularly serious toxic effects associated with PFOS and other long-chain analogues. A number of peer reviewed studies have examined the potential toxicity and indications of human toxicity, immunotoxic properties in vitro, genotoxicity and neurotoxicity of PFBS and PFHxS along with other PFCs.²⁶⁷ However there are still gaps in publically available data.^{268, 269}

334. Elevated levels in humans of PFOS, PFOA, and PFNA beside PFHxS have been found in several peer reviewed studies. PFHxS is associated with elevated odds of high cholesterol in humans and deficit/hyperactivity disorder in children 12-15 years old. Increasing umbilical cord concentrations of PFHxS were associated with decreasing birth weight and decreasing birth length in humans.²⁷⁰

2. Environmental effects of shorter-chain perfluoroalkyl sulfonates

335. Perfluorobutane sulfonamide (FBSA), a precursor to PFBS is shown to be a bioaccumulative contaminant in fish in Canada and possibly in The Netherlands. It is likely sourced from new alternative perfluorobutane-based products, as well as other shorter chain perfluoroalkyl-based products.²⁷¹

336. PFBS is a strongly acidic and highly water-soluble and persistent substance which has a low vapour pressure and is poorly adsorbed to soils and sediments, and is therefore expected to remain in the water compartment on release into the environment. PFBS stays mostly in the water column as its water solubility is much higher than that of higher homologues. PFBS has been widely detected in water and has very low sorption in sediment.²⁷² PFBS is also found in municipal landfill leachates, drinking water and in the Arctic. PFBS has a significantly increasing temporal shifting trends of PFOS to PFBS were observed in the dolphin liver samples. This pattern may be attributed to the substitution of PFOS by its alternative, PFBS.²⁷³

337. PFBS has been found in indoor dust from homes and offices.²⁷⁴ According to the information provided by Germany in 2011 and peer reviewed publications, due to the very limited ability of the PFAS with perfluorinated chains less than 6 carbons to adsorb, it is difficult to remove the chemicals from water.²⁷⁵ Until now, no commercial method is known. In water samples from rivers and certain groundwater, the short-chain PFCs can already be detected. PFHxS and other PFCs are found in polar bears and humans in the Arctic.^{276, 277, 278} Increasing levels of PFHxS have been found in samples from Beluga whales from Alaska between 1989 and 2006.²⁷⁹

²⁶⁶ UNEP/POPS/POPRC.8/INF/17/Rev.1.

²⁶⁷ UNEP/POPS/POPRC.8/INF/17/Rev.1.

²⁶⁸ UNEP/POPS/POPRC.8/INF/17/Rev.1.

²⁶⁹ Posner et.al, "Per- and polyfluorinated substances in the Nordic Countries, Use, occurrence and toxicology", TemaNord 2013:542, ISBN 978-92-893-2562-2, (2013).

²⁷⁰ Lee Yj, Kim MK, Bae J, Yang JH (2013) Concentrations of perfluoroalkyl compounds in maternal and umbilical cord sera and birth outcomes in Korea, *Chemosphere* 90:1603-1609.

²⁷¹ Chu S, Letcher RJ, McGoldrick DJ, Backus SM (2016) A new fluorinated surfactant contaminant in biota: Perfluorobutane sulfonamide in several fish species, *Environ Sci Technol* 50:669-675.

²⁷² <http://www.sciencedirect.com/science/article/pii/S0048969715303880>.

²⁷³ Lam JC, Lyu J, Kwok KY, Lam PK (2016) Perfluoroalkyl substances (PFASs) in marine mammals from the South China Sea and their temporal changes 2002-2014: Concern for alternatives of PFOS?, *Environ Sci Technol* 2016 Feb.

²⁷⁴ UNEP/POPS/POPRC.8/INF/17/Rev.1.

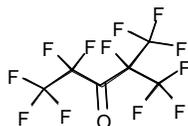
²⁷⁵ UNEP/POPS/POPRC.8/INF/17/Rev.1.

²⁷⁶ Hanssen L, Dudarev AA, Huber S, Odland JO, Nieboer E, Sandanger TM (2013) Partition of perfluoroalkyl substances (PFASs) in whole blood and plasma, assessed in maternal and umbilical cord samples from inhabitants of arctic Russia and Uzbekistan, *Sc Total Environ* doi: 10.1016/j.scitotenv.2013.01.029.

²⁷⁷ Bytingsvik J, van Leeuwen SP, Hamers T, Swart K, Aars J, Lie E, Nilsen EM, Siig O, Derocher AE, Jenssen BM (2012) Perfluoroalkyl substances in polar bear mother-cub pairs: a comparative study based on plasma levels from 1998 and 2008, *Environ Int* 49:92-99.

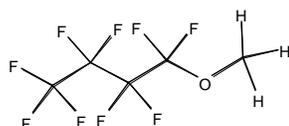
C. Shorter-chain perfluoroalkyl ketones and ethers

338. According to 3M's website, a C₆-fluorinated compound, Novec™ 1230, is used as a gaseous fire suppression agent produced by that company. The compound is dodecafluoro-2-methylpentan-3-one (CAS No: 756-13-8):



Dodecafluoro-2-methylpentan-3-one

339. 3M also markets some C₄-perfluorinated compounds for commercial and industrial cleaning under the trademark Novec™, such as methyl nonafluorobutyl ether (CAS No: 163702-07-6) and methyl nonafluoroisobutyl ether (CAS No: 163702-08-7). Here the methyl group is not fluorinated.



Methyl nonafluorobutyl ether

1. Health effects of shorter-chain perfluoroalkyl ketones and ethers

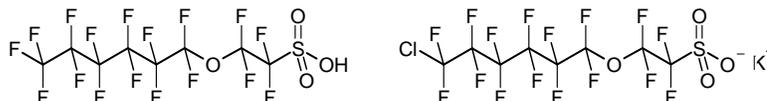
340. Published peer-reviewed data are lacking.

2. Environmental effects of shorter-chain perfluoroalkyl ketones and ethers

341. Published peer-reviewed data are lacking.

D. Polyfluorodialkyl ether sulfonates

342. In China F-53 (potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate) and F-53B (potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate) are available as PFOS alternatives for chrome plating.²⁸⁰ The structure formulas of F-53 and F-53B are, respectively:



1. Health effects of polyfluorodialkyl ether sulfonates

343. No publically available data are available.

2. Environmental effects of polyfluorodialkyl ether sulfonates

344. No published peer-reviewed data exist for persistence (half-lives) in water, sediment, soil and air, bioconcentration factors (BCFs).²⁸¹

E. Fluorotelomers and fluorotelomer phosphates

345. In general, both long and short chain fluorotelomers have been the most common alternatives to PFOS compounds.²⁸² They are not fully fluorinated but contain more reactive hydrocarbon parts and

²⁷⁸ AMAP, 2015. AMAP Assessment 2015: Human Health in the Arctic. AMAP, Oslo. 2015.

²⁷⁹ Reiner JL, O'Connell SG, Moors AJ, Jucklick JR, Becker PR, Keller JM (2011) Spatial and temporal trends of perfluorinated compounds in Beluga whales (*Delphinapterus leucas*) from Alaska, *Environ Sci Technol* 45:8129-8136.

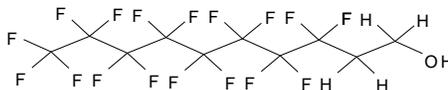
²⁸⁰ Presentation by Jun Huang, Tsinghua University, at the national workshop on nine new persistent organic pollutants and the implementation of the Stockholm Convention in China, Beijing, 1–2 July 2010.

²⁸¹ UNEP/POPS/POPRC.8/INF/17/Rev.1.

²⁸² "Long-chain" has been defined by the Organisation for Economic Cooperation and Development (OECD) for two classes of perfluoroalkyl substances: perfluorocarboxylic acids (PFCAs) and perfluoroalkyl sulfonates

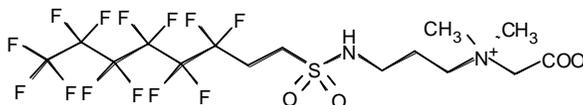
functional groups. The perfluorinated tail, however, is similar to the tail of PFOS and is as persistent, and these chemicals are precursors of perfluorinated carboxylic acids (PFCAs). According to information from the 2006 OECD survey, more than 5,000 tonnes of PFCA precursors were produced and used in 2005.

346. One of the basic structures is 8:2 fluorotelomer alcohol (8:2 FTOH), also named 1*H*,1*H*,2*H*,2*H*-perfluorodecanol; it has a C₈-perfluorinated tail:

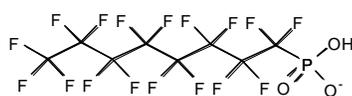


347. Chemours specializes in fluorotelomers and markets a wide range of Capstone[®] products, generally associated with 6:2-fluorotelomer-based products.

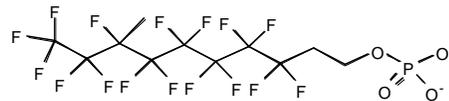
348. Chemours manufactures a range of fluorotelomers called Capstone[™] products, based on perfluorohexyl ethyl sulfonamide, which are used in fire-fighting foam formulations.²⁸³ A possible structure formula for an amphoteric compound 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctane sulfonamidopropyl carboxybetaine, which now replaces the analogously fully fluorinated perfluorooctane compound, is:



349. The polyfluoroalkyl phosphonic acids and phosphoric acids and their diesters (PAPs and diPAPs), used mainly in food packaging,²⁸⁴ have been discovered in the environment and in people.²⁸⁵ Here are examples of structure formulas:



Perfluorooctyl phosphonate



8:2 PAP

(PFASs). The definition is posted on the OECD Portal on Perfluorinated Chemicals at <http://www.oecd.org/ehs/pfc/>.

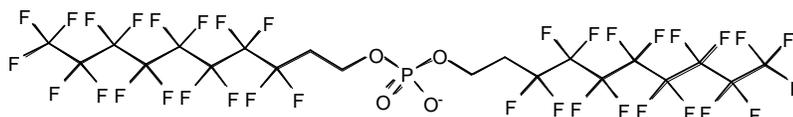
Text from the website: "A distinction is made between long-chain perfluorinated compounds (LC PFCs) and short-chain perfluorinated compounds (SC PFCs), based on the toxicity and bioaccumulation differences between LC PFCs and SC PFCs." Long-chain perfluorinated compounds" refers to:

- (a) Perfluorocarboxylic acids with carbon chain lengths C8 and higher, including perfluorooctanoic acid (PFOA);
- (b) Perfluoroalkyl sulfonates with carbon chain lengths C6 and higher, including perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonate (PFOS); and
- (c) Precursors of these substances that may be produced or present in products.
- (d) For definition purposes "precursor" means a substance that has been recognized as having the potential to degrade to perfluorocarboxylic acids with a carbon chain length of C8 and higher (including PFOA) or perfluoroalkyl sulfonates with a carbon chain length of C6 or higher (including PFHxS and PFOS)." Short-chain therefore is defined as perfluorocarboxylic acids with carbon chain lengths C7 and shorter and perfluoroalkyl sulfonates with carbon lengths C5 and shorter as well as potential precursors to these substances.

²⁸³ www2.dupont.com/Forafac/en_US/index.html.

²⁸⁴ U.S. Fed. Reg. Vol. 81, No. 1, January 4, 2016 p. 5-8;

²⁸⁵ D'eon JC, Crozier PW, Furdulj VI, Reiner EJ, Libelo EL, Mabury SA. 2009. Observation of a commercial fluorinated material, the polyfluoroalkyl phosphoric acid diesters, in human sera, wastewater treatment plant sludge, and paper fibers. *Environmental Science and Technology* 43: 4589–4594.



8:2 diPAP

350. Some of the major producers of fluorochemicals in Japan, United States, and Europe have voluntarily agreed to work towards the elimination of PFOA and C₈-perfluorotelomers, a group of possible alternatives that degrade into PFOA, by 2015. However, the voluntary agreement does not include producers outside these regions and may not prevent other companies from starting or continuing to market long chain PFAS as alternatives to PFOS.

1. Health effects of fluorotelomers and fluorotelomerbased phosphates

351. There is a lack of health data for the many specific and complex fluorotelomers used in practice. Some of their degradation products are known to have adverse health impacts. For example, PFOA is found in breast milk and has been shown to be tumorigenic and immunotoxic in laboratory animals. Higher concentrations of serum PFOA are associated with osteoarthritis in women.²⁸⁶ In humans, in utero exposure to PFOA is associated with lower sperm concentration, lower total sperm count, higher levels of lutenizing hormone, and higher levels of follicle stimulating hormone.²⁸⁷ A study of placental transfer found a strong correlation between PFOA concentrations in pregnant women and the cord blood of their respective newborns.²⁸⁸ Japanese researchers have shown that PFOA can alter the expression of over 500 genes,²⁸⁹ while Chinese researchers investigating the genotoxic potential of PFOA in human liver cells (hepatoma HepG2 cells) in culture have demonstrated that PFOA exerts genotoxic effects on these cells, probably through oxidative DNA damage.²⁹⁰ Increasing toxicological or ecotoxicological information are becoming available for the degradation products other than PFOA. In vitro studies demonstrate impaired reproduction and altered sex hormone levels.^{291,292} They have been regularly detected in human blood, umbilical cord blood and breast milk and the data that exists suggest similar characteristics as previously observed with PFOA. They are also found in consumer products, offices, food packaging and food.^{293,294,295,296,297,298}

²⁸⁶ Uhl SA, James-Todd T, Bell ML (2013) Association of osteoarthritis with perfluorooctanoate and perfluorooctane sulfonate in NHANES 2003-2008.

²⁸⁷ Vested A, Ramlau-Hansen CH, Olsen SF, Bonde JP, Kristensen SL, Halldorsson TI, Becher G, Haug LS, Ernst EH, Toft G (2013) Associations of in utero exposure to perfluorinated alkyl acids with human semen quality and reproductive hormones in adult men, *Environ Health Perspect*, DOI:10.1289/ehp.1205118.

²⁸⁸ Porpora MG, Lucchini R, Abballe A, Ingelido AM, Valentini S, Fuggetta E, Cardi V, Ticino A, Marra V, Fulgenzi AR, Felip ED (2013) Placental transfer of persistent organic pollutants: a preliminary study on mother-newborn pairs, *Int J Environ Res Public Health* 10:699-711.

²⁸⁹ Guruge KS, Yeung LW, Yamanaka N, Miyazaki S, Lam PK, Giesy JP, Jones PD, Yamashita N., Gene Expression Profiles in Rat Liver Treated With Perfluorooctanoic Acid (PFOA). *Toxicol Sci*. 2005 Oct 12; [Epub ahead of print].

²⁹⁰ Yao X. & Zhong L., Genotoxic risk and oxidative DNA damage in HepG2 cells exposed to perfluorooctanoic acid. *MutationResearch/Genetic Toxicology and Environmental Mutagenesis* Volume 587, Issues 1-2, 10 November 2005, Pages 38-44.

²⁹¹ Liu C, Deng J, Yu L, Ramesh M, Zhou B (2010) Endocrine disruption and reproductive impairment in zebrafish by exposure to 8:2 fluorotelomer alcohol, *Aquat Toxicol* 96:70-76.

²⁹² Liu C, Yu L, Deng J, Lam PK, Wu RS, Zhou B (2009) Waterborne exposure to fluorotelomer alcohol 6:2 FTOH alters plasma sex hormone and gene transcription in the hypothalamic-pituitary-gonadal (HPG) axis of zebrafish, *Aquat Toxicol* 93:131-137.

²⁹³ Herzke D, Olsson E, Posner S (2012) Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway – A pilot study, *Chemosphere* 88:980-987.

²⁹⁴ Fraser AJ, Webster TF, Watkins DJ, Nelson JW, Stapleton HM, Calafat AM, Kato K, Shoeib M, Vieira VM, McClean MD (2012) Polyfluorinated compounds in serum linked to indoor air in office environments, *Environ Sci Technol* 46:1209-1215.

²⁹⁵ Gebbink WA, Ullah S, Sandblom O, Berger U (2013) Polyfluoroalkyl phosphate esters and perfluoroalkyl carboxylic acids in target food samples and packaging-method development and screening, *Environ Sci Pollut Res Int*.

²⁹⁶ De Silva AO, Allard CN, Spencer C, Webster GM, Shoeib M (2012) Phosphorus-containing fluorinated organics: polyfluoroalkyl phosphoric acid diesters (diPAPs), perfluorophosphonates (PFPA), and perfluorophosphinates (PFPIAs) in residential indoor dust, *Environ Sci Technol* 46:12575-12582.

2. Environmental effects of fluorotelomers and fluorotelomer based phosphates

352. There is also a lack of publically available environmental data on the fluorotelomers and fluorophosphates used in practice. Some are volatile and may undergo long-range air transportation. They degrade to perfluorinated carboxylic acids, such as perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA), in organisms and in nature. These perfluorinated acids have been widely detected in the environment and wildlife.²⁹⁹ PFOA has been found in the Arctic environment, and reaches very high levels (for example in sea-ice snow pack in the Arctic, PFOA is detected at levels that are higher than already banned POPs, such as PCBs and POP-BDEs).³⁰⁰

353. The environmental hazard, including tendency to bioaccumulation, increases with chain length, and all perfluorinated alkyl chains are completely persistent in nature.

F. Side chain fluorinated polymers

354. The substance 2-propenoic acid, 2-methyl-, hexadecyl ester (hexadecyl methacrylate), polymers with 2-hydroxyethyl methacrylate, γ - ω -perfluoro-C₁₀-C₁₆-alkyl acrylate and stearyl methacrylate (CAS No: 203743-03-7) has been prohibited in Canada under the *Prohibition of Certain Toxic Substances Regulations, 2012* as it is a precursor to long-chain PFCAs. The following substances are also prohibited:

(a) Hexane, 1,6-diisocyanato-, homopolymer, reaction products with α -fluoro- ω -2-hydroxyethyl-poly(difluoromethylene), C16-20-branched alcohols and 1-octadecanol;

(b) 2-propenoic acid, 2-methyl-, 2-methylpropyl ester, polymer with butyl 2-propenoate and 2,5-furandione, γ - ω -perfluoro-C8-14-alkyl esters, tert-Butyl benzenecarboperoxoate-initiated;

(c) 2-propen-1-ol, reaction products with pentafluoroiodoethane tetrafluoroethylene telomer, dehydroiodinated, reaction products with epichlorohydrin and triethylene tetramine.

355. In most instances the exact composition of the products and their active substances have not been disclosed by the private sector.

356. A recent Swedish study from the Swedish Chemicals Agency³⁰¹ identified 229 fluorinated co polymers that are available on the global market. Some lacked CAS number but their chemicals name were well described.

1. Health effects of fluorinated co-polymers

357. There is a lack of publically available specific health data on the active fluorinated substance. Polymers are generally of low availability/uptake and have low toxicity but there is a lack of data to confirm this relation for fluorinated polymers.³⁰²

2. Environmental effects of fluorinated co-polymers

358. There is a lack of publically available data. The ultimate degradation products may be perfluoroalkanoic acids (PFAAs), including PFOA.

G. Fluorinated polyethers

359. Per- and polyfluorinated ether-based fluorinated surfactants typically have 1, 2, or 3 perfluorinated carbon atoms separated by an ether oxygen, depending on the route to the perfluoropolyether intermediate. The photooxidation of tetrafluoroethylene (TFE, taxogen) or hexafluoropropene oxide (HFPO). HFP gives oligomers or polymers with mono or di-acid end groups.

²⁹⁷ Liu W, Takahashi S, Sakuramachi Y, Harada KH, Koizumi A (2013) Polyfluorinated telomers in indoor air of Japanese houses, *Chemosphere* 90:1672-1677.

²⁹⁸ Xu Z, Fiedler S, Pfister G, Henkelmann B, Mosch C, Volkel W, Fromme H, Schramm KW (2013) Human exposure to fluorotelomer alcohols, perfluorooctane sulfonate and perfluorooctanoate via house dust in Bavaria, Germany, *Sci Total Environ* 443:485-490.

²⁹⁹ UNEP/POPS/POPRC.8/INF/17/Rev.1.

³⁰⁰ Information provided by Inuit Circumpolar Council in 2011.

³⁰¹ <http://www.kemi.se/global/rapporter/2014/rapport-6-14-chemicals-in-textiles.pdf>.

³⁰² UNEP/POPS/POPRC.8/INF/17/Rev.1.

These perfluoropolyethers have random sequences of $-\text{CF}_2\text{O}-$ and either $-\text{CF}_2\text{CF}_2\text{O}-$ or $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ units, from TFE or HFP, respectively.³⁰³

360. Per- and poly-fluorinated ether surfactants are the newest commercially available substances in this rapidly expanding group of fluorinated surfactants. For example, the phosphate is used as a grease repellent for food contact paper. Per- and polyfluorinated polyether carboxylates are also used as processing aids in the synthesis of fluoropolymers.³⁰⁴

361. OMNOVA Solutions Inc. produces under the trade name PolyFox™ a family of short-chain fluorosurfactants based on fluorinated polyethers with a molecular weight greater than 1,000 and with C_2F_5 or CF_3 perfluoroalkyl side chain structures. The PolyFox™ product line includes anionic and non-ionic surfactants, UV-radiation curable acrylic monomer derivatives and polyols.

362. The basic structure of PolyFox™ 656 compounds is illustrated in the following figures (x + y equals about 6):



363. It seems that these surfactants have a moderate surface tension that is not quite as low as that of conventional fluorinated surfactants. The new surfactants are claimed to have a broad processing window, with less interference with other compounds. Coating quality is improved as foaming is reduced. The latter is an important factor in producing and processing water-borne coatings.

364. PolyFox™ fluorosurfactants have been used in aqueous and solvent-borne semiconductor coating formulations. In a number of examples excellent wetting, flow and levelling properties have been achieved for semiconductor coatings.

365. In addition, the poly(alkylene oxide) chain of all PolyFox® materials has an inherently low refractive index compared to other commercial polymers such as acrylics. The presence of even very short ($-\text{CF}_3$, $-\text{C}_2\text{F}_5$) side chains further reduces the refractive index, and PolyFox® materials have been used as antireflection layers in photo-resist and LCD screen applications. The PolyFox® formulation is currently being used as a surfactant in floor polish products in the United States, Europe and Asia.

366. PolyFox® products are currently priced competitively in comparison with any new C_6 -based materials but are more expensive than the C_8 -based materials, which is being phased out.³⁰⁵

1. Health effects of fluorinated polyethers

367. The acute toxicity of fluorinated polyethers is low ($\text{LD}_{50} > 2 \text{ g/kg bw}$) but they may irritate skin and the respiratory system. Generally, publically available data are lacking.³⁰⁶

2. Environmental effects of fluorinated polyethers

368. The polymer backbone linkage of the PolyFox® molecules is an ether link, which is more environmentally stable than, for example, the ester/amide links of PFOS and telomer-based fluorosurfactants. This makes the PolyFox® molecule more persistent and resistant to degradation to lower molecular weight carboxylic acids. Polyfluorodialkyl ether sulfonates are outside the domain of applicability of EPI Suite models for the purposes of estimating persistence and bioaccumulation.

H. Silicone polymers

369. Silicones are mainly polymers with the generic formula R_2SiO .³⁰⁷ They may be straight-chain or cyclic compounds and vary in molecular weight from a few hundred to several hundred thousand

³⁰³ Posner et.al, "Per- and polyfluorinated substances in the Nordic Countries, Use, occurrence and toxicology", TemaNord 2013:542, ISBN 978-92-893-2562-2, (2013), <http://norden.diva-portal.org/smash/get/diva2:701876/FULLTEXT01.pdf>.

³⁰⁴ Posner et.al, "Per- and polyfluorinated substances in the Nordic Countries, Use, occurrence and toxicology", TemaNord 2013:542, ISBN 978-92-893-2562-2, (2013), <http://norden.diva-portal.org/smash/get/diva2:701876/FULLTEXT01.pdf>.

³⁰⁵ Personal communication from Richard Thomas, OMNOVA, January 2010.

³⁰⁶ Posner et.al, "Per- and polyfluorinated substances in the Nordic Countries, Use, occurrence and toxicology", TemaNord 2013:542, ISBN 978-92-893-2562-2, (2013), <http://norden.diva-portal.org/smash/get/diva2:701876/FULLTEXT01.pdf>.

g/mol for the polymers. The building blocks of silicones are either siloxanes or silanes. Siloxanes are organic group substituted silica with the chemical formula $[R_2SiO]_n$, where R is an organic substituent such as methyl, ethyl, phenyl, etc. The chemicals formula for silanes is $(R)_n-1SiX_n$, where $n=0-4$, $X=$ Halogen (usually chlorine), $R=$ organic substituent (usually CH_3).

370. A major use of volatile methyl cyclic siloxanes (cVMS) or volatile methyl linear siloxanes (linear VMS) as illustrated in Table 5 below are monomers or manufacturing intermediates in the production of polymeric materials called polydimethylsiloxanes (PDMS).³⁰⁸ The starting material for the manufacture of PDMS is dimethyldichlorosilane. The first step in the process is hydrolysis to form cyclic siloxanes and/or linear siloxanols. PDMS itself is then formed by either the ring-opening polymerisation of cyclic siloxanes or the polycondensation of linear siloxanols in the presence of an endblocker, such as $[(CH_3)_3Si]_2O$ and heat under acid or alkaline conditions.³⁰⁹

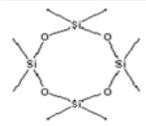
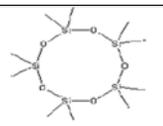
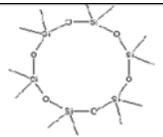
371. Volatile methylsiloxane (VMS) fluids are low molecular weight organosilicon materials with significant vapor pressure under ambient environmental conditions. They are volatile, low-viscosity silicone fluids consisting of $(-CH_3)_2SiO-$ units in either linear or cyclic structures. VMS emissions from industrial sources are limited, because the compounds are manufactured and used as intermediates in enclosed systems.

372. Some VMS fluids are also found in cosmetics and other personal care formulations, often as carriers and emollients in antiperspirant, hair care, and skin care applications.³¹⁰ A family of specialty, high performance polymers which includes silicones, siloxanes and silanes, all of which are widely used as intermediate building blocks in thousands of products from airbags to cookware to textiles.³¹¹

373. Some commercial products of silicone polymers (such as silicone polyethers as identified below), that are alternatives to PFOS, might contain impurities of VMS, although not all polymers potentially used as alternatives will contain VMS impurities. These VMS might be used as raw materials in the manufacturing process of silicone polymers and therefore may be low level impurities in silicone polymers.³¹²

374. These siloxanes are volatile methyl siloxanes with short SiO backbones, in particular the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes MM (or HMDSO), MDM, MD2M and MD3M. They are shown in Table 5.

Table 5: Siloxanes of environmental and health concern, that are manufacturing intermediates in the production of polydimethylsiloxanes (PDMS) and may appear as impurities in commercial PDMS^{313, 314}

Abbreviation	Name	CAS No:	Structure
D4	Octamethyl cyclotetrasiloxane	556-67-2	
D5	Decamethyl cyclopentasiloxane	541-02-6	
D6	Dodecamethyl cyclohexasiloxane	540-97-6	

³⁰⁷ <http://www.dowcorning.com/content/publishedlit/51-960A-01.pdf>.

³⁰⁸ https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290565/scho0309bpqz-e-e.pdf.

³⁰⁹ https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290565/scho0309bpqz-e-e.pdf.

³¹⁰ <https://www.dowcorning.com/content/publishedlit/01-1033b-01.pdf>.

³¹¹ https://www.dowcorning.com.cn/zh_CN/content/about/aboutmedia/FactSheet_EN.pdf.

³¹² https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290565/scho0309bpqz-e-e.pdf.

³¹³ Cousins AP, Kaj L, Broström-Lundén E. 2009. Siloxanes in the Nordic environment. *Norman Bulletin* no. 1. www.norman-network.net.

³¹⁴ https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290565/scho0309bpqz-e-e.pdf

Abbreviation	Name	CAS No:	Structure
MM (or HMDSO)	Hexamethyl disiloxane	107-46-0	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3 - \text{Si} - \text{O} - \text{Si} - \text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
MDM	Octamethyl trisiloxane	107-51-7	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{H}_3\text{C} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$
MD2M	Decamethyl tetrasiloxane	141-62-8	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \\ \text{CH}_3 - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{CH}_3 \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$
MD3M	Dodecamethyl pentasiloxane	141-63-9	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{CH}_3 - \text{Si} - \text{O} - \left(\text{Si} - \text{O} \right)_3 - \text{Si} - \text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$

375. Out of these commercially used siloxanes, D4, D5, and MM (or HMDS) are chemicals produced in high volumes produced at several locations worldwide.^{315, 316} The first two are the most commonly used siloxanes in the Nordic countries.³¹⁷

376. Recent activities in the northern hemisphere have focused on investigating the environmental occurrence of the above-mentioned siloxanes, which are used in a large number of industrial and consumer products such as sealants, fuels, car polishes, cleaners, anti-foaming agents, car waxes and personal care and biomedical products.^{318, 319} The widespread use of siloxanes and their broad application, high volatility and potential for toxic effects have raised concerns about these compounds within various disciplines of environmental science. Recent studies indicate that they are widespread in the environment.

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

378. Worlée-Chemie produced silicone polymers, which in the paint and ink industry can in several cases be used as alternatives to fluorosurfactants as wetting agents. WorléeAdd[®] 340 is a low-viscous non-ionic special modified silicone polyether (containing 3-(polyoxyethylene) propylheptamethyl trisiloxane, CAS No: 67674-67-3) that can improve surface wetting of aqueous systems on difficult substrates like polyethylene and polypropylene or contaminated substrates. It has a low surface tension and is claimed to be highly effective in improving wetting, spreading and levelling of water-borne coatings and eliminating surface defects without foam stabilizing. It is further claimed that the compound normally has no negative effect on recoating.

379. Another product, WorléeAdd[®] 345, was a mixture of a silicone polyether (10–15%) and a dioctyl sulfosuccinate (50–55%) in ethanol and water. This surfactant could be used to improve wetting properties of aqueous coatings for different substrates, where penetration into absorbing surfaces also is improved.

380. Per- and polyfluorinated polyether silanes are used as surface treatments, e.g. for stones or Perfluoroalkyl derivatives of silanes also exist; they include 1H,1H,2H,2H-perfluoroalkyl triethoxysilane, which is effective for glass, stone and surface treatment³²⁰ and additionally as antibiofouling agents for ships.³²¹ The formula is:

³¹⁵ http://www.siliconescarbonbalance.eu/pdf/SIL_nutshell_en.pdf.

³¹⁶ https://www.dowcorning.com.cn/zh_CN/content/about/aboutmedia/FactSheet_EN.pdf.

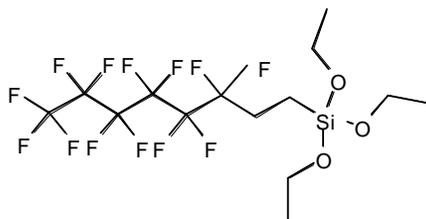
³¹⁷ Kaj L, Schlabach M, Andersson J, Cousins AP, Schmidbauer N, Brorström-Lundén E. 2005. Siloxanes in the Nordic Environment. TemaNord 2005:593.

³¹⁸ Lassen C, Hansen CL, Mikkelsen SH, Maag J. 2005. Siloxanes – consumption, toxicity and alternatives. Environmental Project no. 1031. Danish Environmental Protection Agency.

³¹⁹ <https://www.dowcorning.com/content/publishedlit/01-1033b-01.pdf>.

³²⁰ ABCR 2006–2007 catalogue: Fluorochemicals. Karlsruhe, Germany.

³²¹ Posner et.al, “Per- and polyfluorinated substances in the Nordic Countries, Use, occurrence and toxicology”, TemaNord 2013:542, ISBN 978-92-893-2562-2, (2013), <http://norden.diva-portal.org/smash/get/diva2:701876/FULLTEXT01.pdf>.



1. Health effects of siloxanes and silicone polymers

381. A study carried out by the National Food Institute at the Technical University of Denmark investigated the toxic effects of siloxanes as a group in order to set a health-based quality criterion for ambient air. Toxic effects of D3, D4, D5, D6 and HMDSO were studied using a “read-across” modelling method, which is based on structural similarity and its relation to toxicity. The linear siloxane HMDSO appeared to have lower potential for liver toxicity, but higher potential for lung toxicity, than the cyclic substances. Decreasing toxicity with increasing chain length was also observed. An ambient quality criterion of 0.01 mg/m³ was derived, based on lung toxicity, including a safety factor of 250.³²² Some years ago polysiloxanes or silicone polymers were evaluated in a comprehensive monograph published by the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC).³²³ Low-molecular-weight polydimethylsiloxanes have been studied by siloxane manufacturers and they conclude that the polydimethylsiloxanes studied all possess a very low potential for toxicity.

382. The Scientific Committee on Consumer Products in the European Union has published an Opinion on D4 in which the safety of D4’s use as a cosmetic ingredient has not been questioned.³²⁴ In the United States, the Cosmetic Ingredient Review (CIR) panel, a non-governmental body, is about to publish its final assessment of the safety of cyclic siloxanes, D3, D4, D5, D6 and D7.³²⁵ The panel has concluded that D4, D5, D6 and D7 are safe for use in cosmetics. D3 will be taken off the International Nomenclature of Cosmetic Ingredients (INCI) list because it is not a commercial product.

383. Health Canada concluded in 2008 that D4, D5, D6 and in 2013 that L3 are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health. Environment Canada concluded in a screening assessment report that D4 may be entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. Based on the conclusions of the assessment, a Final Order adding D4 to the List of Toxic Substances in Schedule 1 under the *Canadian Environmental Protection Act, 1999* (CEPA 1999) was published in Part II of the *Canada Gazette* on February 16, 2011.³²⁶ The European Commission has classified D4 as a reproductive toxic substance (repr. 2) (H361f).³²⁷

384. Other studies of siloxanes, however, indicate that they seem to be harmful when inhaled and that exposure may induce serious damage to eyes. Prolonged and frequent skin contact with WorléeAdd® 340 may cause skin irritation.³²⁸

2. Environmental effects of siloxanes and silicone polymers

385. Siloxanes are widely distributed in the northern hemisphere. In general, siloxanes are very stable and persistent compounds that do not degrade in the environment. They are found in the Arctic. However, there are also studies which conclude that siloxanes are unlikely to meet the POP screening criteria for long range transport.^{329, 330} The cyclic- and short-chain linear siloxanes bioconcentrate in

³²² Greve K, Nielsen E, Ladefoged O. 2008. Toxic effects of siloxanes: group evaluation of D3, D4, D5, D6 and HMDS in order to set a health-based quality criterion in ambient air. *Toxicology Letters* 180: S67.

³²³ http://www.ecetoc.org/index.php?mact=MCSOap,cntnt01,details,0&cntnt01by_category=3&cntnt01order_by=Reference%20Desc&cntnt01template=display_list_v2&cntnt01display_template=display_details_v2&cntnt01document_id=5338&cntnt01returnid=91.

³²⁴ http://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_029.pdf.

³²⁵ http://ijt.sagepub.com/content/30/6_suppl/149S.abstract.

³²⁶ <https://www.ec.gc.ca/toxiques-toxics/default.asp?lang=En&n=98E80CC6-1&xml=71D7177A-0334-4668-9579-1508F6D55ABD>.

³²⁷ UNEP/POPS/POPRC.10/INF/8/Rev.1.

³²⁸ UNEP/POPS/POPRC.8/INF/17/Rev.1.

³²⁹ <http://publications.environment-agency.gov.uk/pdf/SCHO0309BPQZ-e-e.pdf>.

³³⁰ <http://publications.environment-agency.gov.uk/pdf/SCHO0309BPQX-e-e.pdf>.

aquatic organisms.³³¹ These siloxanes may be toxic to aquatic organisms; there are, however, still gaps in our knowledge.

386. According to the material safety datasheet for WorléeAdd® 340, the silicone polymer in that product is classified as environmentally dangerous with the R-phrases R51 (“Toxic to aquatic organisms”) and R53 (“May cause long-term adverse effects in the aquatic environment”). The R-phrase R53 indicates that the substance is bioaccumulative.

387. The cyclic siloxanes D4, D5 and D6 have been subjected to an environmental risk assessment by the United Kingdom Environment Agency applying European Union Technical Guidance.³³² Canada has concluded that D4 has the potential to cause harm in the aquatic environment and has implemented a risk management measure to reduce release from industrial effluents. Environment Canada has additionally concluded that D5, D6 and L3 are not entering the environment in a quantity or under conditions that constitute a danger to the environment.³³³

388. A quantitative weight of evidence has been completed on D4, D5 and D6 that suggests that cVMSs are not classifiable as persistent, bioaccumulative, toxic, nor that they undergo LRT in the sense of the legacy POPs (Bridges and Solomon, 2016).³³⁴ There are other relevant studies. For example, peer review publications are available that conclude no risk to the aquatic environment (Fairbrother et al., 2016).³³⁵ In addition, Wang et al published a summary of siloxanes measured in various environmental media in Canada that demonstrates the concentrations measured are less than concentrations of D4 that were associated with effects in organisms in laboratory studies³³⁶. A recent report by Norway assessing biomagnification in the Inner Oslofjord concluded that D4 underwent biodilution³³⁷. Peer review publications are also available which question if the reproductive effects seen in rodents following D4 exposure are relevant to human health (Quinn et al., 2007³³⁸ and Plant, 2008³³⁹). There is a study in which experts question whether the reported presence of siloxanes in Arctic biota are due to long range transport (LRT) and back deposition and suggest any siloxanes reported are a result of local sources (Warner et al., 2010)³⁴⁰. Krogseth et al. (2013)³⁴¹ recently questioned the reliability of D4 measurements in air and indicated the reported presence of D4 is uncertain as concentrations measured were similar to levels found in storage control samples. Another recent report by Norway has reported that overall the levels of siloxanes were below the level of quantitation in a number of Arctic samples (with a few samples reported to have measured concentrations of D5)³⁴². The ECETOC monograph cited above has been updated in 2012 and the

D6 <http://publications.environment-agency.gov.uk/pdf/SCHO0309BPQY-e-e.pdf>.

³³⁰ <http://www.sciencedirect.com/science/article/pii/S0045653512012842>.

<http://www.sciencedirect.com/science/article/pii/S0045653512012957>.

<http://www.sciencedirect.com/science/article/pii/S0045653512012933>.

³³¹ Parrott JL, Alaei M, Wang D, Sverko E (2012) Fathead minnow (*Pimephales promelas*) embryo to adult exposure to decamethylcyclopentasiloxane (D5), *Chemosphere* doi: 10.1016/j.chemosphere.2012.10.053.

³³² <http://www.chemicalsubstanceschimiques.gc.ca/challenge-defi/batch-lot-2/index-eng.php>.

³³³ <http://www.chemicalsubstanceschimiques.gc.ca/challenge-defi/batch-lot-12/index-eng.php>

³³⁴ Bridges, J., Solomon K. 2016, Quantitative Weight of Evidence Analysis of the Persistence, Bioaccumulation, Toxicity and Potential for Long Range Transport of the Cyclic Volatile Methyl Siloxanes. *Journal of Toxicology and Environmental Health, Part B: Critical Reviews*. In Press.

³³⁵ Fairbrother, A. and Woodburn, K.B. (submitted) Assessing the aquatic risk of the cyclic volatile methyl siloxane (D4). Submitted to ES&T Letters August 2016.

³³⁶ Wang et al, 2013, Concentrations of cyclic volatile methylsiloxanes in biosolid amended Soil, influent, effluent, receiving water, and sediment of wastewater treatment plants in Canada, *Chemosphere*.

³³⁷ Environmental Contaminants in An Urban Fjord, 2015; <http://www.miljodirektoratet.no/Documents/publikasjoner/M601/M601.pdf>

³³⁸ Quinn, A.L.; Regan, J.M.; Tobin, J.M.; Marinik, B.J.; McMahon, J.M.; McNett, D.A.; Sushynski, C.M.; Crofoot, S.D.; Jean, P.A.; and Plotzke, K.P. 2007. In vitro and in vivo evaluation of the estrogenic, androgenic, and progestagenic potential of two cyclic siloxanes. *Tox Sci.* 96(1):145-153.

³³⁹ Plant, T. 2012. A comparison of the neuroendocrine mechanism underlying the initiation of the preovulatory LH surge in the human, Old World monkey and rodent. *Frontiers in Neuroendocrinology.* 33:160-168.

³⁴⁰ Warner, N. A.; Evensen, A.; Christensen, G.; Gabrielsen, G. W.; Borga, K.; Leknes, H. 2010. Volatile siloxanes in the European Arctic: Assessment of source and spatial distribution. *Environ. Sci. Technol.* 44, 7705-7710.

³⁴¹ Krogseth, I. S.; Kierkegaard, A.; McLachlan, M. S.; Breivik, K.; Hansen, K. M.; Schlabach, M. 2013, Occurrence and seasonality of cyclic volatile methyl siloxanes in Arctic air. *Environ. Sci. Technol.* 47(1), 502-9.

³⁴² Screening of UV chemicals, bisphenols and siloxanes in the Arctic, 2016 <http://www.miljodirektoratet.no/Documents/publikasjoner/M598/M598.pdf>

new report concluded that overall, PDMS does not present a risk to human health or the environment.³⁴³

389. Hexamethyl disiloxane (MM or HMDS) is undergoing Substance Evaluation by the UK. Decision includes information relevant for PBT/vPvB assessment under REACH. Octamethyl trisiloxane (MDM), Decamethyl tetrasiloxane (MD2M) and Dodecamethyl pentasiloxane (MD3M) are on the CoRAP for Substance Evaluation (UK) due to PBT/vPvB concerns. The UK is performing a PBT assessment for D6. It is currently considered very persistent and bioaccumulative in a REACH context.³⁴⁴

390. The ECHA PBT Working Group concluded, based on a weight of evidence study of the available information that D4 meets the Annex XIII criteria for both a 'persistent, bioaccumulative and toxic' (PBT) and both D4 and D5 as 'very persistent and very bioaccumulative' (vPvB) substances in the environment. Although the T criteria in Annex XIII of REACH are not met for D5, there are some uncertainties relating to the limited publically available data on mammalian, avian and fish reproductive effects, and toxicity has been observed in sediment and soil organisms.^{345, 346, 347} A review of the environmental properties of cyclic siloxanes is available on the Internet.³⁴⁸ In-depth information on the properties of siloxanes is provided in the Technical paper on the identification and assessment of alternatives to PFOS in open applications and in assessment reports of the tenth meeting of the POPs Review Committee.^{349, 350}

3. Results of the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride in 2014

391. The factsheets on alternatives to PFOS, its salts and PFOSF (UNEP/POPS/POPRC.10/INF/8/Rev.1) developed as part of the assessment of alternatives to PFOS, its salts and PFOSF conducted in 2014 provides information on the following siloxanes: decamethyl cyclopentasiloxane (D5); decamethyl tetrasiloxane (MD2M); dodecamethyl cyclohexasiloxane (D6); octamethyl cyclotetrasiloxane (D4); and octamethyl trisiloxane (MDM).

392. According to the factsheets, the overall conclusion and the assessment of persistent organic pollutant properties against Annex D criteria and other hazard indicators were as follows:

- (a) Decamethyl cyclopentasiloxane (D5):
 - (i) Overall conclusion: Class 3 (Substances that are difficult for classification due to insufficient publically available data);
 - (ii) Persistence: A biodegradation study indicates a degradation rate of 0.14% in 28 days in water. This result indicates that D5 slowly degrades in water likely with a persistence half-life more than 2 months. Sediment degradation half-lives of 1200 days under aerobic conditions at 24°C and 3100 days under anaerobic conditions at 24°C were determined in a reliable study conducted according to an appropriate test protocol, and in compliance with Good Laboratory Practices (GLP). D5 is therefore considered to fulfil the persistence criteria according to Annex D 1 (b) (i);
 - (iii) Bioaccumulation: A steady-state bioconcentration factor (BCF) value of 7060 for fathead minnows was determined in a reliable study conducted according to an appropriate test protocol, and in compliance with GLP. D5 is therefore considered to fulfil the bioaccumulation criteria according to Annex D 1 (c) (i);
 - (iv) Long-range transport: D5 has the potential to be transported over long-distances in the atmosphere. In air, D5 is persistent with calculated atmospheric half-lives of more than 3 days. Therefore D5 is considered to fulfil the Annex D 1 (d) (iii) criteria;

³⁴³ <http://www.ecetoc.org/mediaroom/ecetoc-publishes-joint-assessment-of-commodity-chemicals-jacc-report-no-55-on-linear-polydimethylsiloxanes/#>

³⁴⁴ Submission by the European Commission.

³⁴⁵ <http://echa.europa.eu/about-us/who-we-are/member-state-committee/opinions-of-the-msc-adopted-under-specific-echa-s-executive-director-requests>.

³⁴⁶ <http://echa.europa.eu/documents/10162/18ea3a03-0da4-4a8d-a522-5b467c3a9307>

³⁴⁷ UNEP/POPS/POPRC.10/INF/8/Rev.1.

³⁴⁸ www.cyclosiloxanes.eu.

³⁴⁹ UNEP/POPS/POPRC.10/INF/7/Rev.1, UNEP/POPS/POPRC.10/INF/8/Rev.1.

³⁵⁰ UNEP/POPS/POPRC.8/INF/17/Rev.1.

- (v) Ecotoxicity: D5 shows essentially no acute toxicity to aquatic organisms (fish: LC50 >16 µg/L, daphnia EC50 >2.9 µg/L). Also no chronic toxicity with no observed effect concentration (NOEC) of ≥14 µg/L (*Oncorhynchus mykiss*) and a NOEC of ≥2.9 (*Daphnia magna*) was detected when tested at concentrations up to its water solubility limit. The 28d-NOEC for sediment organisms was 70 mg/kg dw. A 28 day effect concentration for terrestrial organisms lethal concentration (LC50) and NOEC > 4000 mg/kg dry weight indicate no terrestrial toxicity. Although the T criteria are not met, there are some uncertainties relating to the limited publically available data on mammalian, avian and fish reproductive effects, and toxicity has been observed in sediment and soil organisms.³⁵¹ D5 is therefore not likely to fulfil the Annex D 1 (e) (ii) criteria;
 - (vi) Toxicity to human health: D5 has not been classified by the International Agency for Research on Cancer (IARC) for carcinogenicity. No international agency has classified D5 for reproductive/developmental toxicity. Data on the endpoints for carcinogenicity/ genotoxicity and reproductive/developmental toxicity show no toxicity. D5 is therefore not likely to fulfil the Annex D 1 (e) (ii) criteria;
- (b) Decamethyl tetrasiloxane (MD2M):
- (i) Overall conclusion: Class 4 (Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e));
 - (ii) Persistence: One experimental data point indicates high persistence in water for decamethyl tetrasiloxane, with a biodegradation rate of 0% in 28 days in water. The substance likely degrades rather fast in soil depending on the water content (1.48 days at 32%RH and 119.5 days at 100%RH).³⁵² There is no publically available data for degradation in sediment. Decamethyl tetrasiloxane (MD2M) cannot therefore be assessed towards the Annex D 1 (b) (i) criteria due to equivocal data;
 - (iii) Bioaccumulation: Steady-state experimental BCF values of 3870 L/kg (0.43 µg/L) and 1610 L/kg (5.3 µg/L) in a reliable study conducted according to an appropriate test protocol, and in compliance with GLP. Decamethyl tetrasiloxane (MD2M) is considered not to fulfil the bioaccumulation criteria according to Annex D 1 (c) (i);
 - (iv) Long-range transport: Estimated half-life in air is 7.150 Days [AopWin v1.92]. Decamethyl tetrasiloxane (MD2M) is considered to fulfil the Annex D 1 (d) (iii) criteria;
 - (v) Ecotoxicity: The LC50 and NOEC values available indicate that MD2M is not toxic to aquatic organisms and terrestrial organisms up to the solubility limit of the substance. Decamethyl tetrasiloxane (MD2M) is not likely to fulfil the Annex D 1 (e) criteria;
 - (vi) Toxicity to human health: MD2M has an LC50 > 2000 mg/kg which indicate low acute toxicity. MD2M has not been classified by IARC for carcinogenicity. Data on the endpoints for carcinogenicity, genotoxicity and reproductive/developmental toxicity show no toxicity effect. Decamethyl tetrasiloxane (MD2M) is not likely to fulfil the Annex D 1 (e) criteria;
- (c) Dodecamethyl cyclohexasiloxane (D6):
- (i) Overall conclusion: Class 4 (Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e));
 - (ii) Persistence: D6 is not readily biodegradable. A number of studies report half-life values of more than 60 days in water for D6. Degradation of D6 in soil depends on the water content, being higher in humid soils. No experimental publically available data are available for persistence in sediment. D6 is therefore considered to fulfil the persistence criteria according to Annex D 1 (b) (i);

³⁵¹ Olsen, G.W., et al., Half-Life of Serum Elimination of Perfluorooctanesulfonate, Perfluorohexanesulfonate, and Perfluorooctanoate in Retired Fluorochemical Production Workers. *Environ Health Perspect*, 2007. 115(9).

³⁵² Herzke et.al, A literature survey on selected chemical compounds - Literature survey of polyfluorinated organic compounds, phosphor containing flame retardants, 3-nitrobenzanthrone, organic tin compounds, platinum and silver, Norwegian Climate and Pollution Agency (KLIF), 2007, report TA-2238/2007.

- (iii) Bioaccumulation: Several empirical bioconcentration factors (BCF) of less than 2500 have been reported. D6 is therefore considered not to fulfil the bioaccumulation criteria according to Annex D 1 (c) (i);
 - (iv) Long-range transport: D6 has the potential to be transported over long-distances in the atmosphere. In air, D6 is persistent with calculated atmospheric half-lives of more than 2 days. Estimations of the transport distance and monitoring data also indicate that D6 can be transport over long distances. D6 is therefore considered to fulfil the Annex D 1 (d) (iii) criteria;
 - (v) Ecotoxicity: The experimental toxicity data showed no adverse effects to pelagic aquatic organisms at concentrations up to 0.0046 mg/L, its approximate water solubility limit. Given the low bioavailability, and low potential for effects, it is concluded that D6 has low potential to cause ecological harm in the aquatic and terrestrial environment. D6 is therefore not likely to fulfil the Annex D 1 (e) (i) criteria;
 - (vi) Toxicity to human health: D6 exhibits low acute toxicity, with LD50 values >2000 mg/kg body weight. D6 has not been classified by IARC for carcinogenicity, genotoxicity or reproductive/developmental toxicity. Data on the endpoints for carcinogenicity, genotoxicity and reproductive/developmental toxicity are negative. Therefore D6 is considered not to be toxic to humans. D6 is therefore not likely to fulfil the Annex D 1 (e) (ii) criteria;
- (d) Octamethyl cyclotetrasiloxane (D4):
- (i) Overall conclusion: Class 1, Substances that are likely to meet all Annex D criteria (b), (c), (d) and (e);
 - (ii) Persistence: A biodegradation rate of 3.7% in 29 days in water indicates that D4 has a half-life in water greater than 2 month. Data available on the degradation of D4 in sediment show that it has a relatively long half-life, of the order of 242 days at 24°C under aerobic conditions, and 365 days at 24°C under anaerobic conditions. However D4 half-life in soil is dependent on the %RH value. D4 is considered to fulfil the persistence criteria according to Annex D 1 (b) (i);
 - (iii) Bioaccumulation: The steady state BCF for D4 has been determined as 12,400 L/kg in fathead minnows. There are also empirical log Kow data that range between 4.34 and 6.49 for D4.³⁵³ D4 is therefore considered to fulfil the bioaccumulation criteria according to Annex D 1 (c) (i);
 - (iv) Long-range transport: The half-life of D4 in the atmosphere is reported to be from 12.7 to 15.8 days. Therefore D4 is therefore considered likely to fulfil the Annex D 1 (d) (iii) criteria;
 - (v) Ecotoxicity: The European Commission has classified D4 as Hazardous to the aquatic environment (Aquatic Chronic 4). Considering D4's potential to bioaccumulate in biota and its toxicity to sensitive aquatic organisms, long-term environmental exposure may cause adverse effects to aquatic organisms. Therefore D4 is likely to fulfil the Annex D 1 (e) (i) criteria;
 - (vi) Toxicity to human health: The European Commission has classified D4 as a reproductive toxic substance (repr. 2) (H361f).³⁵⁴ D4 is therefore likely to fulfil the Annex D 1 (e) (ii) criteria;
- (e) Octamethyl trisiloxane (MDM):
- (i) Overall conclusion: Class 4, Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e).
 - (ii) Persistence: Available data indicate both high and low degradation rates in water for MDM. The substance degrades relatively fast in soil depending on the water content. There is no publically available data available for degradation in

³⁵³ Martin, J.W., et al., Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.*, 2003. 22(1): p. 196-204.

³⁵⁴ Poulsen et al. Substitution of PFOS for use in nondecorative hard chrome plating, 2011, Environmental Project No. 1371 2011, Danish Ministry of Environment.

sediment. MDM cannot be assessed towards the persistence criteria according to Annex D 1 (b) (i) due to equivocal data.

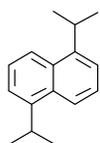
- (iii) Bioaccumulation: Experimental steady state BCF data of 5030 (0.0017 mg/L of MDM) and 7730 (0.021 mg/L) and experimental log Kow of 6.60 are reported for MDM. MDM is considered to fulfil the bioaccumulation criteria according to Annex D 1 (c) (i).
- (iv) Long-range transport: MDM present in air will undergo abiotic degradation through reaction with photochemically-produced atmospheric hydroxyl radicals, with atmospheric half-lives of 6–9 days. MDM is considered to fulfil the Annex D 1 (d) (iii) criteria.
- (v) Ecotoxicity: Measured effect concentration and NOEC values indicate low ecotoxicity for MDM for aquatic organisms. There were no effect concentration values available for terrestrial organisms. Therefore MDM is not likely to fulfil the Annex D 1 (e) (i) criteria.
- (vi) Toxicity to human health: MDM indicate low oral, dermal and inhalation acute toxicity. MDM is not classified for carcinogenicity by IARC. Mutagenicity and reproductive toxicity is negative for MDM. Therefore MDM is not likely to fulfil the Annex D 1 (e) (ii) criteria.

I. Propylated aromatics

393. Rütgers Kureha Solvents produces various aromatic surfactants with the trade name Ruetasolv[®]; based on propylated naphthalenes and biphenyls, these products 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.

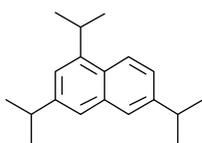
394. They may also be used as plasticizers and film-forming aids in emulsion paints and adhesives. The various isopropyl naphthalenes and isopropyl biphenyls are very hydrophobic substances that are compatible with almost all raw materials such as epoxy resins, polyurethane resins, resin esters, hydrocarbon resins, polystyrene, elastomers, dispersions, emulsions, styrene-acrylate-copolymers, vinyl acetate and ethylene vinyl acetate co-polymers, mineral oils and bitumen.

395. Propylated aromatic products are all colourless liquids with a boiling point of about 300°C and have very low solubility in water.



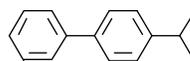
Ruetasolv DI

CAS No: 38640-62-9



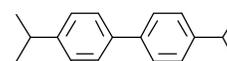
Ruetasolv TPN

CAS No: 35860-37-8



Ruetasolv BP 4201

CAS No: 69009-90-1



Ruetasolv BP 4103

CAS No: 25640-78-2

1. Health effects of propylated aromatics

396. The substances *p*-isopropyl-1,1'-biphenyl (Ruetasolv BP 4103) and *p,p'*-diisopropyl-1,1'-biphenyl (Ruetasolv BP 4201) can cause skin sensitization or dermatitis upon repeated contact with skin, and long-term exposure causes irritation of the eyes, nose, throat, mucous membranes and respiratory tract. *p*-Isopropyl-1,1'-biphenyl has a very low acute toxicity with oral LD₅₀ values for rats of > 4 g/kg. Central nervous system, liver and kidney damage have, however, been reported as chronic effects of that chemical in animals.³⁵⁵

397. Isopropylated naphthalenes are also irritating substances. The acute toxicity of diisopropyl-naphthalene (Ruetasolv DI) is very low, with an oral LD₅₀ value for rats of 3,900 mg/kg.³⁵⁶

398. More in-depth health effect information on the properties of propylated aromatics is provided in assessment reports of POPRC10.³⁵⁷

³⁵⁵ UNEP/POPS/POPRC.8/INF/17/Rev.1.

³⁵⁶ UNEP/POPS/POPRC.8/INF/17/Rev.1.

³⁵⁷ UNEP/POPS/POPRC.10/INF/7/Rev.1, UNEP/POPS/POPRC.10/INF/8/Rev.1.

2. Environmental effects of propylated aromatics

399. The biphenyls and the naphthalenes have high octanol/water partition coefficients (log K_{OW}), and the bioconcentration factor (BCF) for the substances is greater than 100. These chemicals are therefore potentially bioaccumulative. The biphenyl moiety seems to be easily biodegradable, whereas the naphthalene moiety biodegrades slowly. The sparse available information suggests that the biphenyls are acutely toxic to aquatic organisms, whereas naphthalene appears to have no acute toxic effects on the investigated fish species.³⁵⁸

400. More in-depth environmental effect information on the properties of propylated aromatics is provided in assessment reports of the tenth meeting of the POPs Review Committee.³⁵⁹

3. Results of the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride in 2014

401. The factsheets on alternatives to PFOS, its salts and PFOSF (UNEP/POPS/POPRC.10/INF/8/Rev.1) developed as part of the assessment of alternatives to PFOS, its salts and PFOSF conducted in 2014 provides information on the following propylated aromatics: diisopropyl-1,1'-biphenyl; diisopropylnaphthalene (DIPN); 1-isopropyl-2-phenyl-benzene; and triisopropylnaphthalene (TIPN).

402. According to the factsheets, the overall conclusion and the assessment of persistent organic pollutant properties against Annex D criteria and other hazard indicators were as follows:

- (a) Diisopropyl-1,1'-biphenyl:
 - (i) Overall conclusion: Class 4 (Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e));
 - (ii) Persistence: The bench mark isomer I with CAS No: 36876-13-8 biodegraded more than 80% in 48 hours under the River Die-Away Test using both river sediment and river water / Wemcol, 1% diisopropyl. These results indicate that the bench mark isomer is easily degraded in sediment water systems. However there is no publically available data available for diisopropyl-1,1'-biphenyl to verify these biodegradation data. Diisopropyl-1,1'-biphenyl cannot therefore be assessed towards the Annex D 1 (b) criteria due insufficient data;
 - (iii) Bioaccumulation: Only one experimental BCF identified with a value of 104721 for diisopropyl-1,1'-biphenyl. Other available bioaccumulation values are estimated also for the bench mark isomer. Since at least two experimental data points are considered as reliable for assessment towards the Annex D 1 (c) criteria, the conclusion is that there is insufficient publically available data for this substance. Diisopropyl-1,1'-biphenyl cannot therefore be assessed towards the bioaccumulation criteria according to Annex D 1 (c) (i) due to insufficient data;
 - (iv) Long-range transport: Estimated half-life in air is 0.842 days [AopWin v1.92]. The bench-mark diisopropylbiphenyl isomer with CAS No: 36876-13-8 is in vapor-phase degraded in the atmosphere by reaction with photochemically produced hydroxyl radicals with a half-life of about 1 to 2 days. Diisopropyl-1,1'-biphenyl is considered not to fulfil the Annex D 1 (d) (iii) criteria;
 - (v) Ecotoxicity: No publically data available in the references reviewed. Diisopropyl-1,1'-biphenyl cannot therefore be assessed towards the Annex D 1 (e) criteria due to insufficient data;
 - (vi) Toxicity to human health: No publically data available in the references reviewed. Diisopropyl-1,1'-biphenyl cannot therefore be assessed towards the Annex D 1 (e) criteria due to insufficient data;
- (b) Diisopropylnaphthalene (DIPN)
 - (i) Overall conclusion: Class 4 (Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e));

³⁵⁸ UNEP/POPS/POPRC.8/INF/17/Rev.1.

³⁵⁹ UNEP/POPS/POPRC.10/INF/7/Rev.1, UNEP/POPS/POPRC.10/INF/8/Rev.1.

- (ii) Persistence: DIPN is not readily biodegradable. Laboratory scale experimental data in salt and distilled water indicate that DIPN is easily degradable in water. However data from field trials provided by NITE³⁶⁰ indicate that is slow with a half-life of less than 50% in 2 months in water. Thus the half-life in water exceeds the limit set out in annex D criteria of the Stockholm Convention. Since field data are considered more reliable than laboratory scale tests it is concluded that 2, 6 DINP and its isomers are not easily degraded in water under field conditions. There is no publically available data available for soil and sediment. Diisopropylnaphthalene is therefore likely to fulfil the Annex D 1 (b) (ii) criteria;
 - (iii) Bioaccumulation: Steady state BCF values greater than 5000 are reported for DIPN. Diisopropylnaphthalene is therefore likely to fulfil the bioaccumulation criteria according to Annex D 1 (c) (i);
 - (iv) Long-range transport: Estimated half-life in air is 0.162 days [AopWin v1.92]. Half-life for the photolytic reaction in air is estimated to be 5.8 hours. Diisopropylnaphthalene is considered not likely to fulfil the Annex D 1 (d) (iii) criteria;
 - (v) Ecotoxicity: There is one effect concentration value of LD50 in *Seriola quinqueradiata* (Yellowtail) available of approx 2 mL/kg which corresponds to high aquatic toxicity according to the GHS system. The data from NITE³⁶¹ indicate toxicities below 1 mg/L reflecting a very high toxicity to aquatic life. No ecotoxicity data was found for terrestrial compartments. Diisopropylnaphthalene is likely to fulfil the Annex D 1 (e) criteria;
 - (vi) Toxicity to human health: Acute toxicity LD50 exceeded 4000 mg/kg bw which indicate low acute toxicity for the substance. DIPN did not show any carcinogenic, genotoxic or reproductive toxicity effect, which suggests that DIPN is non-toxic. Diisopropylnaphthalene is not likely to fulfil the Annex D 1 (e) criteria;
- (c) 1-Isopropyl-2-phenyl-benzene:
- (i) Overall conclusion: Class 4 (Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e));
 - (ii) Persistence: Experimental data on biodegradation in water and sediment -water samples suggest a rapid degradation of similar monoisopropyl biphenyl isomers. The substances were completely degraded in sediment-water samples within one week that suggest half-life in water and sediment much less than 2 month and 6 month respectively. 1-Isopropyl-2-phenyl-benzene is considered not to fulfil the Annex D 1 (b) criteria for persistence;
 - (iii) Bioaccumulation: In an experimental study, BCF were determined to be 2896 and 10790 respectively. Two experimental log Kow values are available namely 5.33 and 5.51. 1-Isopropyl-2-phenyl-benzene is considered to fulfil the Annex D 1 (c);
 - (iv) Long-range transport: Estimated half-life in air is 1.098 Days [AopWin v1.92]. Vapor-phase isopropylbiphenyl is degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals, the half-life for this reaction in air is estimated to be about 40 hours, a bit less than 2 days. 1-Isopropyl-2-phenyl-benzene is therefore considered not to fulfil the Annex D 1 (d) (iii) criteria;
 - (v) Ecotoxicity: The substance is suggested with the data available to show high toxicity to aquatic organisms. There was no data available for terrestrial organisms. 1-Isopropyl-2-phenyl-benzene is likely to fulfil the Annex D 1 (e) criteria;
 - (vi) Toxicity to human health: The substance show acute toxicity data of more than 5000 mg/kg bw and is therefore considered non-toxic. No cancer classification according to IARC. Mutagenicity tests are negative .There are no data available

³⁶⁰ Lieder, P.H., et al., A two-generation oral gavage reproduction study with potassium perfluorobutanesulfonate (K+PFBS) in Sprague Dawley rats. *Toxicology*, 2009. 259: p. 33-45.

³⁶¹ Lieder, P.H., et al., A two-generation oral gavage reproduction study with potassium perfluorobutanesulfonate (K+PFBS) in Sprague Dawley rats. *Toxicology*, 2009. 259: p. 33-45.

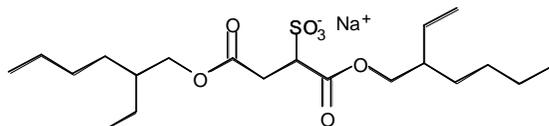
for any other toxicity endpoints. 1-Isopropyl-2-phenyl-benzene is not likely to fulfil the Annex D 1 (e) criteria;

- (d) Triisopropylnaphthalene (TIPN):
- (i) Overall conclusion: Class 4 (Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e));
 - (ii) Persistence: Degradation of 0-23% in 4 weeks in a screening test for biodegradation in water are reported for TIPN. This suggests a degradation of less than 50% in 2 months. Triisopropylnaphthalene is considered likely to meet the Annex D 1 (b) criteria;
 - (iii) Bioaccumulation: Experimental data for bioaccumulation with Rice fish (*Oryzias latipes*) at three different dose levels of the substance namely 1 ppb, 5 ppb and 50 ppb resulted in steady state (10 weeks) BCF values 7600 (1 ppb), 11000 (5 ppb) and 14600 (50 ppb) These BCF values indicate this is a bioaccumulative substance. In Chemspider one experimental BCF is reported namely 138038. Triisopropylnaphthalene is considered to fulfil the Annex D 1 (c) (i) criteria;
 - (iv) Long-range transport: Estimated half-life in air is 0.096 Days [AopWin v1.92]. Triisopropylnaphthalene is considered not likely to fulfil the Annex D 1 (d) (iii) criteria;
 - (v) Ecotoxicity: No experimental publically data available in the references reviewed. Triisopropylnaphthalene cannot therefore be assessed towards the Annex D 1 (e) criteria due to insufficient data;
 - (vi) Toxicity to human health: No experimental publically data available in the references reviewed. Triisopropylnaphthalene cannot therefore be assessed towards the Annex D 1 (e) criteria due to insufficient data.

J. Sulfosuccinates

403. Several companies produce surfactants based on 50–75% of the sodium salt of di(2-ethylhexyl) sulfosuccinate, which can be used as a wetting agent for aqueous systems of detergents, cleaners, paints and coatings. It is also used in pesticides.

404. In the following, the chemical structure of the sodium salt of di(2-ethylhexyl) sulfosuccinate (CAS No: 577-11-7) is presented:



405. In a product from BASF (Lutensit® A-BO) the sulfosuccinate is mixed with water and ethanol, and in a product from Cognis (Hydropalat® 875) the sulfosuccinate is mixed with water and 2,2-dimethylpropane-1,3-diol.

406. The product from Cognis can be used as a wetting agent in aqueous coating systems and is particularly suitable for difficult-to-wet substrates like plastics, metal, cellulose film, silicone-treated papers and glass. This surfactant may also be used as an emulsifier for emulsion polymerization. Another area where it can be used as an alternative to fluorinated surfactants is in optimizing the colour acceptance of aqueous pigment concentrates in different coatings. The product has medium foam formation.

407. Münzing Chemie also produces a surfactant (Edaplan® LA 451) based on a sulfosuccinate derivative in ethanol and water, which also can be used as a wetting agent for aqueous paints and coatings. The identity of the sulfosuccinate has not been disclosed. The product is claimed to have good wetting properties, no increase in foam and good recoatability. The surface tension is moderate. Application areas are decorative paints, wood and furniture coatings, automotive and repair coatings, industrial coatings, printing inks and overprint varnishes.

1. Health effects of sulfosuccinates

408. Toxicological information is scarce. Sulfosuccinates are irritants to eyes, skin and the respiratory system, especially upon prolonged or repeated contact. Dermatitis has been observed as a

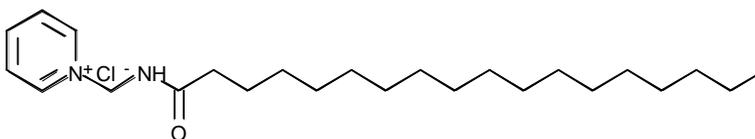
long-term effect, as have central nervous system depression and injury to the heart, the liver and blood-forming organs. The substance di(2-ethylhexyl) sulfosuccinate has low acute toxicity if swallowed (LD_{50} (oral, rat) = 1.9 g/kg).³⁶² Information found in the United States Government's Hazardous Substances Data Bank suggests that di(2-ethylhexyl) sulfosuccinate is mildly toxic (upon ingestion) to humans, with a probable oral lethal dose (in humans) of 0.5–5 g/kg. A possible metabolite is the branched 2-ethylhexanol, which may have reproductive effects.

2. Environmental effects of sulfosuccinates

409. Di(2-ethylhexyl) sulfosuccinate is easily biodegradable and not likely to bioaccumulate; however, a $^{96h}LC_{50}$ value of 10–100 mg/l for *Leuciscus idus* (a small fresh-water cyprinoid fish) shows that the sulfosuccinate is harmful to aquatic organisms.³⁶³ More information is needed in order to make an accurate assessment.³⁶⁴

K. Stearamidomethyl pyridine chloride

410. A classic cationic textile surfactant is 1-(stearamidomethyl) pyridinium chloride, which was previously marketed by ICI as Velan PF:



411. The substance reacted with cellulose at elevated temperatures to form a durable water-repellent finish on cotton. It was later found that the reaction was restricted to the surface of the fibres and that the high cure temperature weakened the fabric. Sodium acetate had to be added to prevent the decomposition of the cellulose by the hydrogen chloride formed. Also, the pyridine liberated during the reaction had an unpleasant odour and the fabric had to be scoured after the cure. The toxicological properties of pyridine ended its use in the 1970s, when government regulation of such substances increased. Pyridine might be evaluated differently now. Further information about its properties is lacking.

1. Health effects of stearamidomethyl pyridine chloride

412. Published data on this chemical are lacking.³⁶⁵

2. Environmental effects of stearamidomethyl pyridine chloride

413. Published data on this chemical are lacking.³⁶⁶

L. Polypropylene glycol ether, amines and sulfates

414. Possible replacements for fluorosurfactants in some applications are anionic surfactants based on aliphatic alcohols. The BASF product Emulphor® FAS 30 is the sodium salt of fatty alcohol polyglycol ether sulfates, which are preferentially used in the emulsion polymerization of acrylate and methacrylate esters, styrene and vinyl esters. These anionic emulsifiers are also combined with non-ionic Emulan® grades in order to achieve desired properties such as a particular particle size or emulsion stability. Because of their “foaming” properties, fatty alcohol polyglycol ether sulfates are also used in cosmetics and fire-fighting foams.

415. A fatty alcohol polyglycol ether sulfate has the following general formula:



in which *R* represents a linear or branched alkyl and/or alkenyl group having, for example, 12 to 16 carbon atoms, *n* represents a number mainly from 2 to 4 and *X* represents a cation selected from the group consisting of sodium, ammonium or substituted ammonium.

³⁶² UNEP/POPS/POPRC.8/INF/17/Rev.1.

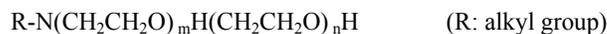
³⁶³ UNEP/POPS/POPRC.8/INF/17/Rev.1.

³⁶⁴ UNEP/POPS/POPRC.10/INF/7/Rev.1.

³⁶⁵ UNEP/POPS/POPRC.10/INF/7/Rev.1.

³⁶⁶ UNEP/POPS/POPRC.10/INF/7/Rev.1.

416. A related non-fluorosurfactant is Enthone[®] (ethoxylated oleyl amine, CAS No: 26635-93-8), used in decorative chrome plating and in many other applications.³⁶⁷ Its general formula is as follows:



1. Health effects of polypropylene glycol ether, amines and sulfates

417. There is a lack of publically available data on this chemical. Emulphor FAS 30 has low acute toxicity by ingestion (oral LD₅₀ > 2 g/kg b.w.) and is not considered to be irritating. Enthone and other polyethylene glycol amines are non-toxic and non-irritating non-ionic emulsifiers.

2. Environmental effects of polypropylene glycol ether, amines and sulfates

418. Emulphor FAS 30 is readily biodegradable (> 70% elimination according to the OECD biodegradation screening test (301E)) and does not seem to be acutely toxic to aquatic organisms, as the reported ^{96h}LC₅₀ value for fish (*Leuciscus idus*) is > 100 mg/L. Enthone is readily degradable, with low toxicity. There is, however, a lack of publically available data on these chemicals.

V. Evaluation and prioritization of alternatives against Annex D criteria

419. The report for the evaluation of information on PFOS, its salts and PFOSF being prepared by the Secretariat for consideration by the Conference of the Parties at its seventh meeting contains the most up-to-date information.³⁶⁸

420. The present chapter is a summary of a report on the assessment of alternatives to PFOS, its salts and PFOSF³⁶⁹ conducted by the Persistent Organic Pollutants Review Committee in accordance with decisions SC-6/4 and POPRC-9/5. The summary was considered by the Conference of the Parties at its seventh meeting.³⁷⁰

421. The assessment of alternatives to PFOS, its salts and PFOSF was undertaken by applying the methodology used by the Committee in the assessment of chemical alternatives to endosulfan.³⁷¹ Accordingly, the Committee assessed chemical alternatives to PFOS, its salts and PFOSF for persistent-organic-pollutant characteristics using experimental data and information from quantitative structure-activity relationship (QSAR) models available at the date of applying the methodology.

422. It is important to note that this classification should not be considered a formal conclusion of the POPRC regarding whether these alternatives meet the Annex D requirements for listing. Therefore, the POPRC would still need to perform a full, rigorous, and open review of any of these chemicals, in accordance with the Convention, should they in the future be nominated by a Party for listing under the Convention.

423. Information on alternatives to PFOS, its salts and PFOSF was provided by parties and observers³⁷² using a format developed by the Committee.³⁷³ In addition, information on the identity of alternatives to PFOS, its salts and PFOSF was compiled from guidance on alternatives to PFOS, its salts and PFOSF and their related chemicals³⁷⁴ and a technical paper on the identification and assessment of alternatives to the use of PFOS, its salts and PFOSF and their related chemicals in open applications.³⁷⁵ Both the guidance and the technical paper were developed on the basis of information about alternatives to PFOS, its salts and PFOSF provided by parties and observers. Additional information was also obtained from recent publications on the topic.³⁷⁶

³⁶⁷ www.enthone.com/pwb/index.aspx.

³⁶⁸ UNEP/POPS/POPRC.10/INF/7/Rev.1.

³⁶⁹ UNEP/POPS/POPRC.10/INF/7/Rev.1.

³⁷⁰ UNEP/POPS/COP.7/8, annex II.

³⁷¹ UNEP/POPS/POPRC.8/INF/28.

³⁷² The information, submitted by 11 parties and 3 others, is available on the website of the Stockholm Convention at: <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/tabid/3565/Default.aspx>.

³⁷³ UNEP/POPS/POPRC.9/INF/10/Rev.1.

³⁷⁴ UNEP/POPS/POPRC.9/INF/11/Rev.1.

³⁷⁵ UNEP/POPS/POPRC.8/INF/17/Rev.1.

³⁷⁶ ENVIRON, Assessment of POP Criteria for Specific Short-Chain Perfluorinated Alkyl Substances, project number: 0134304A, (2014). <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/PFOSSubmission/tabid/3565/Default.aspx>; OECD/UNEP Global PFC Group, "Synthesis paper on per- and polyfluorinated chemicals (PFCs)", (2013),

424. A full report on the results of the assessment may be found in document UNEP/POPS/POPRC.10/INF/7/Rev.1. In addition, fact sheets on nine chemical alternatives to PFOS, its salts and PFOSF that were subjected to detailed assessment are set out in document UNEP/POPS/POPRC.10/INF/8/Rev.1.

A. Assessment of chemical alternatives to PFOS, its salts and PFOSF

425. The methodology used for the assessment consists of a two-step screening process, as mandated³⁷⁷. In the first step, to prioritize the alternatives to PFOS for assessment, alternatives were screened to identify those that had the potential to be persistent organic pollutants and those that were unlikely to be persistent organic pollutants. The second step consisted of a more detailed assessment of the persistent-organic-pollutant characteristics of the alternatives that had been identified as having the potential to be persistent organic pollutants. In the second assessment step, alternatives to PFOS, its salts and PFOSF were classified according to their likelihood to meet all the criteria of Annex D to the Stockholm Convention.

426. A total of 54 chemical alternatives to PFOS, its salts and PFOSF were identified for assessment. The alternatives are used in a wide range of applications that are listed as specific exemptions and acceptable purposes in part I of Annex B to the Convention and most of them are industrial chemicals. Given the range of applications, the alternatives have diverse functions and can have different properties. The alternatives include both fluorinated and non-fluorinated substances. The majority of the alternatives are commercially available. A list of the alternatives is set out in appendix 1 to the full report.

427. In prioritizing chemicals for assessment, the criteria of bioaccumulation (B) and persistence (P) (criteria (c) and (b) of Annex D to the Convention) were used. Experimental data and information from QSAR models were collated for each substance to assess their persistent-organic-pollutant characteristics, which are set out in appendices 2 and 3 to the full report. The chemicals were grouped into four screening categories based on the cut-off values for persistent-organic-pollutant characteristics listed below.

Screening category I: potential persistent organic pollutants

Cut-offs: bioaccumulation: experimental bioconcentration factor (BCF) > 5000 and/or experimental log Kow > 5 and/or biomagnification factor or trophic magnification factor (BMF/TMF) > 1 (for fluorinated substances). Persistence: half-life (experimental) in water greater than two months (60 days), in soil greater than six months (180 days) or sediment greater than six months (180 days). The substances identified in this screening category fulfilled both bioaccumulation and persistence criteria.

Screening category II: candidates for further assessment

Cut-offs: bioaccumulation: experimental BCF > 1000 and/or experimental log Kow > 4 and/or BMF/TMF > 0.5 (for fluorinated substances). Persistence: A PB-score > 1 (P-score > 0.5) and/or half life (experimental and/or estimated) in water greater than two months (60 days), in soil greater than six months (180 days) or in sediment greater than six months (180 days).

Screening category III: candidates for further assessment with limited data

Cut-offs: bioaccumulation: no experimental data for BCF and log Kow and for BMF/TMF (for fluorinated substances).

Screening category IV: not likely to fulfil the criteria on persistence and bioaccumulation in Annex D

Cut-offs: bioaccumulation: experimental BCF < 1000 and/or experimental log Kow < 4.0 (for non-fluorinated substances) and BMF/TMF values ≤ 0.5 (for fluorinated substances) and/or persistence: half life (experimental) in water less than two months (60 days), in soil less than six months (180 days) and in sediment less than six months (180 days).

428. Depending on the screening category in which they had been placed in the prioritization step, the alternatives to PFOS, its salts and PFOSF were further assessed and assigned to one of the four

http://www.oecd.org/env/ehs/risk-management/PFC_FINAL-Web.pdf; Nordic Council of Ministers, *Per- and Polyfluorinated Substances in the Nordic Countries: Use, Occurrence and Toxicology*, TemaNord 2013:542, ISBN: 978-92-893-2562-2, (2013), <http://dx.doi.org/10.6027/TN2013-542>.

³⁷⁷ Decision POPRC-9/5

classes based on their likelihood to meet all the criteria in Annex D to the Convention. The four classes are the following:

Class 1: Substances that the committee considered met all Annex D criteria;

Class 2: Substances that the committee considered might meet all Annex D criteria but remained undetermined due to equivocal or insufficient data;

Class 3: Substances that are difficult to classify because of insufficient data;

Class 4: Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e).

429. The following criteria were used for further assessing the substances classified according to the screening categories described above:

(a) **Categories I and II:** an assessment of persistent-organic-pollutant characteristics and other hazard indicators (toxicity and ecotoxicity) was performed. For each substance, a detailed fact sheet was compiled on the properties selected for assessment;

(b) **Category III:** a more exhaustive search for experimental data on bioaccumulation was performed. If such data were obtained, an evaluation was made of whether the substance met the Annex D (c) (i) criterion or if it biomagnified (TMF/BMF>1). If those criteria were met and the substance was considered likely to be bioaccumulative, the procedure set out in subparagraph (a) above was followed. If no data were obtained, no fact sheet was compiled and the substance was assigned to class 3;

(c) **Category IV:** no further action was taken and the substances were assigned to class 4.

430. Detailed fact sheets were compiled for nine chemicals, as set out in document UNEP/POPS/POPRC.10/INF/8/Rev.1. The results of the analysis based on the fact sheets are summarized in appendix 4 to the full report (UNEP/POPS/POPRC.10/INF/7/Rev.1).

431. The conclusions of the assessment of the 54 alternatives to PFOS, its salts and PFOSF are as follows:

Class 1: Substances that the committee considered met all Annex D criteria

Non-fluorinated alternatives (one substance)	
CAS No:	Substance
556-67-2	Octamethyl cyclotetrasiloxane (D4)*

Class 2: Substances that the committee considered might meet all Annex D criteria but remain undetermined due to equivocal or insufficient data

Pesticides (one substance)	
CAS No:	Substance
2921-88-2	Chlorpyrifos

Class 3: Substances that are difficult to classify because of insufficient data

Fluorinated alternatives (20 substances)	
CAS No:	Substance
29420-49-3	Perfluorobutane sulfonate potassium salt
3871-99-6	Perfluorohexanesulfonate potassium salt*
647-42-7	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanol*
27619-97-2	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulfonate
355-86-2	Tris(octafluoropentyl) phosphate
563-09-7	Tris(heptafluorobutyl) phosphate
40143-77-9	Sodium bis(perfluorohexyl) phosphinate
34455-29-3	Carboxymethyldimethyl-3-[[3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]propylammonium hydroxide
358-63-4	Tris(trifluoroethyl) phosphate
163702-07-6	Methyl nonafluorobutyl ether

163702-08-7	Methyl nonafluoro-isobutyl ether
59587-38-1	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate potassium salt
2043-47-2	1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -Perfluorohexanol or 3,3,4,4,5,5,6,6,6-nonafluorobutyl ethanol*
	2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate
	1,1,2,2,-tetrafluoro-2-(perfluorohexyloxy)-ethane sulfonate
	Perfluorohexane ethyl sulfonyl betaine
756-13-8	Dodecafluoro-2-methylpentan-3-one
40143-76-8	Perfluorohexyl phosphonic acid
	1-chloro-perfluorohexyl phosphonic acid
2144-53-8	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester*
Non-fluorinated alternatives (four substances)	
541-02-6	Decamethyl cyclopentasiloxane (D5)*
577-11-7	Di-2-ethylhexyl sulfosuccinate, sodium salt
4261-72-7	Stearamidomethyl pyridine chloride
67674-67-3	(Hydroxyl) Terminated polydimethylsiloxane
Commercial brands (11 brands)	
	Polyfox®
	Emulphor® FAS
	Enthone®
	Zonyl®
	Capstone®
	Nuva®
	Unidyne®
	Rucoguard®
	Oleophobol®
	Asahiguard®
	Solvera®

Class 4: Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e)

Non-fluorinated alternatives (nine substances)	
CAS No:	Substance
540-97-6	Dodecamethyl cyclohexasiloxane (D6)*
107-46-0	Hexamethyl disiloxane (MM or HMDS)*
107-51-7	Octamethyl trisiloxane (MDM)*
141-62-8	Decamethyl tetrasiloxane (MD2M)*
141-63-9	Dodecamethyl pentasiloxane (MD3M)*
25640-78-2	1-Isopropyl-2-phenyl-benzene
38640-62-9	Diisopropyl-naftalene (DIPN)
35860-37-8	Triisopropyl-naftalene /TIPN)
69009-90-1	Diisopropyl-1,1'-biphenyl
Pesticides (eight substances)	
CAS No:	Substance

52315-07-8	Cypermethrin
52918-63-5	Deltamethrin
95737-68-1	Pyriproxyfen
138261-41-3, 105827-78-9	Imidacloprid
120068-37-3	Fipronil
122-14-5	Fenitrothion
71751-41-2	Abamectine
67485-29-4	Hydramethylnon

*Manufacturing intermediate for alternatives to PFOS.

432. A total of 17 substances were considered unlikely to be persistent organic pollutants. These 17 substances have been reported as alternatives to PFOS, its salts and PFOSE for the following applications: carpets; leather and apparel; textiles and upholstery; coating and coating additives; insecticides for the control of red imported fire ants and termites; and insect bait for the control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. Additional information may be found in document UNEP/POPS/POPRC.10/INF/10.

433. It is important to note that the assessment of the persistent-organic-pollutant characteristics and other hazard indicators of each alternative should not be seen as a comprehensive and detailed assessment of all available information, since only a selected number of databases have been consulted. The fact sheets on which the more detailed assessment of selected alternatives is based provide an analysis on a screening level as to whether or not the assessed substances meet the numerical thresholds in Annex D to the Stockholm Convention, but contain no analysis of monitoring data or other evidence as provided for in Annex D. Accordingly, the failure of a given substance to meet the thresholds should not be taken as evidence that the substance is not a persistent organic pollutant. In addition, substances that, according to the present report, are not likely to meet the criteria on persistence and bioaccumulation in Annex D may still exhibit hazardous characteristics that should be assessed by parties and observers before considering such substances to be suitable alternatives to PFOS, its salts and PFOSE. Conversely, substances that have here been found likely to be persistent organic pollutants may, upon more detailed review, be found to not meet Annex D criteria.

B. Information gaps

434. The methodology used for the assessment of alternatives to endosulfan,³⁷⁸ which was adapted for the current assessment, was developed for a group of chemicals that are all pesticides. Because pesticides are subject to a process of registration and risk assessment in many countries, reliable information about their properties is readily available in a number of public databases. By contrast, the alternatives to PFOS, its salts and PFOSE are mostly industrial chemicals about which much less information is made publicly available. In many cases, relevant information is classified as confidential business information. The low availability of data presented one of the main difficulties in undertaking the assessment of alternatives to PFOS, its salts and PFOSE, as evidenced by the large number of chemicals that the Committee could not assess because of a lack of data.

435. The scarcity of publically available experimental data about alternatives to PFOS, its salts and PFOSE also made it necessary to rely more heavily on modelled data for their assessment than was the case with regard to alternatives to endosulfan. Existing modelling tools provide estimates of bioaccumulation based on log Kow values. Although modelling tools have shown in recent years some improvement in accurately predicting the properties of fluorinated substances, the further development of tools more suited for estimating bioaccumulation and biomagnification values for this group of chemicals should facilitate their assessment.

436. The identification of alternatives to PFOS, its salts and PFOSE in the report is based largely on information provided by parties and observers. Alternatives to PFOS, its salts and PFOSE that are considered not likely to meet all Annex D criteria were identified for several of the applications listed as specific exemptions and acceptable purposes in part I of Annex B to the Convention. Alternatives to PFOS, its salts and PFOSE were not reported for some applications.

437. In assessing each potential alternative to persistent organic pollutants, it should be confirmed that the alternative does not lead to the use of other chemicals that have the properties of persistent organic pollutants as defined by the criteria in Annex D to the Convention. (). In addition, a chemical

³⁷⁸ Decision POPRC-8/6: Assessment of alternatives to endosulfan.

alternative should not have hazardous properties that raise serious concern, such as mutagenicity, carcinogenicity, or adverse effects on the reproductive, developmental, endocrine, immune or nervous systems. Non-chemical alternatives should also be considered and may include alternative industrial processes and innovative practices.³⁷⁹ Alternatives also need to be technically and economically feasible. The majority of alternatives identified in the report are commercially available, which is an important indicator of technical feasibility (UNEP/POPS/POPRC.5/10/Add.1). The technical and economic feasibility of an alternative are heavily influenced by the specific requirements of the user (a company, an industry or sector) of the alternative and the conditions prevailing in the country where the user operates. In addition, determining the technical feasibility of an alternative requires detailed information about the performance of the alternative for a specific use and the expertise to assess that information. The information provided by parties and others on the technical feasibility, cost-effectiveness, efficacy, availability and accessibility of chemical and non-chemical alternatives to PFOS, its salts and PFOSF did not include enough publically available data to enable a comprehensive assessment of the availability, suitability and implementation of such alternatives. While more information on the identity of potential alternatives to PFOS, its salts and PFOSF and their properties may be available in open sources, obtaining such information was beyond the scope of the assessment and the resources and time available.

438. As pointed out in the guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals (UNEP/POPS/POPRC.5/10/Add.1), in identifying and evaluating alternatives to persistent organic pollutants, it is important to describe the specific use and functionality of the persistent organic pollutants in as precise a manner as possible. In the case of PFOS, its salts and PFOSF, the various specific exemptions and acceptable purposes listed in Annex B to the Convention describe broad use categories (for example, fire fighting foams), articles (for example, electric and electronic parts for some colour printers and colour copy machines) and processes (for example, chemically driven oil production) for which PFOS, its salts and PFOSF can have a variety of uses. The lack of information about the precise use and function of PFOS, its salts and PFOSF in these applications makes it difficult to identify corresponding alternatives with a high degree of certainty.

439. Obtaining precise and detailed information about alternatives to the use of PFOS, its salts and PFOSF and their properties is necessary for the assessment of those alternatives by the Committee. It is recommended that the format for collecting information from parties and others be revised to facilitate the provision of such information by, for example, specifying the functionality of PFOS, its salts and PFOSF under the use categories listed as specific exemptions and acceptable purposes. Parties and others should also be encouraged to provide additional information to support the assessment of alternatives to PFOS, its salts and PFOSF.

440. It was acknowledged that degradation products may be relevant in a future screening. However, considering the complexity related to the degradation products, these were set aside for the moment.

VI. Comparative assessment of PFOS and possible alternatives

441. Comparative assessment of PFOS and its possible alternatives with regard to technical, socioeconomic, environmental, health and safety considerations is a very complex task requiring much more data and other information than are normally publically available. Often much more information is available about PFOS than about possible alternatives, which may be newly developed substances covered by patents and for which manufacturers have not provided information. For this reason rigid selection criteria are not useful; information on the alternatives will be scarcer, and it will be of lower scientific quality because much of it will be non-peer-reviewed.

442. In addition, if sufficient information is available then one may have to subjectively weigh short-term economic considerations and practical feasibility against long-term economic and safety considerations that include hazards when handling the chemicals for intended use. None of the alternatives will be perfect and without hazards, but at least they should be less hazardous and less persistent than PFOS. For example, fluorinated alternatives with fluorinated alkyl chains shorter than C₈ may be less toxic and bioaccumulative but still persistent indefinitely in the environment.

443. It might be that the short chain fluorinated alternatives are not sufficiently safe. This is illustrated by the similar half-life of perfluorohexane sulfonate compared to PFOS in human blood. In addition, there is a growing body of observations of toxic effects in humans and animal studies and

³⁷⁹ UNEP/POPS/POPRC.5/10/Add.1.

PFHxS is found in seawater, animals, and humans in the Arctic. Furthermore, chemicals with fluorinated chains longer than C₈ seem to be more toxic and bioaccumulative than PFOS.

444. Further, in evaluating the technical properties, fitness for use and durability of the alternatives for each separate application, it is necessary to evaluate socio-economic considerations, including long-term costs due to environmental and health effects; differences between sectors, enterprises (including size), countries and regions; product importance; economic constraints; and social costs. The availability of alternatives seems to be the same worldwide, because the providers are mainly large international companies.

445. Economically useful publically available data is scarce. In general, very little information about the prices of alternatives was found in the Danish survey³⁸⁰ even though the producers of alternative products were asked specifically about such information. The information received, however, suggests that the alternatives are in general priced comparably to the PFOS-related compounds. One company mentioned that the price of alternatives was intentionally kept at the same level as that of PFOS-related compounds. While it was impossible to obtain exact prices, in the coatings and paints area the non-fluorinated alternatives were found to be cheaper.

446. An comprehensive economic assessment of the non-PFOS alternatives depends on:

- (a) The price of the chemicals and or physical alternatives;
- (b) The amount needed during use;
- (c) The expenses during substitution;
- (d) Expenses to possible continuous addition of chemicals;
- (e) Expenses related to possible break down of a continuous addition system, due to problems related to non-sufficient or excess additions of chemicals.

447. Since most of the data mentioned above is not publically available or difficult to get, the actual cost of each individual case is a big challenge, but needs to be done to carry out comprehensive and fair comparison of different real cases. More recent information indicates that some alternatives may be priced comparably to one other but be more expensive than PFOS derivatives.

448. Especially at the beginning, alternatives might be more expensive to purchase or use; however, this possible short-term cost increase is balanced by eliminating a very hazardous and persistent chemical. The prices of substitutes will decrease in the long run with a growing market and increasing competition.

VII. Conclusions, recommendations and future developments

A. Low surface tension is a key function

449. In addition to stability, a key factor in the performance of fluorosurfactants is their extremely low surface tension, which currently cannot be matched with other non-fluorinated surfactants in currently designed processes. Owing to environmental and health concerns, however, surfactants without fluorine content could be used as alternatives if such low surface tension levels are not needed. Given the relatively high prices of fluorosurfactants, switching can in some cases also have economic benefits.

B. Substitutes for PFOS are available

450. Fluorinated or non-fluorinated alternatives exist for nearly all current uses of PFOS.³⁸¹ While the alternatives may be initially slightly more expensive and less effective, they may be less hazardous, but that has to be assessed accordingly. Common PFOS alternatives in use are both non-fluorinated and fluorinated, depending on use and application. Concerning the fluorinated alternatives to PFOS, C₈-fluorotelomers were a frequent choice but they have been shown, however, to degrade into PFOA, which also has hazardous properties.³⁸² Producers of fluorochemicals in the EU, Japan, and US have agreed with the United States Environmental Protection Agency to commit to working

³⁸⁰ Poulsen PB, Jensen AA, Wallström E. 2005. More environmentally friendly alternatives to PFOS-compounds and PFOA. Environmental Project 1013. Danish Environmental Protection Agency. www.mst.dk/Udgivelser/Publications/2005/06/87-7614-668-5.htm.

³⁸¹ UNEP/POPS/COP.7/INF/21.

³⁸² PFOA meets the Annex D screening criteria, and is currently under evaluation by the POPRC as a candidate for listing in the Stockholm Convention.

toward the elimination of PFOA, chemicals that breakdown to PFOA, and related higher homologues by the end of 2015.³⁸³ The voluntary agreement does not apply to producers who did not sign up for the Stewardship Program. As a result, there has been a shift by these Stewardship program producers to short-chain alternatives such as C₆-, C₄- and C₃-perfluoroalkylated chemicals.

C. Need for better alternatives

451. There is a need for better alternatives to PFOS in line with the “General guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals” UNEP/POPS/POPRC.5/10/Add.1.

452. For some uses non-fluorinated chemicals have been introduced as alternatives such as silicones, aliphatic alcohols and sulfosuccinates. It might also be that a particular use or product is no longer essential, or that a process could be changed to eliminate the need for PFOS, as has happened in the photographic industry and in decorative metal plating.

D. Need for improved information from industry on the alternatives and actions parties can take to deploy alternatives safely

453. There are still considerable gaps in publically available information concerning the specific and particularly exact chemical composition of alternatives to PFOS though some of these alternatives have been established on the market for several years. One major reason is that this information is considered as confidential by manufacturers (CBI). There is a need however to release this information and to properly evaluate health and environmental impact from these alternatives.

454. There is still little or no publicly available independent and reliable information on the toxicological and ecotoxicological characteristics of several fluorinated, especially short chain chemicals, and non fluorinated alternatives to PFOS. Additionally there is essential data not publically available for most alternatives to PFOS concerning quantities produced and uses on the market, mostly due to market trade secrets.

455. Since either little or no information is publically available concerning how these alternatives are actually used and their path ways and environmental fate, it is currently not possible to perform comprehensive risk assessment studies of these alternative substances.

456. It is therefore strongly recommended to improve transparency of chemicals manufacturers on health, environmental and safety information, noting as stated in Article 9 of the Convention, that health and safety information shall not be regarded confidential. In addition, manufacturers should construct improved inventories on how these alternatives actually are used, quantities on the market and additionally encourage further independent scientific toxicological and ecotoxicological studies to get more health and environmental data together with monitoring data in order to improve our knowledge how to implement these alternatives to PFOS in a commercial scale wherever possible.

E. Need for incentives

457. There is a need for incentives to develop safe, affordable and technologically feasible alternative substances and processes and to identify the driving forces for their development. The international requirements applying to all parties to the Stockholm Convention, which must be implemented in national law, constitute one such incentive. Article 3 of the Stockholm Convention states that Parties with regulatory and assessment schemes for new chemical substances shall take measures to regulate with the aim of preventing the production and use of substances that exhibit characteristics of POPs.

F. Labeling and information considerations

458. The Conference of the Parties to the Stockholm Convention encourages parties that have registered or will register for the production and use of PFOS, its salts and PFOSF for acceptable purposes by notifying the Secretariat in accordance with Annex B to the Convention to take measures necessary to ensure that articles containing PFOS, its salts and PFOSF that are allowed to be produced and used can be easily identified by labelling or other means throughout their life cycles.³⁸⁴

459. The objective for a consistent labelling system is how to select and implement transboundary labelling systems for products and articles that contain POPs by enhancing understanding and

³⁸³ <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/and-polyfluoroalkyl-substances-pfass-under-tsca#tab-3>.

³⁸⁴ Decision SC-7/5.

harmonisation of the essential elements of different schemes and their value in facilitating management of POPs.

460. Comprehensive and consistent labelling of POPs in articles and chemicals products may stimulate the promotion of POPs-free products that provides powerful incentives for sales of such products. These incentives may be both voluntary and enforced by law to be fully implemented over time on the global market.

461. Many countries have regulatory systems in place designed to protect human health and the environment from exposure to hazardous chemicals. These systems, however, are known to vary in content and approach across countries and regulatory authorities within a country (e.g. ministries of environment, labour, industry, agriculture, and consumer goods). Such differences may result in inconsistent application of guidelines, legislation, or voluntary approaches to labelling that offer variable protection for human health and the environment.

462. A number of useful documents that address how to improve the information on chemicals in products and articles in the life cycle have been developed within the Chemicals in Products (CiP) project led by the United Nations Environment Programme (UNEP). The CiP is part of the work of the Strategic Approach to International Chemicals Management (SAICM). The Chemicals in Products Programme was finalized in 2015 and the accompanying Programme Guidance can be found on UNEPs web page.³⁸⁵

463. The GHS, the best-known systematic labelling approach for chemicals, including POPs, is being implemented more and more throughout the world. Although it is a voluntary system, many governments have integrated its principles into national legislation, at least for industrial chemicals and, in some countries, for pesticides. Application of the basic concepts of the GHS within the EU Member State regulations is legally binding. A number of useful approaches for labelling of specific POPs in articles based on specific compositions have been advanced.³⁸⁶

464. The labelling requirements for PCBs are stipulated in Annex A, Part II of the Convention, which provides a management plan and inventory designed to keep track of appliances (equipment) containing PCBs so that important information is not lost. Parties to the Convention are required to identify and remove from use equipment containing PCBs, as well as to attach labels indicating the presence of PCBs in appliances. The label states its % in accordance with three stated concentrations, volumes and in accordance with priorities established in the Convention. This requirement is in place only for PCBs. Parties could consider addressing other articles that contain a POP, e.g. PFOS by establishing requirements or setting references.

465. The labelling system must be practical, effective, enforceable, and easy to implement, and independently consider the socio-economic impact on companies. Monitoring and enforcement could be facilitated by monitoring a company's self-inspection scheme, through a liability scheme in cases of fatalities, or through the use of financial incentives. High-level political will is a prerequisite for implementation of a POPs labelling system. The implementation could target "low hanging fruits" first and identify short-, medium- (5 years), and long-term (10 years) goals.

466. The best approach may be to gain experience by first selecting one labelling system option and implementing it on a provisional basis. If this proves successful, legislation and the administrative system could then be adapted, as appropriate. Harmonizing the labelling systems for POPs at the international level, using the Conference of the Parties of the Stockholm Convention as a platform, could be considered.

G. Complex assessment

467. Fluoro chemistry is diverse and complex. There may therefore be a need for a mechanism for continuously updating information regarding the alternatives' substitution properties and hazards. Such a mechanism should be consistent with Article 9, subparagraph 1 (b), of the Convention which states that each Party shall facilitate or undertake the exchange of information relevant to alternatives to persistent organic pollutants, including information relating to their risks as well as to their economic and social cost.

³⁸⁵ <http://www.unep.org/hazardoussubstances/UNEPsWork/ChemicalsInProductsproject/tabid/56141/Default.aspx>.

³⁸⁶ Labelling of products or articles that contain POPs – Initial considerations (Draft 2012), <http://chm.pops.int/Implementation/NIPs/Guidance/Labellingofproductsorarticles/tabid/3174/Default.aspx>.

468. Assessment of the economic implications of switching to alternatives to PFOS rests on cost effectiveness considerations. The cost effectiveness of different measures is expressed by the ratio of manufacturing cost to the reduced load of hazardous substances though this can be harder to estimate. As there are large uncertainties, different scenarios – a worst case scenario (low load reduction effectiveness – high costs) and best case scenario (high load reduction effectiveness – low costs) - are used for the calculation of cost effectiveness of various options. The quantitative assessment is complemented by a comprehensive qualitative evaluation to include sustainability aspects, which is mainly based on experts' estimates rather than on empirical data. Inclusion of life cycle considerations in the assessment may also be useful.³⁸⁷ A major cost effectiveness study, funded by the European Commission, has been published for PFOS and PFOA.³⁸⁸ There is no publicly available cost effectiveness study for other PFCs. Often available useful economic data may also be scarce and biased. The sparse information received to date, however, suggests that the alternatives are in general priced comparably to the PFOS-related compounds. Specifically in the coatings and paints area, the non-fluorinated alternatives are cheaper.

H. Need for more public data and information on alternatives

469. Much fewer data are currently available publicly on the alternatives than on PFOS. Much of the information is from patent literature, and the identities of actual chemicals used are often not disclosed. This reinforces the need for implementation of paragraph 1 of Article 9 on the information exchange regarding alternatives to persistent organic pollutants.

470. Chemicals with structures similar to those of the listed PFOS substances could cause concerns similar to those related to the latter substances. This should be considered in evaluating alternatives. Increasing effort will be needed to study the toxicological and environmental properties of alternatives and to make the resulting information public and trustworthy by publishing it in peer reviewed scientific journals.

471. A strategic integrated approach to testing is needed to speed development of the data required to understand the issues and concerns relating to the various types of alternatives. The private sector has a key responsibility in this regard.

I. Need for better communication in the value chain

472. It is important that the issues associated with PFOS as a globally recognized persistent organic pollutant, including the health and environmental risks, be made fully known to suppliers and industries. Producers need to have better knowledge about the use of PFOS in processes, products and articles. It is also important to provide relevant information to customers and consumers so that they can develop substantiated opinions about the possible need to change products or processes. Industries that are proactive in phasing out the use of a very hazardous chemical such as PFOS are likely to reap future market advantages.

J. Need for more international cooperation

473. PFOS and its substitutes are being studied and evaluated in parallel by authorities in many countries. More international cooperation and private sector transparency can save resources and speed up processes. The OECD Parallel Process for the Notification of New Chemicals is one useful approach (for new chemicals) to consider in developing international collaboration on assessing potential alternatives to PFOS and other polyfluorinated chemicals of concern.

³⁸⁷ <http://www.unep.fr/shared/publications/pdf/DTIx1208xPA-LifeCycleApproach-Howbusinessusesit.pdf>.

³⁸⁸ Cohiba, control of hazardous substances in the Baltic sea region, guidance document 4, http://www.google.se/url?sa=t&rct=j&q=&esrc=s&frm=1&source=web&cd=1&ved=0CDEQFjAA&url=http%3A%2F%2Fwww.cohiba-project.net%2Fpublications%2Fen_GB%2Fpublications%2F_files%2F87107446768797277%2Fdefault%2FPFOA-PFOS.pdf&ei=MCInUdXqEuXd4QTyxYCoAw&usq=AFQjCNGF4ZVXK2Wy6mtcS0Cv31SOefClww&sig2=kXgiPktG2DJswuQF-BYyTw&bvm=bv.42768644,d.bGE.

Appendix 1: Register of specific exemptions and acceptable purposes for PFOS, its salts and PFOSE

A. Specific exemptions for PFOS, its salts and PFOSE as of May 2016

<http://chm.pops.int/Implementation/Exemptionsandacceptablepurposes/RegisterofSpecificExemptions/ChemicalslistedinAnnexB/tabid/4644/Default.aspx>

Activity	Specific exemption	Party	Expiry date	Estimated quantity of production / use	Reason for exemption	Remarks
Production	1. Photo masks in the semiconductor and liquid crystal display (LCD) industries	China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Use	1. Photo masks in the semiconductor and liquid crystal display (LCD) industries	Canada	Not provided	Not provided	Not provided	None
		China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China
		Norway	Expired on 26/08/2015	Not provided	Not provided	Not provided
		Republic of Korea	5 years	Not provided	Research for PFOS, its salts or PFOSE alternative materials is on-going	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Production	2. Metal plating (hard metal plating)	China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China
		European Union	Expired on 26/08/2015	Not provided	Not provided	The EU restriction is not limited to PFOS, its salts and PFOS-F but covers all PFOS derivatives defined as C ₈ F ₁₇ SO ₂ X X = OH, metal salt (O-M ⁺), halide, amide and other derivatives including polymers.
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Use	2. Metal plating (hard metal plating)	Brazil	Two years	Not provided	The product protects the operators of spray chrome in electroplating process	There are some stockpiles to be used
		China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China
		Turkey	Expired on 26/08/2015	Not provided	-	-
		Canada	Expired. Specific exemption for	Not provided	Not provided	Not provided

			use of PFOS in metal plating only required until 2013.				
		Brazil	Withdrawn on 21/08/2015	Not provided	The product protects the operators of spray chrome (highly toxic) in electroplating process. No equivalent product available with the same performance.	Withdrawn notification	
		Czech Republic	Expired on 26/08/2015	Not provided	Not provided	Not provided	
		European Union	Expired on 26/08/2015	Not provided	Not provided	The EU restriction is not limited to PFOS, its salts and PFOS-F but covers all PFOS derivatives defined as C ₈ F ₁₇ SO ₂ X X = OH, metal salt (O-M+), halide, amide and other derivatives including polymers.	
		Iran	Expired on 26/08/2015	Not provided	Country data not yet established	Not provided	
		Switzerland	Expired on 26/08/2015	Not provided	Not provided	Not provided	
		Republic of Korea	5 years	Not provided	Research for PFOS, its salts or PFOF alternative materials is on-going	Not provided	
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory	
Production	3. Metal plating (decorative plating)	China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China	
		European Union	Expired on 26/08/2015	Not provided	Not provided	The EU restriction is not limited to PFOS, its salts and PFOS-F but covers all PFOS derivatives defined as C ₈ F ₁₇ SO ₂ X X = OH, metal salt (O-M+), halide, amide and other derivatives including polymers.	
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory	
Use	3. Metal plating (decorative plating)	Brazil	Two years	Not provided	The product protects the operators of spray chrome in electroplating process	There are some stockpiles to be used	
		China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China	
		Canada	Expired. Specific exemption for use of PFOS in metal plating only required until 2013.	Not provided	Not provided	Not provided	Not provided
		Turkey	Expired on 26/08/2015	Not provided	-	-	

		Brazil	Withdrawn on 21/08/2015	Not provided	The product protects the operators of spray chrome (highly toxic) in electroplating process. No equivalent product available with the same performance.	Withdrawn notification
		Czech Republic	Expired on 26/08/2015	Not provided	Not provided	Not provided
		European Union	Expired on 26/08/2015	Not provided	Not provided	The EU restriction is not limited to PFOS, its salts and PFOS-F but covers all PFOS derivatives defined as C ₈ F ₁₇ SO ₂ X X = OH, metal salt (O-M ⁺), halide, amide and other derivatives including polymers.
		Iran	Expired on 26/08/2015	Not provided	Country data not yet established	Not provided
		Switzerland	Expired on 26/08/2015	Not provided	Not provided	Not provided
		Republic of Korea	5 years	Not provided	Research for PFOS, its salts or PFOF alternative materials is on-going	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Production	4. Electric and electronic parts for some colour printers and colour copy machines	China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Use	4. Electric and electronic parts for some colour printers and colour copy machines	China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China
		Republic of Korea	5 years	Not provided	Research for PFOS, its salts or PFOF alternative materials is on-going	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Production	5. Insecticides for control of red imported fire ants and termites	China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Use	5. Insecticides for control of red imported fire ants and termites	China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China
		Republic of Korea	5 years	Not provided	Research for PFOS, its salts or PFOF alternative materials is on-going	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS

						inventory
Production	6. Chemically driven oil production	China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Use	6. Chemically driven oil production	China	Not provided	Not provided	Currently in use without appropriate alternatives and transition will take some time	Applicable to Hong Kong SAR and Macau SAR of China
		Republic of Korea	5 years	Not provided	Research for PFOS, its salts or PFOF alternative materials is on-going	Not provided
		Nigeria	Expired on 26/08/2015	Not provided	No alternative for now	Not provided
		Iran	Expired on 26/08/2015	Not provided	Country data not yet established	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Production	7. Carpets	Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Use	7. Carpets	Nigeria	Expired on 26/08/2015	Not provided	No alternative for now	Not provided
		Iran	Expired on 26/08/2015	Not provided	Country data not yet established	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Production	8. Leather and apparel	Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Use	8. Leather and apparel	Nigeria	Expired on 26/08/2015	Not provided	No alternative for now	Not provided
		Iran	Expired on 26/08/2015	Not provided	Country data not yet established	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Production	9. Textiles and upholstery	Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Use	9. Textiles and upholstery	Nigeria	Expired on 26/08/2015	Not provided	No alternative for now	Not provided
		Iran	Expired on 26/08/2015	Not provided	Country data not yet established	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Production	10. Paper and packaging	Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Use	10. Paper and packaging	Nigeria	Expired on 26/08/2015	Not provided	No alternative for now	Not provided
		Iran	Expired on 26/08/2015	Not provided	Country data not yet established	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Production	11. Coatings and coating	Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS

	additives					inventory
Use	11. Coatings and coating additives	Nigeria	Expired on 26/08/2015	Not provided	No alternative for now	Not provided
		Iran	Expired on 26/08/2015	Not provided	Country data not yet established	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Production	12. Rubber and plastics	Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory
Use	12. Rubber and plastics	Nigeria	Expired on 26/08/2015	Not provided	No alternative for now	Not provided
		Iran	Expired on 26/08/2015	Not provided	Country data not yet established	Not provided
		Viet Nam	Expired on 26/08/2015	Not provided	Still in use	Vietnam is in the process of PFOS inventory

B. Acceptable purposes for PFOS, its salts and PFOSF available as of May 2016

<http://chm.pops.int/Implementation/Exemptionsandacceptablepurposes/RegistersofAcceptablePurposes/AcceptablePurposesPFOSandPFOSF/tabid/794/Default.aspx>

Party	Production notifications		Use		Acceptable purpose activities	Chemical name of the precursor (if relevant)	Date of notification	Remarks
	(x=received)		notifications					
			(x=received)					
	Ongoing	Planned	Ongoing	Planned				
Brazil	X		X		<ul style="list-style-type: none"> Insect baits for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp. 	Perfluorooctane sulphonyl fluoride (PFOS-F) (*)	18/11/2010	(*) Intermediate in the production of sulfluramid, for the production of insect baits for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp.
Cambodia			X		<ul style="list-style-type: none"> Fire-fighting foam 	No specific chemicals identified in the NIP update.	20/01/2016	The needs for continued use of stockpiles of PFOS containing fire fighting foam was determined by our NIP update submitted to the Secretariat.
Canada			X	10/12/2010	<ul style="list-style-type: none"> Photo-imaging Photo-resist and anti-reflective coatings for semi-conductors Etching agent for compound semi-conductors and ceramic filters Aviation hydraulic fluids Metal plating (hard metal plating) only in closed-loop systems Fire-fighting foam 		21/12/2010	
China, People's Republic of	X		X		<ul style="list-style-type: none"> Photo-imaging Photo-resist and anti-reflective coatings for semi-conductors Etching agent for compound semi-conductors and ceramic filters Aviation hydraulic fluids Metal plating (hard metal plating) only in closed-loop systems 		18/03/2014	Applicable to Hong Kong SAR and Macau SAR of China

					<ul style="list-style-type: none"> • Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio-opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters) • Fire-fighting foam 			
Czech Republic			x		<ul style="list-style-type: none"> • Photo-imaging; • Photo-resist and anti-reflective coatings for semi-conductors; • Aviation hydraulic fluids; • Metal plating (hard metal plating) only in closed-loop systems 		11/08/2010	
European Union	x		x		<ul style="list-style-type: none"> • Photo-imaging; • Photo-resist and anti-reflective coatings for semi-conductors; • Etching agent for compound semi-conductors and ceramic filters; • Aviation hydraulic fluids; • Metal plating (hard metal plating) only in closed-loop systems. 		31/03/2011	<p>The EU restriction is not limited to PFOS, its salts and PFOS-F but covers all PFOS derivatives defined as C₈F₁₇SO₂X, X= OH, metal salt (O-M⁺), halide, amide, and other derivatives including polymers.</p> <p>Please note that the fire-fighting foams that were placed on the EU market before 27 December 2006 may be used until 27 June 2011.</p>
Japan	x		x		<ul style="list-style-type: none"> • Photo-imaging; • Photo-resistant and anti-reflective coatings for semi-conductors; • Etching agent for compound semi-conductors and 	Perfluotooctane-1-sulfonyl fluoride (PFOS-F, CAS No: 307-.35-7)	02/09/2010	

					ceramic filters; • Certain medical devices			
Norway			x		• Photo-imaging; • Photo-resist and anti-reflective coatings for semi-conductors; • Etching agent for compound semi-conductors and ceramic filters; • Aviation hydraulic fluids; • Metal plating (hard metal plating) only in closed-loop systems.		28/10/2010	
Switzerland			x		• Photo-imaging; • Photo-resist and anti-reflective coatings for semi-conductors; • Etching agent for compound semi-conductors and ceramic filters; • Aviation hydraulic fluids; • Metal plating (hard metal plating) only in closed-loop systems; • Fire-fighting foam.		15/03/2011	Although PFOS-based aqueous film forming foams (AFFF) can no longer be manufactured, or purchased in Switzerland, remaining stocks are allowed to be used in cases of an emergency by fire brigades until 2014 and in stationary installations until 2018.
Vietnam	x		x		• Photo-imaging; • Photo-resist and anti-reflective coatings for semi-conductors; • Etching agent for compound semi-conductors and ceramic filters; • Aviation hydraulic fluids; • Metal plating (hard metal plating) only in closed-loop systems; • Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE))	• Perfluorooctane sulfonic acid (CAS No: 1763-23-1); • Potassium perfluorooctane sulfonate (CAS No: 2795-39-3); • Lithium perfluorooctane sulfonate (CAS No: 29457-72-5); • Ammonium perfluorooctane sulfonate (CAS No: 29081-56-9); • Diethanol-ammonium perfluorooctane sulfonate (CAS No: 70225-14-8); • Tetraethyl-ammonium perfluorooctane sulfonate (CAS No: 56773-42-3);	16/04/2013	Vietnam is in the process of PFOS inventory and will update information when available.

					layers and radio-opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters);		
					• Fire-fighting foam;	• Didecyldimethylammonium perfluorooctane sulfonate (CAS No: 251099-16-8)	
					• Insect baits for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp.	• Perfluorooctane sulfonyl fluoride (CAS No: 307-35-7).	
Zambia			x	30/05/2014	• Aviation hydraulic fluids; • Fire-fighting foam.		Zambia is currently conducting PFOS inventory. Information will be provided the inventory is completed.

Appendix 2: Alternatives to PFOS, their occurrence and applications

A. List of alternatives to PFOS, its salts and PFOSEF by applications

Applications	Open application	Use status	Priority action 1. Highest action priority? 2. Possible to replace PFOS technically?	Identified alternatives	CAS No:	Source of information	Class (assessment result) ³⁸⁹
Acceptable purposes							
Photo-imaging	No	A shift to digital techniques has reduced the use drastically.	1. No 2. Yes	Telomer-based products of various perfluoroalkyl chain length C3- and C4-perfluorinated compounds.	N/A	UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
				Hydrocarbon surfactants	N/A	UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
				Silicon products	N/A	UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
				Non chemical: Digital techniques	N/A	UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Photoresist and anti-reflective coatings for semiconductors	No	PFOS is still used but in lower concentrations.	1. No 2. Not possible to answer without detailed chemicals information about the alternatives	Fluorinated compounds are in use.	N/A	UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Etching agent for compound semiconductors and ceramic filters	No	PFOS is still used but in lower concentrations.	1. No 2. Not possible to answer without detailed chemicals information about the alternatives	Short-chain perfluoroalkyl sulfonates	N/A	UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A

³⁸⁹ UNEP/POPS/POPRC.10/INF/7/Rev.1.

Applications	Open application	Use status	Priority action	Identified alternatives	CAS No:	Source of information	Class (assessment result) ³⁸⁹
Aviation hydraulic fluids	Yes	PFOS-related compounds may still be used.	<ol style="list-style-type: none"> Highest action priority? Possible to replace PFOS technically? 	Fluorinated substances and non-fluorinated phosphate compounds could be used.	N/A	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Metal plating (hard metal plating) only in closed-loop systems	No	PFOS-compounds are still used in hard chrome plating.	<ol style="list-style-type: none"> Yes Yes 	6:2 Fluorotelomer sulfonate (6:2 FTS)	27619-97-2	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate potassium salt	59587-38-1	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				1,1,2,2,-tetrafluoro-2-(perfluorohexyloxy)-ethane sulfonate	N/A	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate	N/A	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Non chemical: Physical covers (netting, balls) for metal plating baths (Cr VI) to diminish hydrogen burst and reduce misting need to be further investigated	N/A	UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A

Applications	Open application	Use status	Priority action 1. Highest action priority? 2. Possible to replace PFOS technically?	Identified alternatives	CAS No:	Source of information	Class (assessment result) ³⁸⁹
Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio opaque ETFE production, in-vitro diagnostic medical devices, and CCD color filters)	No	Old video endoscopes at hospitals contain a CCD colour filter that contains a small amount of PFOS. PFOS is also used as a dispersant for contrast agents in radio-opaque catheters.	1. No 2. Yes	Not available	N/A	N/A	N/A
Fire fighting foam	Yes	There is use of PFOS-related substances in new products in many countries. Stocks are still being used.	1. Yes 2. Yes	Dodecafluoro-2-methylpentan-3-one	756-13-8	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Perfluorohexane ethyl sulfonyl betaine	N/A	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Carboxymethyl dimethyl-3-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]propylammonium hydroxide	34455-29-3	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
Insect baits for control of leaf-cutting ants from genus <i>Atta</i> spp. and <i>Acromyrmex</i> spp.	Yes	Brazil is using PFOS to produce sulfluramid which is used for control of leaf-cutting ants from the species	1. Yes 2. For some countries, it seems possible to replace sulfluramid and for some others, not yet.	Fipronil	120068-37-3	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Fenitrothion (thermal fogging)	122-14-5	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Deltamethrin (dried powder)	52918-63-5	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Hydramethylnon	67485-29-4	UNEP/POPS/POPRC.10/INF/7/Rev.1	4

Applications	Open application	Use status	Priority action 1. Highest action priority? 2. Possible to replace PFOS technically?	Identified alternatives	CAS No:	Source of information	Class (assessment result) ³⁸⁹
		of <i>Atta</i> spp. and <i>Acromyrmex</i> spp.		<p>Non chemical: The entomopathogenic <i>Metarrhizium anisopliae</i> can cause the decline and ultimate death of small colonies and recent research indicates that the entomopathogenic fungi <i>Beauveria bassiana</i> and <i>Aspergillus ochraceus</i> can cause 50% mortality within 4-5 days in laboratory conditions.</p> <p>Natural products that can be effective under certain conditions include limonoids extracted from the roots of the South Brazilian endemic plant <i>Raulinoa echinata</i>.</p>	N/A	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Specific exemptions							
Photo masks in the semiconductor and liquid crystal display (LCD) industries	No	PFOS-related compounds may still be used	1. No 2. Not possible to answer without detailed chemicals information about the alternatives	No information available	N/A	N/A	N/A
Metal plating (hard metal plating)	Yes	PFOS-compounds are still used in hard chrome plating.	1. Yes 2. Yes	6:2 Fluorotelomer sulfonate (6:2 FTS)	27619-97-2	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate potassium salt	59587-38-1	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				1,1,2,2,-tetrafluoro-2-(perfluorohexyloxy)-ethane sulfonate	N/A	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate	N/A	UNEP/POPS/POPRC.10/INF/7/Rev.1	3

Applications	Open application	Use status	Priority action 1. Highest action priority? 2. Possible to replace PFOS technically?	Identified alternatives	CAS No:	Source of information	Class (assessment result) ³⁸⁹
				Non chemical: Physical covers (netting, balls) for metal plating baths (chromium (VI)) to diminish hydrogen burst and reduce misting need to be further investigated	N/A	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Metal plating (decorative plating)	Yes	Cr-III has replaced Cr-VI in decorative chrome plating.	1. Yes 2. Yes	Polypropylene glycol ethers Novel technology: chromium (III) bath instead of chromium (VI) bath	N/A	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Electric and electronic parts for some color printers and color copy machines	No	PFOS-related compounds may still be used	1. Yes 2. Not possible to answer without detailed chemicals information about the alternatives	No information available	N/A	N/A	N/A
Insecticides for control of red imported fire ants and termites	Yes	Other fluorosurfactants may be used as inert surfactants in other pesticide products.	1. Yes 2. Yes	Fipronil	120068-37-3	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Abamectin	71751-41-2	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Pyriproxyfen	95737-68-1	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Fenitrothion	122-14-5	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Imidacloprid	138261-41-3, 105827-78-9	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Cypermethrin	52315-07-8	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Deltamethrin	52918-63-5	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Chlorpyrifos	2921-88-2	UNEP/POPS/POPRC.10/INF/7/Rev.1	2

Applications	Open application	Use status	Priority action 1. Highest action priority? 2. Possible to replace PFOS technically?	Identified alternatives	CAS No:	Source of information	Class (assessment result) ³⁸⁹
				Hydramethylnon	67485-29-4	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Bifenthrin	82657-04-3	POPRC-8/6: Assessment of alternatives to endosulfan	4
				Alpha-cypermethrin	67485-29-4	POPRC-8/6: Assessment of alternatives to endosulfan	4
				Indoxacarb	144171-61-9	POPRC-8/6: Assessment of alternatives to endosulfan	4
				Non chemical: The entomopathogenic <i>Metarrhizium anisopliae</i> can cause the decline and ultimate death of small colonies and recent research indicates that the entomopathogenic fungi <i>Beauveria bassiana</i> and <i>Aspergillus ochraceus</i> can cause 50% mortality within 4-5 days in laboratory conditions. Natural products that can be effective under certain conditions include limonoids extracted from the roots of the South Brazilian endemic plant <i>Raulinoa echinata</i> .	N/A	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Chemically driven oil production	Yes	PFOS derivatives may occasionally be used as surfactants in the oil and mining industries.	1. Yes 2. Yes	PFBS derivatives, fluorotelomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids, and thioether acids.	N/A	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Carpets, leather and apparel, textiles and	Yes	PFOS-related substances have been phased out	1. Yes 2. Yes	Perfluorobutane sulfonate potassium salt	29420-49-3	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Perfluorohexanesulfonate potassium salt*	3871-99-6	UNEP/POPS/POPRC.10/INF/7/Rev.1	3

Applications	Open application	Use status	Priority action 1. Highest action priority? 2. Possible to replace PFOS technically?	Identified alternatives	CAS No:	Source of information	Class (assessment result) ³⁸⁹
upholstery.		in many countries		1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -Perfluorohexanol or 3,3,4,4,5,5,6,6,6-nonafluorobutyl ethanol*	2043-47-2	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanol*	647-42-7	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester*	2144-53-8	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Di-2-ethylhexyl sulfosuccinate, sodium salt	577-11-7	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Stearamidomethyl pyridine chloride	4261-72-7	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Octamethyl cyclotetrasiloxane (D4)*	556-67-2	UNEP/POPS/POPRC.10/INF/7/Rev.1	1
				Decamethyl cyclopentasiloxane (D5)*	541-02-6	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Dodecamethyl cyclohexasiloxane (D6)*	540-97-6	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Hexamethyl disiloxane (MM or HMDS)*	107-46-0	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Octamethyl trisiloxane (MDM)*	107-51-7	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Decamethyl tetrasiloxane (MD2M)*	141-62-8	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Dodecamethyl pentasiloxane (MD3M)*	141-63-9	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Non chemical: 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. Dendrimers may be in the region of nano sized materials meaning features with an average diameter between 1 to 100 nm.	N/A	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Paper and packaging	Yes	PFOS-related substances have	1. Yes	Tris(octafluoropentyl) phosphate	355-86-2	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
			2. Yes	Tris(heptafluorobutyl) phosphate	563-09-7	UNEP/POPS/POPRC.10/INF/7/Rev.1	3

Applications	Open application	Use status	Priority action 1. Highest action priority? 2. Possible to replace PFOS technically?	Identified alternatives	CAS No:	Source of information	Class (assessment result) ³⁸⁹
		been phased out in many countries.		Tris(trifluoroethyl) phosphate	358-63-4	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Perfluorohexyl phosphonic acid	40143-76-8	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				1-chloro-perfluorohexyl phosphonic acid	N/A	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Sodium bis(perfluorohexyl) phosphinate	40143-77-9	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Non chemical: 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	N/A	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Coatings and coating additives	Yes	PFOS-related substances have been phased out in many countries.	1. Yes 2. Yes	Perfluorobutane sulfonate potassium salt	29420-49-3	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Methyl nonafluorobutyl ether	163702-07-6	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Methyl nonafluoro isobutyl ether	163702-08-7	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Octamethyl cyclotetrasiloxane (D4)*	556-67-2	UNEP/POPS/POPRC.10/INF/7/Rev.1	1
				Decamethyl cyclopentasiloxane (D5)*	541-02-6	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
				Dodecamethyl cyclohexasiloxane (D6)*	540-97-6	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Hexamethyl disiloxane (MM or HMDS)*	107-46-0	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Octamethyl trisiloxane (MDM)*	107-51-7	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Decamethyl tetrasiloxane (MD2M)*	141-62-8	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Dodecamethyl pentasiloxane (MD3M)*	141-63-9	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Diisopropylnaftalene	38640-62-9	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Triisopropylnaftalene	35860-37-8	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Diisopropyl-1,1'-biphenyl	69009-90-1	UNEP/POPS/POPRC.10/INF/7/Rev.1	4

Applications	Open application	Use status	Priority action 1. Highest action priority? 2. Possible to replace PFOS technically?	Identified alternatives	CAS No:	Source of information	Class (assessment result) ³⁸⁹
				1-Isopropyl-2-phenyl-benzene	25640-78-2	UNEP/POPS/POPRC.10/INF/7/Rev.1	4
				Hydroxyl) Terminated polydimethylsiloxane	67674-67-3	UNEP/POPS/POPRC.10/INF/7/Rev.1	3
Rubber and plastics	Yes	PFOS-related substances have been phased out in many countries.	1. Yes 2. Yes	Perfluorobutane sulphonate (PFBS) derivatives or various C ₄ -perfluorocompounds are used as alternatives to PFOS in rubber moulding defoamers in electroplating and as additives in plastics.	N/A	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A
Not exempted							
Cleaning agents, waxes and polishes for cars and floors	Yes	PFOS-related substances have been phased out in many countries.	1. Yes 2. Yes	Fluorotelomer-based substances, fluorinated polyethers, C ₄ -perfluorinated compounds. A shift to softer waxes that are more biodegradable or entirely biodegradable may completely eliminate the need for persistent polyfluorinated compounds. In these products, the fluorinated surfactants are replaced with non-ionic or anionic surfactants, which have good wetting properties	N/A	UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A

B. List of alternatives to PFOS, its salts and PFOSF by chemicals

Compound			Functionality	Occurrence	Applications ³⁹⁰	Class (results of the assessment)
CAS No:	Name	Abbr.				
29420-49-3	Perfluorobutane sulfonate potassium salt	PFBS K	Fluorosurfactant ³⁹¹	commercial product	Coating and coating agents, carpets, leather and apparel, textiles and upholstery, paper and packaging, rubber and plastics. ^{A,B}	3
3871-99-6	Perfluorohexanesulfonate potassium salt	PFHxS K	Fluorosurfactant ³⁹²	commercial product	Carpets, leather and apparel, textiles and upholstery ^B ,	3
307-24-4	Perfluorohexanoic acid	PFHxA		transformation product	Not applicable	
2923-26-4	Perfluorohexanoic acid sodium salt	PFHxA Na		transformation product	Not applicable	
375-22-4	Perfluorobutanoic acid	PFBA		transformation product	Not applicable	
375-85-9	Perfluoroheptanoic acid	PFHpA		transformation product	Not applicable	
2043-47-2	1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -Perfluorohexanol or 3,3,4,4,5,5,6,6,6-nonafluorobutyl ethanol	4:2 FTOH	Raw material for surfactant and surface protection products ³⁹³	manufacturing intermediate	Carpets, leather and apparel, textiles and upholstery ^A ,	3
647-42-7	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanol	6:2 FTOH	Raw material for surfactant and surface protection products ³⁹⁴	manufacturing intermediate	Carpets, leather and apparel, textiles and upholstery ^{A,B}	3
2144-53-8	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester	6:2 FMA	Raw material for surfactant and surface protection products ³⁹⁵	manufacturing intermediate	Carpets, leather and apparel, textiles and upholstery ^A	3

³⁹⁰ Applications listed in part I of Annex B to the Convention for which the alternative is relevant. (A) Information from the Guidance on alternatives to PFOS, its salts and PFOSF and their related chemicals (UNEP/POPS/POPRC.9/INF/11/rev1); (B) Information from the technical paper on the identification and assessment of alternatives to the use of PFOS, its salts and PFOSF and their related chemicals in open applications UNEP/POPS/POPRC.8/INF/17.

³⁹¹ Buck et al. "Perfluoroalkyl and polyfluoroalkyl Substances in the Environment: Terminology, Classification and Origins", Integrated Environmental Assessment and Management, Vol 7, Number 4 – pp 513-541 (2011).

Buck et al. "Perfluoroalkyl and polyfluoroalkyl Substances in the Environment: Terminology, Classification and Origins", Integrated Environmental Assessment and Management, Vol 7, Number 4 – pp 513-541 (2011).

³⁹² Buck et al. "Perfluoroalkyl and polyfluoroalkyl Substances in the Environment: Terminology, Classification and Origins", Integrated Environmental Assessment and Management, Vol 7, Number 4 – pp 513-541 (2011).

³⁹³ Buck et al. "Perfluoroalkyl and polyfluoroalkyl Substances in the Environment: Terminology, Classification and Origins", Integrated Environmental Assessment and Management, Vol 7, Number 4 – pp 513-541 (2011).

³⁹⁴ Buck et al. "Perfluoroalkyl and polyfluoroalkyl Substances in the Environment: Terminology, Classification and Origins", Integrated Environmental Assessment and Management, Vol 7, Number 4 – pp 513-541 (2011).

Compound			Functionality	Occurrence	Applications ³⁹⁰	Class (results of the assessment)
CAS No:	Name	Abbr.				
756-13-8	Dodecafluoro-2-methylpentan-3-one		Fluorosurfactant	commercial product	Fire fighting foams ^{A,B}	3
	Perfluorohexane ethyl sulfonyl betaine		Fluorosurfactant	commercial product	Fire fighting foams ^{A,B}	3
34455-29-3	Carboxymethyldimethyl-3- [[[(3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctyl)sulfonyl]amino]propylammoniu m hydroxide		Fluorosurfactant	commercial product	Fire fighting foams ^{A,B}	3
163702-07-6	Methyl nonafluorobutyl ether		Fluorosurfactant	commercial product	Coating and coating additives ^{A,B}	3
163702-08-7	Methyl nonafluoro isobutyl ether		Fluorosurfactant	commercial product	Coating and coating additives ^{A,B}	3
27619-97-2	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1- sulphonate	6:2 FTS	Fluorosurfactant	commercial product	Metal plating ^{A,B}	3
59587-38-1	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1- sulphonate potassium salt	6:2 FTS K	Fluorosurfactant	commercial product	Metal plating ^{A,B}	3
	1,1,2,2,-tetrafluoro-2-(perfluorohexyloxy)-ethane sulfonate	F-53	Fluorosurfactant	commercial product	Metal plating ^{A,B}	3
	2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6- dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate	F-53B	Fluorosurfactant	commercial product	Metal plating ^{A,B}	3
355-86-2	Tris(octafluoropentyl) phosphate	POFPP (PAPs)	Fluorosurfactant	commercial product	Paper and packaging ^{A,B}	3
563-09-7	Tris(heptafluorobutyl) phosphate	PHFBP (PAPs)	Fluorosurfactant	commercial product	Paper and packaging ^{A,B}	3
358-63-4	Tris(trifluoroethyl) phosphate	PTEHP (PAPs)	Fluorosurfactant	commercial product	Paper and packaging ^{A,B}	3
40143-76-8	Perfluorohexyl phosphonic acid	PFHxPA (PAPs)	Fluorosurfactant	commercial product	Paper and packaging ^{A,B} ,	3
	1-chloro-perfluorohexyl phosphonic acid	Cl-PFHxPA (PAPs)	Fluorosurfactant	commercial product	Paper and packaging ^{A,B}	3
40143-77-9	Sodium bis(perfluorohexyl) phosphinate	6:6 PFPi	Fluorosurfactant	commercial product	Paper and packaging ^{A,B} ,	3

³⁹⁵ Buck et al. "Perfluoroalkyl and polyfluoroalkyl Substances in the Environment: Terminology, Classification and Origins", Integrated Environmental Assessment and Management, Vol 7, Number 4 – pp 513-541 (2011).

Compound			Functionality	Occurrence	Applications ³⁹⁰	Class (results of the assessment)
CAS No:	Name	Abbr.				
		(PAPs)				
577-11-7	Di-2-ethylhexyl sulfosuccinate, sodium salt		Waxes and resins	commercial product	Carpets, leather and apparel textiles and upholstery ^B ,	3
4261-72-7	Stearamidomethyl pyridine chloride		Waxes and resins	commercial product	Carpets, leather and apparel, textiles and upholstery ^{A,B} ,	3
556-67-2	Octamethyl cyclotetrasiloxane	D4	Manufacturing intermediate for the production of silicone polymers ³⁹⁶	manufacturing intermediate	Carpets, leather and apparel, textiles and upholstery, coating and coating additives ^{A,B} .	1
541-02-6	Decamethyl cyclopentasiloxane	D5	Manufacturing intermediate for the production of silicone polymers ³⁹⁷	manufacturing intermediate	Carpets, leather and apparel, textiles and upholstery, coating and coating additives ^{A,B} .	3
540-97-6	Dodecamethyl cyclohexasiloxane	D6	Manufacturing intermediate for the production of silicone polymers ³⁹⁸	manufacturing intermediate	Carpets, leather and apparel, textiles and upholstery, coating and coating additives ^{A,B} .	4
107-46-0	Hexamethyl disiloxane	MM (or HMDS)	Manufacturing intermediate for the production of silicone polymers ³⁹⁹	manufacturing intermediate	Carpets, leather and apparel, textiles and upholstery, coating and coating additives ^{A,B} .	4
107-51-7	Octamethyl trisiloxane	MDM	Manufacturing intermediate for the production of silicone polymers.	manufacturing intermediate	Carpets, leather and apparel, textiles and upholstery, coating and coating additives ^{A,B} .	4

³⁹⁶ Wang, De-Gao, et al. "Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment." *Chemosphere* Vol. 93, Issue 5, October 2013: 711–725.

URL: <http://www.sciencedirect.com/science/article/pii/S0045653512012805>.

³⁹⁷ Wang, De-Gao, et al. "Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment." *Chemosphere* Vol. 93, Issue 5, October 2013: 711–725.

URL: <http://www.sciencedirect.com/science/article/pii/S0045653512012805>.

³⁹⁸ Wang, De-Gao, et al. "Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment." *Chemosphere* Vol. 93, Issue 5, October 2013: 711–725.

URL: <http://www.sciencedirect.com/science/article/pii/S0045653512012805>.

³⁹⁹ <http://echa.europa.eu/documents/10162/c98c53e1-7228-4985-8f87-6e202788106f>.

Compound			Functionality	Occurrence	Applications ³⁹⁰	Class (results of the assessment)
CAS No:	Name	Abbr.				
141-62-8	Decamethyl tetrasiloxane	MD2M	Manufacturing intermediate for the production of silicone polymers. ⁴⁰⁰	manufacturing intermediate	Carpets, leather and apparel, textiles and upholstery, coating and coating additives A,B	4
141-63-9	Dodecamethyl pentasiloxane	MD3M	Manufacturing intermediate for the production of silicone polymers. ⁴⁰¹	manufacturing intermediate	Carpets, leather and apparel, textiles and upholstery, coating and coating additives A,B	4
38640-62-9	Diisopropylnaftalene		Waxes and resins	commercial product	Coating and coating additives A,B	4
35860-37-8	Triisopropylnaftalene		Waxes and resins	commercial product	Coating and coating additives A,B	4
69009-90-1	Diisopropyl-1,1'-biphenyl		Waxes and resins	commercial product	Coating and coating additives A,B	4
25640-78-2	1-Isopropyl-2-phenyl-benzene		Waxes and resins	commercial product	Coating and coating additives A,B	4
67674-67-3	(Hydroxyl) Terminated polydimethylsiloxane		Non ionic surfactant ⁴⁰²	commercial product	Coating and coating additives A,B	3
Pesticides						
120068-37-3	Fipronil		Pesticides	commercial product	Insecticides for control of red imported fire ants and termites. Insect bait for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp. ^B	4
71751-41-2	Abamectin		Pesticides	commercial product	Insecticides for control of red imported fire ants and termites	4

⁴⁰⁰ <http://echa.europa.eu/documents/10162/c98c53e1-7228-4985-8f87-6e202788106f>.

⁴⁰¹ https://echa.europa.eu/documents/10162/13632/intentions_2013_en.pdf.

⁴⁰² <http://www.cdms.net/ldat/mp9fi001.pdf>.

<http://www.siltech.com/msds/P2002.2.pdf>.

<http://www.hitochem.com/uploadfile/20120411191716530.pdf>.

Compound			Functionality	Occurrence	Applications ³⁹⁰	Class (results of the assessment)
CAS No:	Name	Abbr.				
95737-68-1	Pyriproxyfen		Pesticides	commercial product	Insecticides for control of red imported fire ants and termites ^B	4
122-14-5	Fenitrothion ⁴⁰³		Pesticides	commercial product	Insecticides for control of red imported fire ants and termites. Insect bait for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp. ^B	4
138261-41-3, 105827-78-9	Imidacloprid		Pesticides	commercial product	Insecticides for control of red imported fire ants and termites ^B	4
52315-07-8	Cypermethrin		Pesticides	commercial product	Insecticides for control of red imported fire ants and termites ^A	4
52918-63-5	Deltamethrin		Pesticides	commercial product	Insecticides for control of red imported fire ants and termites. Insect bait for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp. ^B	4
2921-88-2	Chlorpyrifos		Pesticides	commercial product	Insecticides for control of red imported fire ants and termites ^B	2
67485-29-4	Hydramethylnon ⁴⁰³		Pesticides	commercial product	Insecticides for control of red imported fire ants and termites. Insect bait for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp. ^{A404}	4
Commercial brands						
	Polyfox®		Polymer coating	commercial product	Coating and coating additives ^{A,B}	3

⁴⁰³ According to ABRAISCA, this substance is not an insect bait.

⁴⁰⁴ Submission by Ecuador, <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/tabid/2266/Default.aspx>.

Compound			Functionality	Occurrence	Applications ³⁹⁰	Class (results of the assessment)
CAS No:	Name	Abbr.				
	Emulphor® FAS		Polymer coating	commercial product	Coating and coating additives _{A,B} Metal plating ^{A,B}	3
	Enthone®		Polymer coating	commercial product	Coating and coating additives _{A,B} Metal plating ^{A,B}	3
	Zonyl®		Polymer coating	commercial product	Carpets, leather and apparel, textiles and upholstery ^{A,B}	3
	Capstone®		Polymer coating	commercial product	Coating and coating additives, carpets, leather and apparel, textiles and upholstery, and metal plating _{A,B}	3
	Nuva®		Polymer coating	commercial product	Carpets, leather and apparel, textiles and upholstery ^{A,B}	3
	Unidyne®		Polymer coating	commercial product	Carpets, leather and apparel, textiles and upholstery ^{A,B}	3
	Rucoguard®		Polymer coating	commercial product	Carpets, leather and apparel, textiles and upholstery ^{A,B}	3
	Oleophobol®		Polymer coating	commercial product	Carpets, leather and apparel, textiles and upholstery ^{A,B}	3
	Asahiguard®		Polymer coating	commercial product	Carpets, leather and apparel, textiles and upholstery ^{A,B}	3
	Solvera®		Polymer coating	commercial product	Paper and packaging ^{A,B}	3

Appendix 3: Characteristics of alternatives to PFOS for various applications

Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
Aviation hydraulic fluids	Literature describes phosphate compounds e.g. tri-alkyl phosphates, tri-aryl phosphates, and mixtures of alkyl-aryl-phosphates	N/A	59	<p>Health and environmental hazards: Information gaps since due to lack of publically available information detailing the the real composition of commercial surfactants for aviation hydraulic fluids.</p> <p>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 hydrolyzed they transform into strong acids and may have a local impact if not taken care of in a safe and correct way.</p>
Metal plating	6:2-Fluorotelomer sulfonate (6:2 FTS)	27619-97-2	9, 24, 50,52, 67	<p>Toxicology: Acute and repeated-dose mammalian and aquatic toxicity has been reported</p> <p>Degradation in the environment: Degradation of fluoroalkylthioamido- sulphonates into 6:2 FTS is suggested and 6:2 FTS is susceptible to biodegradation under sulphur-limiting and aerobic conditions.</p> <p>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, 6:2 FTS can be expected in the aqueous environment.. 6:2 FTS has been shown to degrade to the stable perfluorohexane acid (PFHxA) in the environment.</p> <p>Monitoring data: 6:2 FTS has been detected in environmental samples including water, soil, air particulates and biota.</p> <p>During the EU-project PERFORCE⁴⁰⁶, 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 publically available data is needed to determine its origin and whether it is a LRT substance or not.</p>
Metal plating	Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate (F-53)	N/A	64	<p>Toxicology: The substance is poorly characterized.</p> <p>Environmental hazards: Probably persistent. The substance is poorly characterized.</p>
Metal plating	Potassium 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate (F-53B)	N/A	64	<p>Toxicology: The substance is poorly characterized. A recent study estimates the mean biological half-live via all routes of excretion (total elimination) in humans to be 18.5 years⁴⁰⁷.</p> <p>Environmental hazards: Probably persistent. The substance is poorly characterized. F-53B was found in high concentrations (43-78 and 65-112 µg/L for the effluent and influent,</p>

⁴⁰⁵ This table provides a selection of the characteristics, a full overview of the characteristics of the substances is provided in UNEP/POPS/POPRC.10/INF/7/Rev.1 and UNEP/POPS/POPRC.10/INF/8/Rev.1.

⁴⁰⁶ <http://www.science.uva.nl/perforce/index.htm?http%3A//www.science.uva.nl/perforce/events.htm>.

⁴⁰⁷ Y. Shi et al., Env. Sci. Technol., 50, 2016, 2396-2404

Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
				respectively) in wastewater from the chrome plating industry in the city of Wenzhou, China. F-53B was not successfully removed by the wastewater treatments in place ⁴⁰⁸ . Consequently, it was detected in surface water that receives the treated wastewater at similar levels to PFOS (ca. 10-50 ng/L) and the concentration decreased with the increasing distance from the wastewater discharge point along the river. Only one 96-h study is available, reporting that F-53B has a similar toxicity to zebrafish (LC50=15.5 mg/L) as PFOS (LC50=17mg/L) and is as resistant to degradation as PFOS. ^{409,410}
Metal plating	Non-fluorinated surfactants (Mainly alkane sulfonates)	N/A		Toxicity: The substances cannot be assessed since there are considerable gaps in publically available data of their chemical composition. Environmental hazards: The substances cannot be assessed since there are considerable data gaps of their chemical composition.
Firefighting foams	Perfluorohexanoic acid (PFHxA)	307-24-4		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 distinct binding sites were identified by NMR in human albumin for PFOA and PFHxA. Both acids readily displace endogenous oleic acid from its usual binding site, raising questions about possible interferences with the pharmacokinetics of fatty acids and drugs. Both acids changed the secondary structure of the protein, PFOA to a larger extent than PFOA. Association with phospholipids in fish has also been established. ⁴¹¹ 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. Concomitant with increased production, short-F-chain substances, such as PFHxA, are now increasingly often detected in the environment. PFHxA levels were substantial in drinking water downstream of a fluoropolymer manufacturing plant. ⁴¹² Therefore it cannot be excluded that PFHxA bioconcentrate, bioaccumulate or biomagnify Degradation in the environment: Persistent. Perfluorohexanoate (PFHxA) is the terminal 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 (NH ₄ PFHx, ammonium perfluorohexanoate) have been presented at scientific meetings in the past year.

⁴⁰⁸ <http://www.ncbi.nlm.nih.gov/pubmed/23952109>.

⁴⁰⁹ <http://www.greensciencepolicy.org/wp-content/uploads/2014/10/Wang2015.pdf>.

⁴¹⁰ <http://www.ncbi.nlm.nih.gov/pubmed/23952109>.

⁴¹¹ Marie Pierre Krafft, Jean G. Riess, Per- and polyfluorinated substances (PFASs): Environmental challenges, Current Opinion in Colloid & Interface Science 20 (2015) 192–212.

⁴¹² Marie Pierre Krafft, Jean G. Riess, Per- and polyfluorinated substances (PFASs): Environmental challenges, Current Opinion in Colloid & Interface Science 20 (2015) 192–212.

Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
Firefighting foams	Dodecafluoro-2-methylpentan-3-one. IUPAC name: 1,1,1,2,2,4,5,5,5-nonafluoro – 4 – (trifluoromethyl) – 3 – pentanone	756-13-8		Toxicology: Information gaps though the MSDS lists a variety of liver effects and hydrogen fluoride and carbon monoxide as decomposition products. ⁴¹³ Degradation in the environment: Probably persistent Emissions: Modeling data indicate volatility Monitoring data: Information gaps in publically available data
Firefighting foams	Fluorine free surfactants	N/A	-	Information gaps due to lack in publically available data of the real composition of commercial fire fighting foams.
Insect baits for control of leaf-cutting ants	Fipronil Deltamethrin ⁴¹⁴ Fenitrothion ⁴¹⁵ Hydramethylnon	120068-37-3 52918-63-5 122-14-5 67485-29-4	64	Toxicology: Hydramethylnon is considered as low toxic to humans and mammals. ⁴¹⁶ Environmental hazards: Fipronil is considered more acutely toxic to humans and the environment than sulfluramid. Deltamethrin, fenitrothion and fipronil, were not likely considered to fulfil the criteria on persistence and bioaccumulation in Annex D of the Stockholm Convention. ⁴¹⁷ Fenitrothion is banned in the EU since 2007 ⁴¹⁸
Insecticides for control of red imported fire ants and termites	S-Methoprene Pyriproxyfen Fipronil Imidacloprid Chlorpyrifos Cypermethrin	65733-16-6 95737-68-1 120068-37-3 138261-41-3, 105827-78-9 2921-88-2 52315-07-8	-	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. Hydramethylnon is considered as low toxic to humans and mammals. ⁴²¹ Environmental hazards: Fipronil and chlorpyrifos are considered more acutely toxic to humans and the environment than sulfluramid. Bifenthrin and chlorpyrifos were considered that they might meet all Annex D criteria in the Stockholm Convention but remained undetermined due to equivocal or insufficient data. ⁴²²

⁴¹³ http://www.chemcas.org/msds_archive/msds_01/cas/gb_msds/756-13-8.asp.

⁴¹⁴ Deltamethrin as insect bait exclusively formulated in dried powder formulations.

⁴¹⁵ Fenitrothion has a exclusively formulation in thermonebulizable solutions (thermal fogging).

⁴¹⁶ <http://npic.orst.edu/factsheets/hydragen.pdf>

⁴¹⁷ Decision POPRC-8/6: Assessment of alternatives to endosulfan.

⁴¹⁸ : <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:141:0076:0077:EN:PDF>

Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
	Deltamethrin ⁴¹⁹ Fenitrothion ⁴²⁰ Abamectin (commercial mixture) and their mixtures Bifenthrin Hydramethylnon Alpha-cypermethrin Indoxacarb	52918-63-5 122-14-5 71751-41-2 82657-04-3 67485-29-4 67375-30-80 144171-61-9		Alpha-cypermethrin, abamectin, cypermethrin, deltamethrin, fenitrothion, fipronil, imidacloprid and indoxacarb were not likely considered to fulfil the criteria on persistence and bioaccumulation in Annex D of the Stockholm Convention. ⁴²³ Fenitrothion is banned in the EU since 2007 ⁴²⁴
Chemically driven oil production	Perfluorobutane sulfonate (PFBS)	29420-49-3	1, 4, 5, 7, 15, 24, 25, 35, 41, 42, 49, 50, 51, 57, 64	<p>Category: The principal terminal degradation product of N-methyl perfluorobutane sulphonamidoethanol and PFBS-based products.</p> <p>Toxicology: The substance is well characterized. PFBS suppressed differentiation of a neuronotypic cell line used to characterize neurotoxicity.</p> <p>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.</p> <p>Emissions: Emission to the environment may be expected from chemically driven oil production and PFBS manufacturing</p> <p>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. PFBS has been found in blood plasma that has been reported in some recent studies, where also half lives of 24 days for men and 46 days for women have been reported. PFBS like PFOS and PFOA acted as an aromatase inhibitor in placental cells (Gorochategui <i>et al.</i> 2014). This inhibitory effect of the short chain PFBS was considered particularly important, because it is often considered a safe substitute of PFOS.⁴²⁵ Observations in the Arctic may qualify PFBS as a LRT substance.</p>

⁴²¹ <http://npic.orst.edu/factsheets/hydragen.pdf>.

⁴²² Decision POPRC-8/6: Assessment of alternatives to endosulfan.

⁴¹⁹ Deltamethrin as insect bait exclusively formulated in dried powder formulations.

⁴²⁰ Fenitrothion has a exclusively formulation in thermonebulizable solutions (thermal fogging).

⁴²³ Decision POPRC-8/6: Assessment of alternatives to endosulfan.

⁴²⁴ : <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:141:0076:0077:EN:PDF>

⁴²⁵ Danish Ministry of Environment, "Short-chain Polyfluoroalkyl Substances (PFAS).

Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
Chemically driven oil production	6:2-Fluorotelomer sulfonate (6:2 FTS)	27619-97-2	9, 24, 50, 52, 67	<p>Toxicology: Acute and repeated-dose mammalian and aquatic toxicity has been reported</p> <p>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.</p> <p>Emissions: Emission to the environment may be expected from chemically driven oil production and in manufacturing.</p> <p>Emission of 6:2 FTS from STP effluents is found. FTS can be expected in the aqueous environment. .. 6:2 FTS has been shown to degrade to the stable perfluorohexane acid (PFHxA) in the environment.</p> <p>Monitoring data: 6:2 FTS has been detected in environmental samples including water, soil, air particulates and biota.</p> <p>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. 6:2 FTS observations has been done in the Arctic. More publically available data is needed to determine its origin and whether it is a LRT substance or not.</p>
Chemically driven oil production	Fluorotelomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids, and thioether acids	N/A	63	<p>Toxicology: Information gaps since there are no specific surfactant substances identified</p> <p>Environmental hazards: Information gaps since there are no specific surfactant substances identified</p>
Carpets, leather and apparel, textiles and upholstery	Dendrimers: Hyperbranched hydrophobic polymers (dendritic i.e. highly branched polymers)	N/A	39, 48, 62, 68	<p>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.</p> <p>Environmental hazards: Information gaps in publically available information.</p>
Carpets, leather and apparel, textiles and upholstery	Siloxanes ⁴²⁶ (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 ⁴²⁷	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)	8, 13, 62, 64	<p>Toxicology: The European Commission has classified D4 as a reproductive toxic substance (repr. 2) (H361f)⁴²⁸ and is likely to fulfill the Annex D 1(e) (i) and (ii) criteria.^{429,430} Some siloxanes will be metabolized and the metabolites (hydroxylation metabolites) are expected to be found in blood and urine. California State EPA⁴³¹ notes the weak estrogenic activity of D4 combined with long half life and uterine tumors resulting from D5 exposure. The Government of Canada⁴³² concluded that D4 is inherently toxic to aquatic biota.</p> <p>Degradation in the environment: D4 and D5 are considered to fulfil the persistence criterium according to Annex D to the Stockholm Convention.⁴³³ Siloxane polymers are considered as inert.</p>

A literature review of information on human health effects and environmental fate and effect aspects of short-chain PFAS” Environmental project No. 1707, 2015, <http://www2.mst.dk/Udgiv/publications/2015/05/978-87-93352-15-5.pdf>

⁴²⁶ Manufacturing intermediates in the production of PDMS

⁴²⁷ http://extra.ivf.se/kemi/common/downloads/Kunskapsarkiv/Polysiloxaner/presentation_polysiloxanes.pdf

Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
				<p>The California State EPA notes that cyclosiloxanes appear to have long half lives in people.</p> <p>Emissions: Siloxanes are volatile.</p> <p>Monitoring data: D4 and D5 is considered to fulfil the Annex D on bioaccumulation, Long Range Transport (LRT) and D4 additionally is likely to fulfil the ecotoxicity criterium of the Stockholm Convention⁴³⁴. 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.⁴³⁵ 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. Certain siloxanes are persistent in the environment, resisting oxidation, reduction, and photodegradation. Varying information exists on the susceptibility of siloxanes to hydrolysis.</p>
Carpets, leather and apparel, textiles and upholstery	Fluorotelomer alcohols (FTOH)	2043-47-2 (4:2 FTOH) 647-42-7 (6:2 FTOH)	2, 18, 19, 21, 23, 24, 45, 47, 56, 64	<p>Category: precursors for fluorotelomer-based polymers.</p> <p>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 shows that 4:2 FTOH is more potent than 6:2 and 8:2 for cytotoxicity. FTOHs have been shown to be xenobiotics causing effects down to 0.03 mg/L, and 6:2 FTOH to be more potent than 8:2 FTOH⁴³⁶.</p> <p>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).</p> <p>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.</p> <p>Monitoring data: FTOHs were found in the North American atmosphere. However, present</p>

⁴²⁸ Harmonized Classification according to GHS Regulation (EC) No 1272/2008.

<http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database>.

⁴²⁹ UNEP/POPS/POPRC.10/INF/7/Rev.1.

⁴³⁰ UNEP/POPS/POPRC.10/INF/8/Rev.1.

⁴³¹ <http://oehha.ca.gov/multimedia/biomon/pdf/1208cyclosiloxanes.pdf>.

⁴³² <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>.

⁴³³ UNEP/POPS/POPRC.10/INF/8/Rev.1.

⁴³⁴ UNEP/POPS/POPRC.10/INF/8/Rev.1.

⁴³⁵ Cyclosiloxanes, Materials for the December 4-5, 2008, Meeting of the California Environmental Contaminant Biomonitoring Program (CECBP) Scientific Guidance Panel (SGP).

⁴³⁶ Danish Ministry of Environment, "Short-chain Polyfluoroalkyl Substances (PFAS).

A literature review of information on human health effects and environmental fate and effect aspects of short-chain PFAS" Environmental project No. 1707, 2015, <http://www2.mst.dk/Udgiv/publications/2015/05/978-87-93352-15-5.pdf>.

Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
				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.
Carpets, leather and apparel, textiles and upholstery	Perfluorobutane sulfonate (PFBS) as processing agent for perfluorobutane sulfonyl (PFBS)-based polymers	29420-49-3	1, 4, 5, 7, 15, 24, 25, 35, 41, 42, 49, 50, 51, 57, 64	<p>Category: precursor for perfluorobutane sulfonyl (PFBS)-based polymers and terminal degradation product.</p> <p>Toxicology: The substance is well characterized. PFBS suppressed differentiation of a neuronotypic cell line used to characterize neurotoxicity.</p> <p>Degradation in the environment: PFBS is considered as persistent in the environment. PFBS is considered the terminal degradation product of PFBS-based products.</p> <p>Emissions: Poorly characterized though emissions are expected from PFBS manufacturing.</p> <p>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. PFBS has been found in blood plasma that has been reported in some recent studies, where also half lives of 24 days for men and 46 days for women have been reported. PFBS like PFOS and PFOA acted as an aromatase inhibitor in placental cells (Gorrochategui <i>et al.</i> 2014). This inhibitory effect of the short chain PFBS was considered particularly important, because it is often considered a safe substitute of PFOS.⁴³⁷ Observations in the Arctic may qualify PFBS as a LRT substance.</p>
Carpets, leather and apparel, textiles and upholstery	Perfluorohexane sulfonic acid (PFHxS)	3871-99-6	10, 24, 34, 50, 55, 58,	<p>Category: precursor for perfluorohexylsulfonyl (PFHxS)-based polymers and terminal degradation product</p> <p>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). PFHxS is much more liver toxic than PFBS and PFOS.⁴³⁸</p>

⁴³⁷ Danish Ministry of Environment, “Short-chain Polyfluoroalkyl Substances (PFAS).

A literature review of information on human health effects and environmental fate and effect aspects of short-chain PFAS” Environmental project No. 1707, 2015, <http://www2.mst.dk/Udgiv/publications/2015/05/978-87-93352-15-5.pdf>.

⁴³⁸ Danish Ministry of Environment, “Short-chain Polyfluoroalkyl Substances (PFAS).

Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
				<p>Degradation in the environment: PFHxS is considered as persistent and stable in the environment and is regarded as the terminal degradation product of PFHxS-based products.</p> <p>Emissions: Possible from treated textiles and manufacturing.</p> <p>Monitoring data: There is a high potential for contamination of surface and ground water⁴³⁹. 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 (PFSAs) 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.</p>
Paper and packaging	Fluorotelomer based phosphate esters such as diesters of polyfluoroalkyl phosphonic acids and phosphoric acids (diPAPs) and polyfluoroalkyl phosphonic acids (PAPs)	Some examples of PAPs and diPAPs are listed in UNEP/POPS/POPRC.8/INF/17/Rev.1, appendix 1.	6, 14, 14, 38, 40, 44, 54, 61, 62, 64	<p>Toxicology: diPAPs facilitates human exposure to perfluorocarboxylates (PFCAs) since PAPs have been proved to be metabolized to PFCAs in an in vivo metabolism experiment.</p> <p>Degradation into the environment: PAPs and diPAPs transform into the corresponding PFCAs</p> <p>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.</p> <p>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.</p>
Paper and packaging	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)	2, 18, 19, 21, 23, 24, 45, 47, 56, 64	<p>Category: precursors for fluorotelomer-based polymers.</p> <p>Toxicology: 4:2 FTOH is poorly characterized. 6:2 FTOH is wellcharacterized Acute and repeated-dose mammalian toxicity, pharma- and toxicokinetics studies have been conducted. Recent research shows that 4:2 FTOH is more potent than 6:2 and 8:2 for cytotoxicity. FTOHs have been shown to be xenoes-trogens causing effects down to 0.03 mg/L, and 6:2 FTOH to be more potent than 8:2 FTOH⁴⁴⁰.</p> <p>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).</p> <p>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</p>

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⁴³⁹ 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>.

⁴⁴⁰ Danish Ministry of Environment, “Short-chain Polyfluoroalkyl Substances (PFAS).

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Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
				<p>compartment only under conditions where no sorptive medium is present.</p> <p>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.</p>
Rubber and plastics	Perfluorobutane sulfonate (PFBS)	29420-49-3	1, 4, 5, 7, 15, 24, 25, 35, 41, 42, 49, 50, 51, 57, 64	<p>Category: precursor for perfluorobutane sulfonyl (PFBS)-based polymers and terminal degradation product.</p> <p>Toxicology: The substance is well characterized PFBS suppressed differentiation of a neuronotypic cell line used to characterize neurotoxicity.</p> <p>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.</p> <p>Emissions: Emission to the environment may be expected from rubber and plastic products and from PFBS manufacturing.</p> <p>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. PFBS has been found in blood plasma that has been reported in some recent studies, where also half lives of 24 days for men and 46 days for women have been reported. PFBS like PFOS and PFOA acted as an aromatase inhibitor in placental cells (Gorochategui <i>et al.</i> 2014). This inhibitory effect of the short chain PFBS was considered particularly important, because it is often considered a safe substitute of PFOS.⁴⁴¹</p> <p>Observations in the Arctic may qualify PFBS as a LRT substance.</p>
Coating and coating additives	Dendrimers : Hyperbranched hydrophobic polymers (dendritic i, e. highly branched polymers)	N/A	39, 48, 62, 68	<p>Toxicology: 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.</p> <p>Environmental hazards: Information gaps in publically available information.</p>
Coating and	Siloxanes ⁴⁴²	556-67-2 (D4)	8, 13, 62	<p>Toxicology: The European Commission has classified D4 as a reproductive toxic substance (repr.</p>

⁴⁴¹ Danish Ministry of Environment, "Short-chain Polyfluoroalkyl Substances (PFAS).

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<http://www2.mst.dk/Udgiv/publications/2015/05/978-87-93352-15-5.pdf>.

⁴⁴² Manufacturing intermediates in the production of PDMS

Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
coating additives	(cyclic : D3, D4, D5 and D6 linear: MM, MDM, MD2M and MD3M) and silicone polymers	541-02-6 (D5) 540-97-6 (D6) 107-46-0 (MM) 107-51-7 (MDM) 141-62-8 (M2DM) 141-63-9 (M3DM)		<p>2) (H361f)⁴⁴³ and is likely to fulfill the Annex D 1(e) (i) and (ii) criteria.⁴⁴⁴⁴⁴⁵ 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.</p> <p>Degradation in the environment: D4 and D5 are considered to fulfil the persistence criteria according to Annex D to the Stockholm Convention.⁴⁴⁶ Siloxane polymers are considered as inert. The California State EPA notes that cyclosiloxanes appear to have long half lives in people.</p> <p>Emissions: Siloxanes are volatile.</p> <p>Monitoring data: D4 and D5 is considered to fulfil the Annex D on bioaccumulation, Long Range Transport (LRT) and D4 additionally is likely to fulfil the ecotoxicity criteria of the Stockholm Convention⁴⁴⁷. 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. Certain siloxanes are persistent in the environment, resisting oxidation, reduction, and photodegradation. Varying information exists on the susceptibility of siloxanes to hydrolysis.</p>
Coating and coating additives	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)	2, 18, 19, 21, 23, 24, 45, 47, 56, 64	<p>Category: precursors for fluorotelomer based polymers</p> <p>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 shows that 4:2 FTOH is more potent than 6:2 and 8:2 for cytotoxicity. FTOHs have been shown to be xenoestrogens causing effects down to 0.03 mg/L, and 6:2 FTOH to be more potent than 8:2 FTOH⁴⁴⁸.</p> <p>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)</p> <p>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</p>

⁴⁴³ Harmonized Classification according to GHS Regulation (EC) No 1272/2008.

<http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database>.

⁴⁴⁴ UNEP/POPS/POPRC.10/INF/7/Rev.1.

⁴⁴⁵ UNEP/POPS/POPRC.10/INF/8/Rev.1.

⁴⁴⁶ UNEP/POPS/POPRC.10/INF/8/Rev.1.

⁴⁴⁷ UNEP/POPS/POPRC.10/INF/8/Rev.1.

⁴⁴⁸ Danish Ministry of Environment, "Short-chain Polyfluoroalkyl Substances (PFAS).

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Applications	Alternative chemicals	CAS No:	References	Characteristics ⁴⁰⁵
				<p>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.</p> <p>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.</p>
Coating and coating additives	Propylated naphthalenes and propylated biphenyls	N/A	64	<p>Toxicology: The substances are poorly characterized</p> <p>Environmental hazards: There are gaps in publically available information. However Diisopropylnaphthalene (DIPN) and Triisopropylnaphthalene (TIPN) are likely to fulfil the Annex D for persistence according to the Stockholm Convention. Diisopropylnaphthalene (DIPN), 1-Isopropyl-2-phenyl-benzene and Triisopropylnaphthalene (TIPN) are likely to fulfil the bioaccumulation criteria according to Annex D in the Stockholm Convention.</p> <p>Diisopropylnaphthalene (DIPN) and 1-Isopropyl-2-phenyl-benzene are likely to fulfil the Annex D for ecotoxicity according to the Stockholm Convention. However it was concluded that these substances are not likely to meet all the annex D criteria and are most likely not POPs.⁴⁴⁹</p> <p>Diisopropylnaphthalene (DIPN) is undergoing Substance Evaluation (SE) due to PBT/vPvB concerns.</p>

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Appendix 4: Non-exhaustive list of alternatives to the use of PFOS in some major open applications

A. Fire-fighting foams

Composition	Trade names	Manufacturer
Fluorosurfactants		
Perfluorohexane ethyl sulfonyle betaine and C ₆ -fluorotelomers often used in combination with hydrocarbons.	Capstone™ products	Chemours
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 ⁴⁵⁰	
Information gaps	Towalex AFFF 3%	Tyco Fire integrated Solutions
Information gaps	FS- series	Chemguard
Information gaps	DX- series	Dynax
A fluorosynthetic versatile AR foam concentrate containing 5-10% 2-(2-butoxyethoxy)ethanol (CAS No: 11234-5; EC 203-961-6)	BIO HYDROPOL 6	Bio Ex
Fluorine-free fire-fighting foams⁴⁵¹		
Protein-based foams	Sthamex F-15	Dr. Sthamer
Products that contain glycols	Hi Combat ATM, "Trainol" ⁴⁵²	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	Centriffoam_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. ⁴⁵³	
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	

⁴⁵⁰ www.kidde.com.ar/utefs/ws-639/Assets/Filmfoam%20813%20-%20DS%20-%2004%20.pdf.

⁴⁵¹ www.kidde.com.ar/utefs/ws-639/Assets/Filmfoam%20813%20-%20DS%20-%2004%20.pdf.

⁴⁵² <http://angusfire.co.uk/products/foam-concentrates/product-range/>.

⁴⁵³ <http://www.solbergfoam.com/>.

	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
Information gaps	HS-series	Chemguard
2-6% Hexylene glycol (CAS No: 107-41-5, EC 203489-0); hydrolyzed protein [70-80%], metallic salt: NaCl+MgCl ₂ [8-15%]; FeSO ₄ *7H ₂ O[0-2%]	PROFOAM 806G	Gepro Group

B. Metal plating⁴⁵⁴

Composition	Trade names	Manufacturers	Comments
Fluorine-free products			
Mainly alkane sulfonates	Sureact CR-H Slotochrom SV31 ⁴⁵⁵ Antifog CR SurTec 850 SK4 Ankor Wetting Agent FF TIB Suract CRH	TIB Schlötter Chemisol <i>SurTec</i> Enthone Inc. TIB	Some of the products in this section are not resistant in chrome sulfuric acid pickling and hard chrome baths ⁴⁵⁶
Fluor-based non-PFOS⁴⁵⁷			
6:2 FTS	Capstone FS10 Proquel OF	Chemours Kiesow	Not resistant to hard chromium plating, less effective in decorative chromium plating
Potassium 1,1,2,2-tetrafluoro-2-(perfluorohexyloxy) 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-tetrafluoroethane sulfonate	FC-53b	China product	
1H,1H,2H,2H-perfluorooctane sulfonic acid	Fumetrol®21	Atotech	

C. Carpets, leather and apparel, textiles and upholstery

Composition	Trade names	Traders	Comments
Fluorine-free products			
Hyperbranched hydrophobic polymers (dendritic i, e. highly branched polymers)	RUCO-DRY ECO	Rudolf GmbH (Germany)	Superhydrophobic surfaces, meaning contact angles larger than 150°.

⁴⁵⁴ Additional information on the use of PFOS and alternatives is available from the National Association for Surface Finishing (<http://www.nasf.org/>).

⁴⁵⁵ This product is only useful for decorative chrome plating.

⁴⁵⁶ Communication with Lanxess.

⁴⁵⁷ There are many more fluorinated substances listed in the Danish Ministry of Environment report.

and specifically adjusted comb polymers as active components. Glycols are added as solvents and cationic surfactants in small amounts act as emulsifiers.			Rudolf Chemie describes the coating as a bionic Lotus coating addressed after the Lotus plant leaves. Applied in coatings, textile and leather.
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	Capstone®	Chemours	
Fluorinated polymers	Foraperle® 225, etc.	Chemours	Impregnation of leather and indoor car upholstery

D. Coating additives

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.
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	Capstone™® PolyFox™	Chemours	
Fluorinated polyethers			
Fluorinated polymers	Capstone™ 225, etc.	Chemours	Impregnation of leather and indoor car upholstery

Appendix 5: Overview of main chemical alternatives to PFOS compounds with identified trade name and company information

Exemptions under the Stockholm Convention	Chemical alternatives to PFOS and related substances	Identified product trade names	Identified companies	Known uses
<p>Coatings and coating additives (surface coatings, paint and varnish)</p> <p>Carpets, leather and apparel, textiles and upholstery (impregnation)</p> <p>Paper and packaging, rubber and plastics (impregnation)</p> <p>Hard metal plating</p> <p>Cleaning agents, waxes and polishes for cars and floors</p>	Perfluorobutane sulfonate (PFBS) derivatives or other alternatives based on various C ₄ -perfluoro compounds	Novec [®] Scotchgard [®]	3M	Paint and coatings industry, electronic coatings, industrial and commercial cleaning, stain protectors for carpets and leather, furniture, automotive uses, hard surfaces and other apparels, catalysts, flame retardants, additives in plastics, industrial coatings, mist suppression, rubber moulding defoamers in electroplating, etc.
Cleaning agents, waxes and polishes for cars and floors	Perfluorobutyl methyl ethers	Novec [®]	3M	Industrial cleaning
Fire fighting foams	Dodecafluoro-2-methylpentan-3-one	Novec [®] 1230	3M	Fire-fighting foams
Hard metal plating	Polyfluorodialkyl ether sulfonates	F-53, F-53B	Shanghai SYNICA ⁴⁵⁸	Mist suppressant hard chrome plating
Aviation hydraulic fluids	Potassium perfluoroethyl cyclohexyl sulfonate	FC-98	3M	Hydraulic fluids
<p>Coatings and coating additives (surface coatings, paint and varnish)</p> <p>Carpets, leather and apparel, textiles and upholstery (impregnation)</p> <p>Paper and packaging, rubber and plastics (impregnation)</p> <p>Hard metal plating</p>	Fluorotelomer alcohol (FTOH) based chemicals and polymers	Capstone [®]	Chemours ⁴⁵⁹	Surfactants, coatings, printing, textile and chemical industries, chrome plating
Fire fighting foams	C ₆ fluorotelomer sulfonamide compounds	Forafac [™] 1157, 1183, 1157N and 1203	Chemours	Fire-fighting foams
Fire fighting foams	Hydrocarbon surfactants, water, solvent, sugars, a preservative, and a corrosion inhibitor	RE-HEALING [™] Foam (RF) ⁴⁶⁰	Solberg	Fire-fighting foams

⁴⁵⁸ www.synica.com.cn/zk/cn/products.asp?id=5&id2=72.

⁴⁵⁹ Chemours has replaced DuPont on the market.

⁴⁶⁰ S. Presidential Green Chemistry Challenge award winner. <https://www.epa.gov/greenchemistry/presidential-green-chemistry-challenge-2014-designing-greener-chemicals-award>.

Exemptions under the Stockholm Convention	Chemical alternatives to PFOS and related substances	Identified product trade names	Identified companies	Known uses
Carpets, leather and apparel, textiles and upholstery (impregnation)	Fluorinated co-polymers	Foraperle® 225, etc.	Chemours	Impregnation of leather and indoor car upholstery
Carpets, leather and apparel, textiles and upholstery (impregnation) Paper and packaging, rubber and plastics (impregnation)	Fluorinated co-polymers	AsahiGuard E-SERIES®	Asahi Glass	Textile, paper and packaging and chemical industries
Coatings and coating additives (surface coatings, paint and varnish)	CF ₃ or C ₂ F ₅ fluoroalkyl polyethers	PolyFox®	OMNOVA Solutions Inc.	Surfactant and wetting additives for coating formulations and floor polish
Coatings and coating additives (surface coatings, paint and varnish)	Propylated naphthalenes or biphenyls	Ruetasolv®	Rütgers Kureha Solvents	Water-repelling agents for rust protection systems, marine paints, coatings, etc.
Coatings and coating additives (surface coatings, paint and varnish)	Sulfosuccinates	Lutensit®	BASF	Levelling and wetting agents
Coatings and coating additives (surface coatings, paint and varnish)		Edaplan® LA 451	Münzing Chemie	Paint and coating industry: wetting and dispersing agents for water-based applications such as wood primers
Coatings and coating additives (surface coatings, paint and varnish)		Hydropalat®875	Cognis	
Coatings and coating additives (surface coatings, paint and varnish) Carpets, leather and apparel, textiles and upholstery (impregnation) Paper and packaging, rubber and plastics (impregnation)	Sulfosuccinates Silicone polymers.	WorléeAdd®	Worlée-Chemie	Wetting agents in the paint and ink industry Surfactants for the impregnation of textile fabrics, leather, carpets, rugs and upholstery and similar articles Wood primers and printing inks
Decorative metal plating	Polypropylene glycol ethers	Emulphor® Enthone	BASF Cookson Electronics	Levelling and wetting agents Decorative chrome plating, etc.
Exemptions under the Stockholm Convention lacking of product trade name and company data				

Exemptions under the Stockholm Convention	Chemical alternatives to PFOS and related substances	Identified product trade names	Identified companies	Known uses
Photo-imaging	Telomer-based surfactant products, hydrocarbon surfactants, silicone products, ⁴⁶¹ C ₃ -C ₄ -fluorinated chemicals.	No information available	No information available	Photographic industry
Photoresist and anti-reflective coatings for semiconductors	No substitutes with comparable effectiveness have been identified for critical uses	No information available	No information available	Semiconductor industry
Etching agent for compound semi-conductors and ceramic filters	No substitutes with comparable effectiveness have been identified for critical uses.	No information available	No information available	Semiconductor industry
Photo masks in the semiconductor and liquid crystal display (LCD) industries	No information available	No information available	No information available	Semiconductor industry
Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters)	For radio-opaque ethylene tetrafluoroethylene, PFBS can replace PFOS.	No information available	No information available	Medical devices
Insect baits for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp.	Synthetic piperonyl compounds such as S-Methoprene, Pyriproxyfen, Fipronil are alternative active substances used, sometimes used in combination. Alternative surfactants may exist.	No information available	No information available	Pesticides
Insecticides for control of red imported fire ants and termites	Several pesticides are used. Other fluorosurfactants may be used as inert surfactants in other pesticide products.	No information available	No information available	Pesticides
Chemically driven oil production	PFBS, telomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids and thioether acids	No information available	No information available	Oil industry

⁴⁶¹ There are considerable datagaps of siloxane compounds used on the market for photographic applications, see reference UNEP/POPS/POPRC.8/INF/17/Rev.1.

Appendix 6: Summary of information on non-chemical alternatives to PFOS submitted during the intersessional period between POPRC-9 and 10

Use	Alternatives ⁴⁶²
Photographic industry	
Photo imaging	Non-chemical alternatives to PFOS include shifting to digital photography
Photolithography	Non-chemical alternatives to PFOS include shifting to digital photography
Semiconductor industry	
Photoresist and anti-reflective coatings for semiconductors	No information available
Etching agent for compound semi-conductors and ceramic filters	No information available
Photo masks in the semiconductor and liquid crystal display (LCD) industries	No information available
Aviation hydraulic fluids	No information available
Hard metal plating	Physical covers (netting, balls) for metal plating baths (Cr VI) to diminish hydrogen burst and reduce misting need to be further investigated ^(A)
Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters)	No information available
Fire-fighting foam	No information available
Pesticides	
Insect baits for control methods for leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp.	<p>The entomopathogenic <i>Metarrhizium anisopliae</i> can cause the decline and ultimate death of small colonies and recent research indicates that the entomopathogenic fungi <i>Beauveria bassiana</i> and <i>Aspergillus ochraceus</i> can cause 50% mortality within 4-5 days in laboratory conditions^(A).</p> <p>Natural products that can be effective under certain conditions include limonoids extracted from the roots of the South Brazilian endemic plant <i>Raulinoa echinata</i>^(A).</p>
Insecticides for control of red imported fire ants and termites	<p>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 ^(B).</p> <p>Biological controls for red imported fire ant (RIFA) include a group of decapitating phorid flies (<i>Pseudacteon</i> spp) which parasitize the ants. The microsporidian protozoan <i>Thelohania solenopsae</i> and the fungus <i>Beauveria bassiana</i> are also promising controls for RIFA. <i>B. bassiana</i> has been shown to control RIFA under field conditions in Taiwan Province of China. 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. Other</p>

⁴⁶² Available information is extracted from (A) Guidance on alternatives to PFOS, its salts and PFOSF and their related chemicals (UNEP/POPS/POPRC.9/INF/11/rev1) or (B) Information from the technical paper on the identification and assessment of alternatives to the use of PFOS, its salts and PFOSF and their related chemicals in open applications UNEP/POPS/POPRC.8/INF/17.

	potential biological controls include the endoparasitic fungi <i>Myrmecomyces annellisae</i> and <i>Myrmicinosporidium durum</i> , and the parasite <i>Mattesia</i> sp ^(B) .
Carpets, leather and apparel, textiles and upholstery and coating and coating additives	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. Dendrimers may be in the region of nano sized materials meaning features with an average diameter between 1 to 100 nm ^(B) .
Paper and packaging	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 ^(B) .
Coatings and coating additives (surface coatings, paint and varnish)	No information available

Appendix 7: Information on use or import of sulfluramid

Table 1. Information submitted by Brazil on export of insect baits for control of leaf-cutting ants from Brazil to Latin American countries (indicated as sulfluramid (kg) active ingredient)

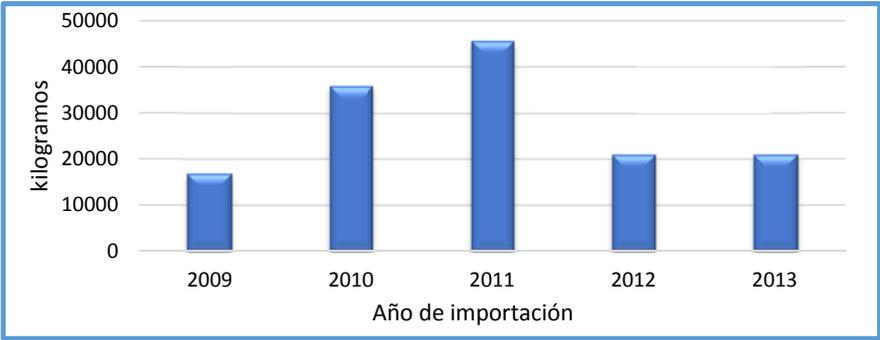
Country	Sulfluramid (kg) active ingredient exported from Brazil			
	2013	2014	2015	Total
Bolivia	30	45	45	120
Colombia	216	324	102	642
Costa Rica	130	95	90	315
Ecuador	216	270	216	702
El Salvador		30	30	60
Guatemala	72	87	96	255
Honduras	63	105	105	273
Panama	51	90	90	231
Paraguay	15		9	24
Peru	36			36
Suriname		27		27
Uruguay	0.09			0.09
Total	829	1073	783	2685

Note-1: Insect baits for control of leaf-cutting ants contain sulfluramid of 3 g active ingredient/kg. (0.3% a.i.)

Note-2: Quantities of sulfluramid used or imported in other countries were not available.

Table 2. Information submitted by Latin American countries and from other sources on export, import and use of insect baits for control of leaf-cutting ants

Country	Information
Antigua and Barbuda	Not imported in Antigua and Barbuda.
Argentina	Registered in Argentina under the following trade names: Mix Hor-Tal; Manchester Cebo Mirex; Mirex Glex Linea Jardin; Mirex Young Linea Jardin; El Buitre Mata; Flumirex LJ; Sulfa Mirex Sh; Parque Mirex Plus; Hormifav S; Mamboreta Mirex -S; Mirex Sul Grhesa; Delente Mirex Jardin; Mix Hor-Tal Jardin; Agrimex-S; Atta Kill Mir-x-S; Fluramin; Huagro sulfa max; Mirenex Sulf. All contains sulfluramid as active ingredient at 0.3 %.
Bahamas	N/A
Barbados	N/A
Belize	Registered in Belize under the trade name Mirex-S 0.3 gr. active ingredient sulfluramid. It is a saturated bait used for the control of leaf cutting ants. It is registered for use in citrus and other fruit tree orchards. The quantities of the active ingredient sulfluramid imported from Guatemala were as follows: 2012: 3.5 kg; 2013: 3 kg; 2014: 3.9 kg; 2015: 5.1kg.
Bolivia	Import data submitted by Brazil (see table 1). Registered in Bolivia under the trade name Mirex-S formulated by Atta Kill Ind. E Comercio de Defensivos Agricolas Ltda in Brazil. Will expire 12/11/2020
Brazil	Registered in Brazil under the following trade names: Fortmex-S; Fluramim; Formicida Granulado Dinagro-S; Formicida Gran. Pikapau-S; Grão Verde AG; Isca Formicida Atta Mex-S; Isca Formicida Exatta; Isca Tamanduá Bandeira-S; Mirex-S Plus; Mirex-S Max; Mirex-S. All contains sulfluramid as active ingredient at 0.3 %. Submitted information on export from Brazil to Bolivia, Colombia, Costa Rica, El Salvador, Ecuador, Guatemala, Honduras, Panama, Paraguay, Peru, Suriname, and Uruguay.
Chile	N/A. Sulfluramid not found in the database of the Ministry of Agriculture (SAG).
Colombia	During the process of the NIP update, the following information was found: <ul style="list-style-type: none"> In the review that was done on December 2014 of the annual reports of pesticide marketing, developed by the Colombian Agricultural Institute (ICA), we found that in the latest report that this the insect bait for leaf-cutting was imported in 2011 (54 tons),

Country	Information
	<p>which correspond to 162 kg of sulfluramid. In the revised data reports we did not find any kind of production or export of that compound after the year 2009.</p> <ul style="list-style-type: none"> • In the ICA database on sales records of chemical pesticides for agricultural use, sales registration No. 3276 of January 14, 1999 was found. This registration is granted to the company Agrocorp SA for the insecticide brand name Atta-Kill and contains 0.3% of Sulfluramid as active ingredient in a Bait Granules formulation (GB). The Ministry of Environment and Sustainable Development is evaluating its validity and if necessary actions concerning cancellation. • The agrochemical Companies members of the Chamber of the National Association of Industrialists (ANDI) and the Association of Pharmaceutical Industries of Colombia (ASINFAR), representing approximately 95% of the pesticide industry in Colombia, reported in 2014 that none of the surveyed companies have stocks of POPs pesticides, including sulfluramid. • In the same vein, 53% of the regional environmental authorities consulted by the MADS, claimed not to have stocks of POPs pesticides including sulfluramid, or storage of any of these pesticides. These authorities have a commitment to disclose related information in their jurisdiction and report to the Ministry of Environment if some finding is present in this area.
Costa Rica	<p>According to the NIP, 623 kg of sulfluramid (equivalent to 207 tonnes of Mirex S) was imported in 2013. An agrochemical formulating Company sales Mirex S in Costa Rica: http://www.agrotico.net/Productos/Proteccion/Insecticidas/MIREX-S_0.36_B.html See also: http://orton.catie.ac.cr/REPDOC/A3765E/A3765E.PDF</p>
Cuba	N/A
Dominica	N/A
Dominican Republic	N/A
Ecuador	Import data submitted by Brazil (see table 1).
El Salvador	Import data submitted by Brazil (see table 1).
Guatemala	Import data submitted by Brazil (see table 1).
Guyana	Imported a small quantity many years ago for a research to develop ant bait for acoushi ant. Not used since then and there is no obsolete stock.
Honduras	<p>Import data submitted by Brazil (see table 1).</p> <p>Perfluorooctane sulfonamide of N-ethyl (EtFOSA; CAS No. 4151-50-2) is marketed in Honduras through the generic name sulfluramid and under the trade names Mirex-S and Martdrim, both products originating in Brazil.</p> <p>According to SENASA-SAG, a total of 140,387 kg of Mirex-S was imported during the period 2009-2013. Mirex-S is registered by Duwest Honduras (DuPont Company), with 0.3% active ingredient sulfluramid in 250-500 gram packages with a trade name ATTA KILL. It is imported from Brazil (94%) and Guatemala (6%).</p>  <p>Figure. Quantities of Mirex-S (kg) imported during the period 2009-2013</p> <p>With regard to the second trade name registered in the database of SENASA-SAG, Martdrim, the registrant is INQUISA, originating in Brazil. The registration expired in July 2010 and it has not been renewed. There is no information of import of Martdrim.</p>
Jamaica	N/A
Mexico	Registered in Mexico as technical sulfluramid and sulfluramid (cofepris.gob.mx).

Country	Information
Nicaragua	Imported 3.5 tonnes of insect bait for leaf-cutting ants (equivalent to 10.50 kg of sulfluramid) in 2013 (http://www.magfor.gob.ni/descargas/publicaciones/ImportacionesPlagFert/agosto2013.pdf) Registered in Nicaragua under the trade name Mirex-S 0.3 G.B (http://www.ramac.com.ni/).
Panama	Import data submitted by Brazil (see table 1). In Panama it is used as an insecticide for leaf-cutting ants with trade name Mirex-S 0.3 GB bait in granules. It is imported from Brazil. The registration will be expired on 16 March 2026.
Paraguay	Import data submitted by Brazil (see table 1).
Peru	Import data submitted by Brazil (see table 1). Registered in Peru under the trade name Mirex-S (002-96-AG-SENASA).
Saint Kitts and Nevis	Not registered in Saint Kitts and Nevis.
Saint Lucia	Two products with sulfluramid as the active ingredient were registered in Saint Lucia in 1998; however, available records indicate that these products have not been imported into the country for the last 10 years. Product name: Volcano ant bait (0.5% sulfluramid) used for controlling urban ant infestations in residential, industrial and commercial areas. Product name: Volcano cockroach bait (1% sulfluramid) used for controlling cockroaches in residential, industrial and commercial areas.
Saint Vincent and Grenadines	N/A
Suriname	Import data submitted by Brazil (see table 1). Banned in Suriname since June 2015. Blitz (fipronil) is used as an alternative but it is not very effective. Need information on environmentally sound alternatives to sulfluramid.
Trinidad and Tobago	N/A
Uruguay	Import data submitted by Brazil (see table 1).
Venezuela (Bolivarian Republic of)	N/A

Note: N/A: no answer.

Appendix 8: Parties' reports on the implementation of alternatives to PFOS, its salts and PFOSF^{463, 464}

Application	Parties' reports on the implementation of alternatives to PFOS, its salts and PFOSF
A. Photo-imaging	<p>Netherlands: Within the industry, new techniques have been developed which do not require PFOS in photolithographic procedures.</p> <p>Sweden: Photographic film continue to disappear and the present use is practically limited to special products (medical uses and similar (scientific)). The total amount of PFOS in films imported to Sweden is estimated to be a few grams in 2013.</p>
B. Semi-conductors (Photo-resist and anti-reflective coatings for semiconductors, etching agent for compound semi-conductors and ceramic filters, photo masks in the semiconductor and liquid crystal display industries)	<p>Germany: In the semiconductor industry it is pointed out that there is a need for the existing exemption for critical applications, because, so far, neither the industry nor their chemical suppliers have made significant efforts of substitution. There are merely hints that currently new PFOS-free techniques are being developed. This issue should be discussed with the stakeholders, which are affected.⁴⁶⁵</p> <p>Ireland: In 2006 the World Semiconductor Council (WSC) announced a plan to end non-critical uses of perfluorooctyl sulfonate (PFOS) chemicals in semiconductor manufacturing and to work to identify substitutes for PFOS in all critical uses. Very small amounts of PFOS compounds are critical ingredients in leading edge photo-resists and anti-reflective coatings, materials used in the photolithographic process for imprinting circuitry on silicon wafers. PFOS is used in photo-resist either as a photo-acid generator or a surfactant. Photo-acid generators are used in photo-resists for 248nm and shorter wavelengths which rely on chemical amplification. During exposure the photo-acid generator forms an acid catalyst which aids in creating the desired image that is to be patterned onto the silicon wafer. Photo-acid generators used for this purpose are typically sulfonic acids and PFOS has been the most effective chemical that provides the necessary acidity and stability. In terms of surfactants, surface tension can produce unwanted thickness variations that emanate from the center of the silicon wafer during the spin-on application of the resist. PFOS is particularly effective in lowering the surface tension, reducing thickness variation, and also creating more uniform films.</p> <p>Under the Stockholm Convention the 'acceptable purpose' which allowed for the continued use of PFOS was defined as 'photo-resist and anti-reflective coatings for semiconductors'. While availing of this exemption for critical applications where no replacement was available, other uses of PFOS at the semiconductor manufacturing facility located in Ireland had previously been eliminated prior to 2010. Since 2010 this facility has been striving to eliminate the small uses of PFOS in these remaining critical applications.</p> <p>A total of nine photolithography process steps were re-designed at the facility thereby reducing PFOS use from less than 3 kilograms per year in 2010 to less than 300 grams by the end of 2012. The final and most challenging process step to re-design was not completed before the technology reached end of life at the facility in 2013. The re-design of each process step had to be addressed individually as each process step has its own unique set of chemistries and process and design specifications that need to be met and in each case the mostly suitable alternate resist chemistry had to be identified. The facility has now been re-furbished and is running the latest company technology which was designed from the outset to be PFOS free.</p> <p>In general terms replacement of PFOS has been achieved through a variety of means including the use of shorter-chain compounds (C-4 to C-1 carbon chains), the use of non-fluorinated substitutes and the elimination of the surfactant function within the photo-resist.⁴⁶⁶</p> <p>Netherlands: Within the semi-conductor industry, every product has its own specific</p>

⁴⁶³ <http://chm.pops.int/Countries/Reporting/NationalReports/tabid/3668/Default.aspx>

⁴⁶⁴ <http://chm.pops.int/Countries/NationalReports/ThirdRoundPartyReports/tabid/4470/Default.aspx>

⁴⁶⁵ <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC8/POPRC8Followup/SubmissionBDEsPFOS/tabid/3064/Default.aspx>.

⁴⁶⁶ Further information on the replacement of PFOS containing photo-resist within the semiconductor industry can be found in the following document: The World Semiconductor Council Joint Statement: http://www.semiconductorcouncil.org/wsc/uploads/WSC_2011_Joint_Statement.pdf See pp. 7, 16-20.

Application	Parties' reports on the implementation of alternatives to PFOS, its salts and PFOSF
	<p>applications. Therefore, for every product, a PFOS-free alternative has to be developed. The industry, together with suppliers, is working on PFOS-free solutions; however industry claims that they need more time to develop a full range of qualitatively comparable alternatives.</p> <p>Spain: Telomer-based products of various perfluoroalkyl chain length. C3- and C4-perfluorinated compounds. Hydrocarbon surfactants. Silicone products.</p> <p>Sweden: No production of photoresist exists in Sweden. No PFOS is remaining in today's import of photoresist.</p> <p>The amount of PFOS in resists usually have been of the magnitude of 0,05-0,1 % which means that PFOS may or may not be declared in the MSDS (depending on who made the MSDS - minor constituents are to be reported only if they contain some hazardous property).</p> <p>In the MSDS for liquid resist there are no statements about PFOS as a component. On a special request for an MSDS on film resist, PFOS was not included in the specification either.</p> <p>One cannot exclude that information from the manufacturers is insufficient or even faulty but with reference to the general PFOS debate it might be more likely that the (international) manufacturers of photoresist actually have substituted PFOS. A substitution to polyfluorinated compounds in photoresist seems likely to have occurred.</p> <p>The situation for the use of PFOS as desmear is a bit unclear. From the suppliers of chemicals to the printed circuit manufacturers it is stated that no PFOS is sold. One of the suppliers claims that PFOS may be omitted by a smaller change in technique when the wafers are cleaned and another one states that PFOS-free desmear has been marketed before. This has not been verified by the manufacturers of printed circuits but the information sounded reliable. Actually, the suppliers of chemicals and technique have conveyed a more profound knowledge about the processes than the manufacturers. This is not surprising since the core business for the manufacturers of printed circuits include more than the actual manufacture.</p> <p>From the suppliers of chemicals to the printed circuit manufacturers it is stated that no PFOS is sold. One of the suppliers claims that PFOS may be omitted by a smaller change in technique when the wafers are cleaned and another one states that PFOS-free desmear has been marketed before. This has not been verified by the manufacturers of printed circuits.</p>
<p>C. Aviation hydraulic fluids</p>	<p>Germany: An example of an exemption no longer being relevant is the use of PFOS applications in the aviation industry. Currently, in Germany, given the small number of players and the high degree of standardization in the industry, a complete substitution may already have been achieved. However, the question cannot be conclusively resolved at this stage. Statements of the manufacturers of hydraulic fluids and talks with Airbus and Lufthansa suggest this. From discussions with the aviation industry it can be concluded that, at least in Germany, mainly two products are being used and others are representing niche applications only. There should be a dialogue with the stakeholders, if and how a deletion of the exemption for hydraulic fluids would affect this industrial branch.⁴⁶⁷</p> <p>Netherlands: According to a producer, PFOS is not an ingredient of the hydraulic fluid. The product does contain a PFOS related molecule (a prefluoroalkyl sulphonate) in an amount lower than 0.1% w/w. This ingredient is not indicated on the Material Safety data Sheet and the producer stated that the substitute molecule was not listed in part I of Annex B to the Stockholm Convention. Despite extensive research, no substitutes for prefluoroalkyl sulphonates (PFOS related molecules) have been identified yet. The use of PFOS in hydraulic fluids seems to be outdated.</p> <p>Norway: According to a recent survey in 2015, the aviation industry informed us that the aviation hydraulic fluids do not contain PFOS anymore. However, we do not have any information about the complete chemical composition of the fluids but the producers have</p>

⁴⁶⁷<http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC8/POPRC8Followup/SubmissionBDEsPFOS/tabid/3064/Default.aspx>.

Application	Parties' reports on the implementation of alternatives to PFOS, its salts and PFOSF
	<p>declared that they to not use PFOS substances.</p> <p>Spain: Fluorinated phosphate esters</p> <p>Sweden: With reference to an official document from one of the suppliers, dated 130522, PFOS has been phased out from phosphate esters based hydraulic fluids. It has been replaced by other fluorinated compounds, PFSA. The phasing out of PFOS by this supplier has not been widely advertised, the customers in question have been informed separately. As far as can be tracked, the substitution of PFOS in this case occurred in 2012/beginning of 2013. The hydraulic fluids existed before PFOS was industrially available and the oil based fluids might be an alternative.</p>
D. Metal plating	<p>Australia: Some users have switched to PFOS-free chemicals.</p> <p>Canada: Five-year time-limited exemptions were enacted under the <i>Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations</i> to allow industry sufficient time to transition to alternatives. This time-limited exemption expired in May 2013. One alternative substance that has been identified for use is “3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate”, (or 1H,1H,2H,2H- Perfluorooctanesulfonic Acid, CAS No: 27619-97-2), which is used at 1-5 wt% in FUMETROL 21. Another alternative substance that has been identified for use is perfluorobutane sulfonate, CAS No: 29420-49-3.</p> <p>Finland: Metal plating industry is phasing out PFOS and moving into more sustainable alternatives. However, it would be beneficial to have a common definition for "closed loop" metal plating processes.</p> <p>Germany: The German Federal Environment Agency commissioned a research report on alternatives to PFOS in the metal plating industry (hard metal plating, decorative plating). In the metal plating industry, PFOS can either be substituted by H4PFOS (CAS No: 276-19-97-2), or with non-fluorinated tensides, the basic elements of which are alkylsulfonates (CH₃(CH₂)_nSO₃H). H4PFOS is not considered a suitable substitution chemical for PFOS by Germany, given its persistence and estimated substance characteristics, which are similar to PFOS. Alkylsulfonates are commonly used, degradable surfactants. TIB Chemicals has filed a patent and has declared the exact formulation as confidential business information, thus our information refers to the general group of alkylsulfonates. According to the progress report mentioned above, the substitution of PFOS in the metal plating industry with non-fluorinated surfactants is feasible for both bright chrome plating and hard chrome plating.</p> <p>The Federal Environment Agency initiated, in the context of the "cleaner production germany" project, a number of projects to support the substitution of PFOS in the metal plating industry.⁴⁶⁸</p> <p>Netherlands: Suppliers do offer PFOS-free products. However, according to users, not all processes are suitable for the use of PFOS-free mist suppressants/wetting agents. Main reason is the reduced quality of chrome plating with PFOS-free products. Another reason is that the reduction of surface tension by alternatives is lower and could therefore lead to higher exposure to chromium (VI) for the worker.</p> <p>Norway: Hard metal plating in closed loop: Alternatives have been tested but have been found to be less efficient. The use of PFOS in this process is none the less very low. The hard-metal plating industry in Norway is small and the use of PFOS substances in this application is less than 10 kg/year. Survey has revealed that the industry would benefit from updated information/fact sheet about the BAT/BEP guidelines for the closed-loop. It seems that the industry is not aware that the waste water from this process contains PFOS and that</p>

⁴⁶⁸ Information is available at: <http://www.cleaner-production.de/projekte-publikationen/projekte/galvanotechnik/einsatz-cr6-freier-elektrolyte-zur-verchromung-von-hochwertigen-automobil-komponenten.html>; <http://www.cleaner-production.de/projekte-publikationen/projekte/galvanotechnik/umruestung-einer-galvanik-auf-umweltfreundliche-beize.html>; http://www.cleaner-production.de/fileadmin/assets/pdfs/Abschlussberichte/20_441_2_4_-_Implementierung_eines_neuen_Kunststoffmetallisierungsverfahrens.pdf; http://www.bubw.de/PDF_Dateien/Downloadbereich/Downloads_2011/Abschlussbericht_PFOS.pdf.

Application	Parties' reports on the implementation of alternatives to PFOS, its salts and PFOSF
	<p>PFOS is a POP and that waste management apply.</p> <p>Romania: VpCl - 414 containing 2-6% 2- Amino-ethanol (CAS No: 141-43-5; EC 205-483-3) Physicochemical properties for 2- Amino-ethanol - Vap.pres. = 0.58 hPa at 26.9°C - Wat.sol.ct.= miscible at 20 °C - logPow = - 1.91 at 25 °C - air photodegradation :50% after 26.6 hours Quantities of use per year: 56 kg VpCl – 414</p> <p>Spain: For decorative plating, use of trivalent chromium, in which case it is not necessary to use a mist catcher.</p> <p>Sweden: Partially fluorinated alternatives (fluorotelomers), have shown sufficient properties. The requirements of "closed loop systems" with regards to PFOS need to be clarified - see comment below. Partially fluorinated alternatives (fluorotelomers) have shown sufficient properties. Experiments on both laboratory scale and pilot scale in a hard chrome plating shop were performed in Denmark and reported in 2012.⁴⁶⁹ The telomer is now used by i.a. two middle size hard chrome platers in Sweden. Two of the hard chrome platers use covering balls in combination with additional cover of the baths. With increased ventilation they claim that the work environment is acceptable without mist suppressant agent.</p> <p>Two plating shops with several years of good experience of full scale plating with a fluorotelomer state that the costs are actually lower than with PFOS. The electroplaters still using PFOS are bigger on plating than the other ones. About 8 kg of the partially fluorinated alternative (fluorinated telomer) is estimated to have been purchased to substitute former use of PFOS. This chemical was introduced in 2009 by one supplier. Two hard chrome platers started test runs the same year and 2011 and the PFOS was totally replaced by this telomer. One other of the small suppliers plans to introduce the same kind of mist suppressant agent soon - after having positive experiences from Finland.</p> <p>In decorative chrome electroplating the chromium layer is a few µm in contrast to the about 35 µm in hard chrome. This enables a somewhat milder electroplating where chromium (III) is used instead of chromium (VI) and consequently the aerosols are not as hazardous. By the use of chromium (III) the demisting foam may be omitted and thereby the need for PFOS. With the thinner chrome layer, the intensity of the process is also less which enables other means of surface cover than foam. Plastic balls are one example that may be used in decorative electroplating.</p>
E. Certain medical devices	<p>Spain: PFOS-free filters. Alternatively, PFBS are tested as surfactant in coating products.</p>
F. Fire-fighting foams	<p>Australia: Major users have switched to PFOS-free foams.</p> <p>Canada: Five-year time-limited exemptions were enacted under the Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations to allow industry sufficient time to transition to alternatives. This time-limited exemption expired in May 2013; however an exemption remains in place for PFOS in AFFF at a concentration of 0.5 ppm to account for residual contamination from previously used PFOS-based AFFF. An alternative substance that has been identified for use is perfluorobutane sulfonate, CAS No: 29420-49-3.</p> <p>Norway: Norway does not use PFOS-containing fire fighting foams. A number of alternatives are available, both fluor-containing foam and foams without fluor. Due to trade secrets we do not have information about the exact chemical composition of the foams.</p> <p>Romania: BIO HYDROPOL 6 containing 5-10% 2-(2-butoxyethoxy)ethanol (CAS No: 11234-5; EC 203-961-6)</p> <p>Physicochemical properties of 2-(2-butoxyethoxy)ethanol: Vap.pres. = 0.02 hPa at 26.9°C;</p>

⁴⁶⁹ Poulsen *et. al.*, "Substitution of PFOS for use in nondecorative hard chrome plating", The Danish Environmental Protection Agency, Environmental Project No. 1371 (2011).

Application	Parties' reports on the implementation of alternatives to PFOS, its salts and PFOSF
	<p>Wat.sol.ct.= miscible at 20 °C; logPow = 0.15-0.4</p> <p>Quantities of use per year: 5729 kg BIO HYDROPOL 6</p> <p>PROFOAM 806G containing 2-6% Hexylene glycol (CAS No: 107-41-5, EC 203489-0); hydrolyzed protein [70-80%], metallic salt: NaCl+MgCl₂ [8-15%]; FeSO₄*7H₂O[0-2%]</p> <p>Physicochemical properties of Hexylene glycol: Vap.pres. = 0.07 hPa at 26.9°C; Wat.sol.ct.= Miscible with water in all properties; logPow < 0.14 at 25 °C</p> <p>Quantities of use per year: 15799 kg PROFOAM 806G</p> <p>Netherlands: Many regulators and authorities require tests or practice with fire-fighting foam installations. On an industrial scale, this requires huge amounts of foam to be spent and spilled into the environment. Not only PFOS-containing foams but also non-PFOS containing foams based on other fluoro compounds damage the environment. Various suppliers of fire-fighting foams advertise 'practice' or 'test' foams with environmentally less hazardous ingredients.</p> <p>Spain: Short chain fluorosurfactants, C6 fluorotelomer and dodecafluoro-2- methylpentan-3-on. Fluoride-free fire-fighting foams (silicone based), hydrocarbon based surfactants, synthetic detergent foams and protein foams.</p> <p>Sweden: Import of PFOS-containing fire-fighting foam ended in 2003. A survey of the chemical content of relevant FFFs on the market has been made.</p>
G. Insect baits for control of leaf-cutting ants	<p>Brazil: The Ministry of Agriculture in collaboration with some Universities has developed studies to test chemicals alternative, pursuant to the recommendations of the Review Committee on Persistent Organic Pollutants in its decision POPRC-8/8 and adopted by COP, which invited Parties that still use PFOS, its salts, PFOSF and its related chemicals for the control of leaf-cutting ants <i>Atta spp.</i> and <i>Acromyrmex spp.</i> to conduct studies, including pilot projects, to develop peer-reviewed information on the feasibility of using alternatives to PFOS, its salts, PFOSF and its related chemicals within an integrated pest management approach.</p> <p>There are basic studies being developed in research centers and universities evaluating biological products, such as entomopathogenic fungi, and natural products such as plant extracts for the control of leaf-cutting ants. The results, however, have been inconsistent, demonstrating technical infeasibility, economic and operational (Boarettto and Forti, 1997; Moreira et al.2004). Fenoxycarb, pyriproxyfen, diflubenzuron, teflubenzuron, silaneafone, thidiazuron, tefluron, prodrone, abamectin, methoprene, Hydramethylnon, boric acid, some insecticides from the group of neonicotinoids, pyrethroids, Spinosyns, etc., had been tested for leaf-cutting ants, but they were not effective.</p>
H. Insecticides for control of red imported fire ants and termites	None
I. Electric and electronic parts for some colour printers and colour copy machines	Spain: Environmentally sound product design.
J. Chemically driven oil production	Spain: Perfluorobutane sulfonate (PFBS), telomer based fluorosurfactants and other perfluoro compounds for uses in oil recovery such as perfluoroalkyl-substituted amines, acids, amino acids and thioether acids.
K. Uses not exempted: carpets, leather and apparel, textiles and upholstery	<p>Spain: Perfluorobutane sulfonate (PFBS) based substances, fluorotelomer-based substances, silicone based or other fluorinated copolymers.</p> <p>Sweden: In most domestic houses stain repellent carpets are not common.</p>
L. Uses not	Spain: Fluorinated products with 1 – 1.5% of fluorochemical. N-Methyl perfluorooctane

Application	Parties' reports on the implementation of alternatives to PFOS, its salts and PFOSF
exempted: paper and packaging, rubber and plastics	sulfonamidoethanol acrylate polymers or short chain telomere based substances
M. Uses not exempted: coatings and coating additives	None

Appendix 9: List of existing documents and decisions of the Committee and the Conference of the Parties relevant to alternatives to PFOS, its salts, PFOF

Table 1. List of existing documents relevant to alternatives to PFOS, its salts, PFOF

Document type	Document symbol	Document title	Remarks
POPRC document	UNEP/POPS/POPRC.10/INF/7/Rev.1	Report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride	Report on the assessment submitted to COP-7.
POPRC document	UNEP/POPS/POPRC.10/INF/8/Rev.1	Factsheets on alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride	Report on the assessment submitted to COP-7.
POPRC document	UNEP/POPS/POPRC.9/INF/11/Rev.1	Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals	Commissioned paper Guidance on PFOF alternatives. Theoretical alternatives. No information from parties.
POPRC document	UNEP/POPS/POPRC.8/INF/17/Rev.1	Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals in open applications	Commissioned paper.
POPRC document	UNEP/POPS/POPRC.5/10/Add.1	General guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals	Guidance on alternatives in general developed by POPRC.
COP document	UNEP/POPS/COP.7/8	Evaluation of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride pursuant to paragraphs 5 and 6 of part III of Annex B to the Convention	Annex II: Summary report of the assessment of alternatives to PFOS, its salts and PFOF Annex III: Conclusions to the Secretariat's report for the evaluation of information on PFOS, its salts and PFOF
COP document	UNEP/POPS/COP.7/INF/11	Report for the evaluation of information on perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride	Secretariat's report. Limited amount of information submitted by Parties on use under Article 15.
COP document	UNEP/POPS/COP.7/INF/12	Compilation of information submitted by parties on their experiences in implementing the recommendations set out in	Party submissions compiled by the Secretariat.

Document type	Document symbol	Document title	Remarks
		the annex to decision POPRC-6/2 on the elimination of brominated diphenyl ethers from the waste stream and on risk reduction for perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride	
COP document	UNEP/POPS/COP.7/INF/21	Revised draft guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid and related chemicals listed under the Stockholm Convention	BAT/BEP Guidance on PFOS. Theoretical alternatives. No information from parties. Possible options provided.
COP document	UNEP/POPS/COP.7/INF/26	Inventory guidance PFOS	Commissioned paper. Inventory guidance. How to conduct an inventory. Practical information, useful links and questionnaires.
COP document	UNEP/POPS/COP.7/27	Reporting pursuant to Article 15 of the Stockholm Convention	Party submissions compiled by the Secretariat.
COP document	UNEP/POPS/COP.7/INF/36 (from page 29)	Report prepared by the Secretariat pursuant to paragraph 2 (d) of Article 20 on the information provided in the reports submitted by parties pursuant to Article 15 of the Convention	Party submissions compiled by the Secretariat.

Table 2. List of decisions of the Committee relevant to alternatives to PFOS, its salts, PFOSF

Decision	Title	Remarks
POPRC-10/4	Process for the evaluation of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride pursuant to paragraphs 5 and 6 of part III of Annex B to the Stockholm Convention on Persistent Organic Pollutants	Finalized and submitted the summary of the report on the assessment of alternatives to PFOS (annex to the decision), its salts and PFOSF together with the full assessment report (UNEP/POPS/POPRC.10/INF/7/Rev.1) and fact sheets on nine of the alternatives assessed (UNEP/POPS/POPRC.10/INF/8/Rev.1) to COP-7.
POPRC-10/5	Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals	Concluded that the guidance on alternatives to PFOS, its salts, PFOSF and their related chemicals should be revised to incorporate pertinent information contained in the report on the assessment of alternatives to PFOS, its salts, PFOSF, in addition to the information contained in the technical paper on the identification and assessment of alternatives to the use of PFOS, its salts, PFOSF and their related chemicals in open applications.

Decision	Title	Remarks
POPRC-9/5	Process for the evaluation of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride for the various acceptable purposes and specific exemptions	Endorsed the TOR for the assessment of alternatives to PFOS, its salts and PFOSF.
POPRC-9/6	Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals	Endorsed the revised guidance on alternatives to PFOS, its salts, PFOSF and their related chemicals (UNEP/POPS/POPRC.9/INF/11/Rev.1).
POPRC-8/8	Perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals in open applications	Adopted the recommendations on alternatives to the use of PFOS, its salts, PFOSF and their related chemicals in open applications, prepared on the basis of the technical paper (UNEP/POPS/POPRC.8/INF/17/Rev.1) Recommendations included phase out of PFOS open application in the following uses: (i) Fire-fighting foams; (ii) Insecticides for the control of red imported fire ants and termites; (iii) Decorative metal plating; (iv) Carpets; (v) Leather and apparel; (vi) Textiles and upholstery. The recommendations were submitted to the COP.
POPRC-8/9	Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals	Decided to revise the guidance on the basis of the comments submitted by parties and observers and any additional information made available to the working group.
POPRC-7/6	Guidance on alternatives to perfluorooctane sulfonate and its derivatives	Invited parties and observers to provide comments on the guidance and information on experience in replacing PFOS and its derivatives with additional alternative products and/or processes, including information about their health and environmental effects.
POPRC-6/5	Substitution and alternatives	Endorsed the revised guidance document on alternatives to perfluorooctane sulfonate and its derivatives and invites parties and observers to disseminate and make use of that document (UNEP/POPS/POPRC.6/13/Add.3).
POPRC-5/2	Substitution and alternatives	Endorsed General guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals (UNEP/POPS/POPRC.5/10/Add.1).

Table 3. List of decisions of the Conference of the Parties relevant to alternatives to PFOS, its salts, PFOSF

Decision	Title	Remarks
SC-7/1	Exemptions	Took note that no new registration may be made with respect to specific exemptions for PFOS, its salts and PFOSF for carpets, leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives, and rubber and plastics.
SC-7/5	Evaluation of PFOS, its salts and PFOSF pursuant to paragraphs 5 and 6 of part III of Annex B to the Convention:	Concluded that parties may need to continue to produce and/or use PFOS, its salts and PFOSF for acceptable purposes as provided in Annex B. Amended the schedule of the process for the evaluation of

Decision	Title	Remarks
		<p>PFOS, its salts and PFOSF.</p> <p>Encouraged parties to label articles containing PFOS, its salts and PFOSF.</p> <p>Requested the Secretariat to revise the format for the collection of information on alternatives to the use of PFOS, its salts, PFOSF and their related chemicals.</p>
SC-6/4	Process for the evaluation of the continued need for perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride for the various acceptable purposes and specific exemptions	<p>Adopted the process for the evaluation of the continued need for PFOS, its salts and PFOSF for the various acceptable purposes and specific exemptions.</p> <p>The process included the POPRC to develop a report on assessment of alternatives to PFOS, its salts and PFOSF, and to comment on the Secretariat's report on the evaluation of PFOS, its salts and PFOSF.</p>
SC-6/7	Work programme on brominated diphenyl ethers and perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride	Took note of the recommendations in POPRC-8/8 and encouraged parties to consider stopping certain uses of PFOS, its salts and PFOSF. Requested the Committee to revise the guidance on alternatives to PFOS, its salts, PFOSF and their related chemicals.
SC-6/10	Guidelines on best available techniques and provisional guidance on best environmental practices	Adopted the workplan for revising the guidance on BAT/BEP relevant to the newly listed POPs including for the use of PFOS and related chemicals listed under the Stockholm Convention.
SC-5/5	Work programme on brominated diphenyl ethers and perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride	Requested the Committee to develop TOR for a technical paper on the identification and assessment of alternatives to the use of PFOS in open applications, develop recommendations on the basis of the technical paper for consideration at COP-6.
SC-4/17	Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride	Listed PFOS, its salts and PFOSF in Annex B with acceptable purposes and specific exemptions.
SC-4/19	Establishing indicative elements of a work programme to facilitate the elimination of listed brominated diphenyl ethers and the restriction or elimination of perfluorooctane sulfonic acid and its salts, perfluorooctane sulfonyl fluoride and other chemicals listed in Annexes A or B of the Convention at the fourth meeting of the Conference of the Parties	<p>Work programme on BDE, PFOS and other new POPs.</p> <p>The work programme included collection of information on PFOS, its salts and PFOSF e.g. types and quantities of articles containing PFOS, its salts and PFOSF, types of processes using PFOS, its salts and PFOSF, cost effectiveness of different management options, methods for sampling and analysis of PFOS, its salts and PFOSF in articles, Identification of remediation methods for contaminated sites as listed.</p>

Appendix 10: Reference list of recent publications on perfluorinated chemicals (PFCs)

Complementary to the reference list in UNEP/POPS/POPRC.8/INF/17/Rev.1

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